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RARE-EARTH RESEARCH AT THE UNIVERSITY OF SÃO PAULO

E. Giesbrecht, G. Vicentini & L.B. Zinner

Instituto de Química, Universidade de São Paulo
Caixa Postal 20.780, São Paulo, Brazil

The lanthanide chemistry studies at the University of São Paulo started in 1960, at the Department of Chemistry of the former Faculdade de Filosofia, Ciências e Letras, and continues until now at the Chemistry Institute.

The lanthanides — Ce-Lu, atomic numbers 58-71 and also La (58) and Y(39) — are very similar elements. Species containing the typical oxidation state (+3), which are classified as a-type acceptors according to Ahrland et al. or hard acids, according to Pearson, were investigated.

Investigations involving polyphosphates, using conductometric and potentiometric procedures, followed by attempts to isolate the detected species, characterization of the compounds obtained by analytical procedures and TG and IR techniques were performed. Tables 1-3 contain a summary of the results.

Synthesis of new lanthanide salts, containing inorganic and organic anions, were made. Hydrated salts, prepared from aqueous solutions, by treating lanthanide oxides or basic carbonates with the corresponding acids, or by metathetical reactions, were mostly isolated (Table 4).

Systematic research on coordination chemistry also started in the 1960's. Reactions between several salts with neutral ligands, generally in non-aqueous media, were performed. It began with the preparation of adducts with cyclic ethers (Table 5). The bonding between the ligands and the metal ions is considered to be very weak.

The trend continued with ligands containing a C—O group (Tables 6-15) like amides, ketones and miscelaneous. IR data indicate a relatively intense interaction between ligands and the central ions.

Complexes derived from ligands with P—O groups (Tables 16-25), can find applications in the extraction of lanthanides. Several adducts containing amides of phosphorus and phosphine oxides were isolated. The bond between the PO oxygen and the lanthanide ions is considerably stable.

A number of sulfoxide complexes with various rare-earth salts have been isolated (Tables 26-33). Sulfoxides contain a "soft" sulfur and "hard" oxygen, both able to act as nucleophiles. However, only oxygen coordinated sulfoxide compounds are formed with lanthanides.

Aliphatic and aromatic amine—N—oxides were also utilized as ligands (Tables 34-40). Bonding through the oxygen is again observed in all cases.

Electrochemical studies involving samarium, europium and ytterbium using current reversal chronopotentiometry and cyclic voltammetry were also performed. The results obtained are summarized in Table 41.

The precipitation of a lanthanide coordination compound from solution depends on the solvent characteristics, such as dielectric constant and donor properties. Since water has a high dielectric constant and appreciable donor charater towards the lanthanides, it is often difficult to precipitate the complexes with neutral ligands from aqueous solution. A few bidentates such as pyrazine-dioxide, trans-dithiane-dioxide and piperazinedi-one, precipitate the corresponding complexes from the concentrated aqueous solution. Lanthanide complexes have often been crystallized after dissolving the appropriate salt in an excess of the ligand, for example, dimethyl-formamide, dimethylacetamide, tetramethylurea, tetra-methylenesulfoxide, lutidine—N—oxide, and pumping off the excess ligand in vacuo. In some cases, the adducts crystalize from the solution. In most cases, the addition compound could be precipitate upon mixing the solution of the metal salt in suitable solvents like ethanol (ex. TMSO), methanol, acetone, acetonitrile (ex.: piperazine-dione, isoniazide) with the ligands. In some cases, a dehydrating agent, such as 2,2-dimethoxypropane or triethyl-orthoformate was added to precipitate the complexes from solution.

The lanthanide compounds present a variety of stoichio-metries, depending on the size of the metal ion, the size of the ligand, the nature of the anion and in some cases of the synthethic procedure used. As the size of Ln^{3+} decreases from La^{3+} to Lu^{3+}, the ligand-ligand repulsion becomes more important for the heavier complexes. When the repulsion becomes large enough to make a particular structure unstable the coordination number and consequently the structure changes. In the perchlorate complexes with DMA, for example, the lighter lanthanides present formula $Ln(ClO_4)_3 \cdot 8DMA$, the intermediate $Ln(ClO_4)_3 \cdot 7DMA$, while those with heavier lanthanide have the composition $Ln(ClO_4)_3 \cdot 6DMA$. But the reverse case is true in quite a few series of complexes, for example, in the trifluoromethanesulfonates with TMU, the Ln:L relation is higher for the heavier lanthanides where no partial anion coordination exists.

In a few cases, it was possible to precipitate different complexes by choosing different solvents or employing different precipitation conditions. The preparation of the complexes of composition $\{LnI(TMSO)_5(H_2O)_3\}I_2$ and $\{Ln(TMSO)_n\}I_3$, for example, depends on the order of the reagents addition.

Fractionary number of ligands, specially in sulfoxide complexes, were also observed. This was interpreted as one ligand acting as a bridge between two lanthanide ions.

It is generally observed that complexes with higher number of neutral ligands are obtained when anions such as PF_6^-, $\sim Ph_4B^- > ClO_4^-$, $\sim CF_3SO_3^- > I^- > ReO_4^-$ are used. This is due to their poor coordination ability. When anions like chlorides, bromides, isothiocyanates, nitrates, tri-fluoroacetates, methanesulfonates are used, the number of neutral ligands is reduced.

The most frequent apparent coordination numbers observed are 6, 7, 8 and 9, specially 8 for small or bidentate ligands. Obviously, the bulky ligands, causing steric hindrance, give lower coordination numbers. The coordination sphere, around the lanthanide ion is described in terms of a polyhedron whose vertexes are occupied by the donor atoms. The idealized geometry results from a compromise between maximum shielding with minimum repulsion between ligands. The most common polyhedron proposed is the trigonal prism, followed by the octahedron and the dodecahedron capped or not.

Infrared spectral data have been extremely useful in order to establish the coordination sites of the ligands, including those which contain two or more potential donor sites. Shifts of the stretching vibrations νCO, νNO, νPO, νSO toward lower frequencies, as compared to the free ligand, were detected in almost all complexes. However, in certain cases the shifts are very small, as in the case of aliphatic amine-oxides, probably due to coupling with other vibrations of the ligand or there is no strong ligand interaction with the metal ion (f. ex., dioxane and thioxane). Large shifts were observed for TMU, HMPA, DPPM, TMAPO or DDPA adducts. Changes in anion symmetry, due to coordination, leads to modifications in the vibrational spectra and may indicate if they are uni, bidentate, etc., or bridging. With thiocyanate ions the IR spectra are useful to decide if they are coordinated through nitrogen or sulfur.

The electronic spectra of the rare-earths are due to 4f-4f transitions. The bands are generally sharp and with low intensity. Absorption and emission spectra of lanthanide compounds were investigated, with emphasis on neodymium (III) and europium (III), respectively. The spectra of the solids were determined at room temperature and at 77K, and also in solution, generally employing nitromethane and in some cases acetonitrile and methanol as solvents. From the neodymium spectra some conclusions were obtained in relation to symmetry of the species and also the nefelauxetic parameters β, covalent factors, $b^{1/2}$, and Sinha's parameters. The values obtained indicate that bonding between ligands and central ions is predominantly electrostatic. Only in a few cases,

specially when halide ions (chloride and bromide) were involved, higher covalent factors were detected.

The oscillator strengths of the hypersensitive transitions in neodymium compounds ($^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$) were investigated in nitromethane and acetonitrile solutions, but not systematically. The influence of the anion basicity in band intensity is remarkable, following the order $NO_3^- >$ $NCS^- > I^-$, ClO_4^-, PF_6^-. Only with the adducts containing pyzNO this fact was not observed, the band presenting about the same intensities for the different compounds prepared.

Fluorescence under UV excitation is also due to 4f-4f transitions. The europium emission spectra were used in the tentative attribution of the symmetries of the species and together with conductance, IR and neodymium spectra data, it was possible to propose a geometry for the species.

This review shows that a large number of lanthanide compounds were prepared along about twenty five years. Regarding the study of these compounds by various techniques, only IR spectroscopy, conductance measurements and X-ray powder patterns have been widely used. The studies involving electronic absorption and fluorescente spectra began only recently. Many other series are under investigation using the mentioned above techniques, but much more has to be done in order to understanding the structure and bonding in lanthanide compounds.

TABLE 1

TRIPOLYPHOSPHATES

FORMULAS	PROPERTIES	REF.
$Ln_5(P_3O_{10})_3 . xH_2O$ Ln = La, Nd, Sm, Eu, Gd, Dy, Y x = 8 (La); x = 16 (Y) x = 17 (Sm); x = 20 (Nd, Eu, Gd, Dy)	By conductometric and potentiometric procedures, it was observed the formation of soluble species with the ratio $Ln^{3+}:P_3O_{10}^5 = 1:2$, including Ce^{3+}. Other species, with the ratio $Ln^{3+}:P_3O_{10}^5 = 1:1$ were detected, in most cases, only in very dilute solutions. By X-RAY it was observed that the La and Y are crystalline; all the others are amorphous.	1-6
$Ln_3Na(P_3O_{10})_2 . xH_2O$ Ln = Pr, Tb, Ho, Er, Tm, Yb, Lu x = 10 (Yb); x = 12 (Pr, Er) x = 13 (Tm); x = 14 (Tb, Ho)		

TABLE 2

TRIMETAPHOSPHATES

FORMULAS	PROPERTIES	REF.
$LnP_3O_9 . 3H_2O$ Ln = La–Lu, Y	IR: In accordance with a D_{3h} symmetry already observed. CONDUCTANCE: Conductometric titration in aqueous solution confirms the raio $Ln^{3+}:P_3O_9{}^{3-} = 1:1$, with no evidence of other species;. CN: It is suggested that the CN in Nd P_3O_9 is nine. X-RAY: The La, Ce and Pr compounds are isomorphous. TG: Decomposition in accordance with: $LnP_3O_9 . 3H_2O \xrightarrow{200°-600°} LnP_3O_9 \xrightarrow{>850°} LnPO_4$	7

TABLE 3

TETRAMETAPHOSPHATES

FORMULAS	PROPERTIES	REF.
$La_4(P_4O_{12})_3.14H_2O$ $Ln_4(P_4O_{12})_3.13H_2O$ $Ln = Ce-Lu$ $Ln^{3+}:P_4O^4{}^-_{12} = 1:1$ only in solution	IR: La to Ho tetrametaphosphates present i.r. bands very similar to the $P_4O^4{}^-_{12}$ ring in aqueous solution. Large modifications in the i.r. spectra occur as the metal ionic radii decrease. ELETRONIC SPECTRA (Nd) : $Nd_4(P_4O_{12})_3$ and $Nd(BrO_3)_3$ spectra are very similar; they were recorded in the region of the hypersensitive band $^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$ (14.9 KK). CN: There are evidences that the CN in $Nd_4(P_4O_{12})_3$ is nine. CONDUCTANCE: Conductometric titration in aqueous solution shows the formation of soluble species $Ln^{3+}:P_4O^4{}^-_{12} = 1:1$. TG: Total evolution of P_4O_{10} with a residue of the corresponding oxide.	8

TABLE 4

LANTHANIDE SALTS

FORMULAS	PROPERTIES	REF.
$Ln_2(SeO_3)_3.nH_2O$ n = 4 Ln = La, Nd, Eu n = 4.5 Ln = Gd n = 5 Ln = Pr, Sm	Conductometric and potentiometric titrations were used to determine the stoichiometry. DTA and TG — under N_2 to 500°C, than air. Compounds loose water between 230-290°C. $\sim$ 500°C occurs disproportionation; $4 M_2(SeO_3)_2 \rightarrow 3 M_2(SeO_4)_3 + M_2S_3$. > 500 a complex misture is formed: oxides, selenides, selenates and oxyselenates.	9
$YNa(SeO_3)_2.3H_2O$ $Ce_3H(SeO_3)_5.5H_2O$ $M_2(SeO_3)_3.4H_2O$ M = Tb-Lu	Conductometric and potentiometric titrations were performed to determine the stoichiometry. DTA and TG — water is completely evolved at $\sim$200°C. Between 1 100- 1 200°C the oxides are formed.	10
$Ln_2(SeO_3)_3.H_2SeO_3.nH_2O$ n = 4 Ln = Y, Pr, Nd, Sm, Tb n = 3 Ln = La n = o Ce, La n = 5 Dy-Lu	IR: Band attributions are made for the several SeO stretchings. X-RAY: a) Ce = La (anhydrous); b) Pr-Lu, Y — form an isomorphous series. TG — first the normal selenites are formed. > 1000°C the oxides are obtained.	11
$Ln(SCN)_3.nH_2O$ n = 7 Ln = La-Nd n = 6 Ln = Sm-Lu, Y	IR: νCN at $\sim$2020, 2030, 2040 — SCN not coordinated. X-RAY: Two isomorphous series: a) $7H_2O$; b) $6H_2O$. Morphology and optical properties are described.	12
$Ln_2(SeO_4)_3.nH_2O$ n = 8 Ln = Y, Ho n = 10 Ln = La n = 7 Ln = Pr, Sm, Eu, Gd, Tb, Dy, Tm, Yb n = 9 Ln = Lu n = 6 Ln = Ce n = 5 Ln = Nd	IR: Strong band at 875 cm^{-1} (ν_3) SeO$^-_4$ — Td symmetry. TG — Between 1000–1050°C the lanthanide oxides are formed. Solubilities in water at various temperatures were determined. X-RAY: Four different types of patterns: a) La–Nd; b) Sm–Gd; c) Tb–Yb; d) Lu.	13

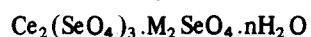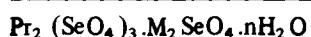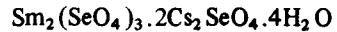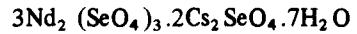|		
$La_2(SeO_4)_3 M_2 SeO_4 nH_2 O$ n = 8 M = Li, Rb n = 5 M = Na n = 9 M = K n = 1 M = Cs	TG-DTA curves are showed. Several steps (9) are proposed for the thermal decomposition. Final product $La_2 O_3$.	14
$Ce_2(SeO_4)_3 . M_2 SeO_4 . nH_2 O$ n = 4 M = Na n = 8 M = K, Rb n = 1 M = Cs	TG-DTA curves. Several steps (5) are proposed for the thermal decomposition. Final residue CeO_2.	15
$Pr_2 (SeO_4)_3 . M_2 SeO_4 . nH_2 O$ n = 4 M = Na n = 7 M = K n = 3 M = Rb n = 0 M = Cs	TG-DTA curves. Several steps (8) are proposed for the thermal decomposition. Final residue $Pr_6 O_{11}$.	16
$Nd_2 (SeO_4)_3 . M_2 SeO_4 . nH_2 O$ $3Nd_2 (SeO_4)_3 . 2Cs_2 SeO_4 . 7H_2 O$ $Sm_2 (SeO_4)_3 . M_2 SeO_4 . mH_2 O$ $Sm_2 (SeO_4)_3 . 2Cs_2 SeO_4 . 4H_2 O$ n = 4 M = Na n = 7 M = K n = 1 M = Rb m = 4 M = Na m = 5 M = K, Rb	TG-DTA curves. Several steps are proposed for the thermal decomposition. Residues: $Na_2 O.Nd_2 O_3$, $Na_2 O.Sm_2 O_3$. Other compounds give $Nd_2 O_3$ and $Sm_2 O_3$.	17
$Eu_2 (SeO_4)_3 . M_2 SeO_4 . nH_2 O$ n = 5 M = Li, Rb n = 6 M = Na n = 7 M = K n = 2 M = Cs	DTA and TG curves. Several steps are proposed for the thermal decomposition. Residues: $Li_2 O$, $Eu_2 O_3$, $Na_2 O$. $Eu_2 O_3$ and $Eu_2 O_3$ for the other salts.	18
$Ln_2 (C_{19} H_{15} O_3 P)_3 . 14H_2 O$ Ln = La–Yb, Y $Lu_2 (C_{19} H_{15} O_3 P)_3 . 15H_2 O$	*Conductometric titration* showed only the formation of insoluble compounds with the ratio $Ln^{3+} : C_{19} H_{15} O_3 P^{2-} =$ = 2 : 3. TG: above 1050°C the residue is formed by the lanthanon ortophosphate. The residues isolated at the various temperatures were submitted to an IR: It was observed that the samples obtained at 650°C, 800°C and 950°C showed bands that corresponded to a mixture of meta-and orthophosphates. All the residues, when heated during many hours at 1050°C showed only bands corresponding to the pure orthophosphates.	19
$Ln(SO_3 NH_2)_3 . nH_2 O$ n = 2 Ln = Y, Pr, Nd, Gd, Yb n = 1.5 Ln = Sm, Dy, Ho n = 2.5 Ln = La, Ce, Er	IR: The bands of the water and sulfamate ion are present. X-RAY: Two different patterns: a) La, Ce; b) the others. The solubility at 30°C and 80°C were determined.	20
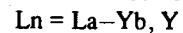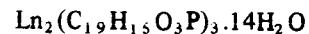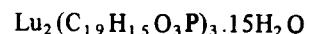
$Lnb_2(ClO_4).nH_2O$ $b = C_4H_3N_2O_3$ = barbiturate n = 3 Ln = La-Pr n = 5 Ln = Nd-Lu, Y	IR: Bands due to water and barbiturate ions. ClO_4^- maintain it's Td symmetry and is not coordinated. X-RAY: Two series: a) La-Pr; b) Nd-Lu, Y.	21
$Lnb_2Cl.nH_2O$ b = barbiturate n = 5 Ln = La-Dy n = 8 Ln = Ho-Lu, Y	IR: Present bands due to water and barbiturate ions. CONDUCTANCE: 1 : 3 electrolyte in water. X-RAY: Three series of patterns: a) La, Ce; b) Pr-Dy; c) Ho-Lu, Y	22
$Lnb_2(SCN).5H_2O$ n = barbiturate Ln = Nd, Sm, Gd-Yb	IR: Bands due to barbiturate ions and water are present. The SCN^- ions are bonded through the nitrogen. X-RAY: All compounds are isomorphous.	23
$Ln_2(C_4H_2O_4)_3.nH_2O$ $C_4H_2O_4$ = fumarate n = 6 Ln = La, Pr, Nd, Tb, Dy n = 5 Ln = Ce, Gd n = 3 Ln = Ho, Er, Tm n = 1 Ln = Yb, Lu, Y	IR: ν_{as} and ν_s CO lowered to small frequencies. X-RAY: Four types of patterns: a) La-Nd; b) Gd-Dy; c) Ho-Tm; d) Yb, Lu, Y.	24
I Ln(LH)$_2$Cl(H$_2$O) I Ln = La-Lu LH = N-Salicylidene- anthranilate	NMR: Only the -COOH portion is neutralized. The phenolic oxygen weakly bonded. Three sites of the ligand bonded. CONDUCTANCE: Non-electrolytes in nitrobenzene. ELECTRONIC SPECTRA (Nd^{3+}): Reflectance - large nephelauxetic effect is observed. Fair degree of covalency. Same species in ethanol and dimethulsulfoxide (Same P).	25
I Ln(LH)$_2$(ClO$_4$) (H$_2$O) I Ln = Nd, Sm, Ho LH = N-Salicylidene- anthranilate	IR: ClO_4 - C_{3v} symmetry - monodentate. Characteristic bands of the N-salicylideneanthranilate are observed. CONDUCTANCE: Non-electrolytes in nitrobenzene. ELECTRONIC SPECTRA (Nd^{3+}) : C.N. = 8 is suggested on basis in the spectra.	26
$Ln_2(C_6H_8S_2O_4)_3$ Ln = La-Sm, Gd, Dy, Yb, Y $C_6H_8S_2O_4{}^{2-}$ = ethylenedithio- diacetate	IR: ν_{as} and ν_s COO shifted to lower frequencies. Splitting of the bands are observed. CONDUCTOMETRIC TITRATIONS: Evidences of the existence of species 2 : 3. X-RAY: The compounds are not crystalline.	27
$Ln(C_{12}H_{10}O_2P)_3.H_2O$ Ln = La-Lu, Y $C_{12}H_{10}O_2P$ = diphenylphos- phinate	IR: Spectra present water bands. ν_{as} PO at ~1140 and ν_s PO at ~1050 cm^{-1} (splitting are observed). X-RAY: Only one isomorphous series was observed.	28
$Ln(C_{12}H_{10}O_4P)_3$ Ln = La-Lu, Y $C_{12}H_{10}O_4P$ = diphenoxy- phosphinates	IR: ν_{as} PO at ~1240 ν_s PO at ~1105; ν_{as} PO-Ph at 1204 and ν_s PO-Ph at 940 cm^{-1}. X-RAY: Three series of patterns: a) La-Eu; b) Ce; c) Gd-Lu, Y.	29
$Ln_2(C_4H_2O_4)_3.nH_2O$ n = 5 Ln = La, Eu n = 4 Ln = Nd, Dy n = 6 Ln = Sm, Y $C_4H_2O_4$ = maleates	IR: ν CO shifted to lower frequencies. X-RAY: Two types of patterns: a) La, Nd, Sm, Eu; b) Dy, Y.	30

$LnH_3(C_4H_2O_4)_3 \cdot nH_2O$ n = 1 Ln = La n = 3 Ln = Y n = 7 Ln = Nd, Dy n = 8 Ln = Sm, Gd $C_4H_2O_4$ = maleates	X-RAY: One isomophous series.	30
$Ln(PNBT)_2Cl.4H_2O$ Ln = Sm$-$Lu PNBT = phenylbutazone anion	IR: Bands due to water and phenylbutazone ion. X-RAY: All compounds are isomorphous. TG $-$ For the compounds of Eu, Tb, Dy $-$ the residues at 600° are LnOCl.	31
$Ln(PNBT)_3.4H_2O$ Ln = La$-$Lu, Y	IR: ν CO at 1600$-$1500. CONDUCTANCE: Non-electrolytes in methanol. X-RAY: All compounds are isomorphous, except Yb and Lu. TG $-$ The adducts loose water at $\sim$200. At higher temperatures the residues are the oxydes. ELECTRONIC SPECTRA (Nd^{3+}): The central ion are involved in a cubic site. The parameters β, $b^{1/2}$, δ were determined. EMISSION SPECTRUM (Eu) : C_{2v} monocapped trigonal prism; C_{3v} also possible.	32
$Ln(H_2V)Cl.6H_2O$ Ln = Eu$-$Lu, Y H_2V = dihydrogenviolurate	IR: ν_{NO} shifted to higher and ν_{CN} to lower frequencies. ν_{CO} $-$ splitting. CONDUCTANCE: 1 : 1 electrolytes in methanol. X-RAY: All compounds are isomorphous. EMISSION SPECTRUM (Eu) : D_{2d}	33
$Ln(H_2V)_3.4H_2O$ Ln = Sm$-$Lu	IR: ν_{Ln-O} at 400 cm^{-1}. Bands due to H_2V^- ions are observed. X-RAY: All compounds are isomorphous.	34
$Ln(H_3C-SO_3)_3 \cdot nH_2O$ n = 2 Ln = La$-$Pr n = 3 Ln = Nd$-$Lu, Y	IR: H_3C-SO_3 $-$ C_{3v} with small distortion-tridentate. Spectra show water bands. CONDUCTANCE: 1 : 3 electrolytes in water, non-electrolytes in methanol. X-RAY: Three types of patterns: a) La$-$Pr; b) Nd$-$Ho, Y; c) Er$-$Lu. ELECTRONIC SPECTRA (Nd^{3+}): The parameters β, $b^{1/2}$, δ and also P in water were determined. TG $-$ loose water at $\sim$100°C. Residue to 370°C the anhydrous salts. EMISSION SPECTRUM (Eu) : proposed symmetry D_3.	35
$Ln(H_3C-SO_3)_3$ Ln = La$-$Lu, Y	IR: Lowering of C_{3v} symmetry, except for La. Three oxygen bonded, but not in an equivalent way. CONDUCTANCE: Non-electrolytes in methanol. X-RAY: Three types of patters: a) La; b) Ce$-$Sm; c) Eu$-$Lu, Y. ELECTRONIC SPECTRA (Nd^{3+}) : Identical to the hydrated, same P value. TG$-$DTA $-$ Compound stable up to $\sim$300°C $-$ Residue $-$ in N_2 atmosphere sulfides, in air sulfides and sulfates. EMISSION SPECTRUM (Eu) : proposed symmetry and geometry D_3 or D_{3h} tricapped trigonal prism.	36
$Ln(C_9H_7O_4)_3.2H_2O$ Ln = La$-$Lu, Y $C_9H_7O_4$ = 1,4-Benzodioxin- -2,3-dihydro-2-carboxylate	IR: COO acting as bridge. CONDUCTANCE: Non-electrolytes in nitromethane. X-RAY: All compounds are isomorphous. TG$-$DTA $-$ Final residues $-$ lanthanide oxides. EMISSIONS SPECTRUM (Eu) : proposed symmetry D_{3h} or C_{3h}.	37

TABLE 5

1,4-DIOXANE AND 1,4-THIOXANE

FORMULAS	PROPERTIES	SIMMETRY AND GEOMETRY (Eu)	REF.
$Ln(ClO_4)_3 \cdot 9H_2O \cdot 4C_4H_8O_2$ Ln = La–Lu, Y	IR: The binding of the dioxane is relatively weak. The spectra are practically identical to that of the free dioxane. X-RAY: Two isomorphous series were obtained: a) La–Dy, Y; b) Ho–Lu.		38 39
$Ln(NO_3)_3 \cdot xH_2O \cdot nC_4H_8O_2$ n = 1, x = 2 Ln = La, Ce n = 2, x = 2 Ln = Pr–Sm n = 2.5, x = 3 Ln = Gd–Yb, Y	IR: Dioxane spectrum without essential modification NO_3^- coordinated to central ion.		40
$LnCl_3 \cdot nC_4H_8O_2$ n = 1 Ln = La–Gd n = 2 Ln = Dy, Er, Y	IR: Dioxane spectrum without essential modification. X-RAY: Two isomorphous series, corresponding to the different compositions.		41
$Ln(NCS)_3 \cdot 2H_2O \cdot 4C_4H_8O_2$ Ln = La–Nd	IR: NCS – coordinated through the nitrogen. X-RAY: The adducts are all isomorphous.		42
$Ln(ClO_4)_3 \cdot 8H_2O \cdot 4C_4H_8SO$ Ln = La–Lu, Y	IR: Thioxane spectrum without essential modification. X-RAY: All the adducts are isomorphous.		43

TABLE 6

N,N-DIMETHYLACETAMIDE (DMA)

FORMULAS	PROPERTIES	SYMMETRY AND GEOMETRY (Eu)	REF.
$\vert Ln(DMA)_n \vert (ClO_4)_3$ n = 8 Ln = La–Nd n = 7 Ln = Sm–Er, Y n = 6 Ln = Tm–Lu	IR: Partial interaction involving ClO_4^- ions. X-RAY: Two isomorphous series: a) n = 8 and 7; b) n = 6. ELECTRONIC SPECTRA (Nd) : The parameters β, $b^{1/2}$, δ , and P in nitromethane were determined.	C_{3v} Monocapped trigonal prism.	44 45
$\vert Ln(NO_3)_3 (DMA)_n \vert$ n = 4 Ln = Ce, Pr n = 3 Ln = Nd–Lu, Y	IR: NO_3^- coordinated to central ions. CONDUCTANCE: Non-electrolytes in nitromethane. In DMA interaction with the solvent. Evidences of the existence of the species $\vert Ln(NO_3) \vert^{2+}$, $\vert Ln(NO_3) \vert^+$ and $\vert Ln(NO_3)_3 \vert$ in DMA. X-RAY: Three isomorphous series was evidenced: a) Ce, Pr; b) Nd–Tb; c) Dy–Lu, Y. ELECTRONIC SPECTRA (Nd) : The parameters β, $b^{1/2}$, δ , and P in nitromethane were determined.	C_{3v} Tricapped trigonal prism	46 47 48 45
$\vert Ln(C_2H_3O_2)DMA \vert$ Ln = La, Ce–Gd	TG: Decomposition giving anhydrous acetate, lanthanide basic carbonate and oxides. ELECTRONIC SPECTRA (Nd) : The parameters β, $b^{1/2}$, δ , were determined.	D_3 Trigonal prismatic	49 50 45

$LnCl_3(DMA)_n$ $n = 4$ $Ln = La$ $n = 3.5$ $Ln = Ce-Dy$ $n = 3$ $Ln = Ho-Lu, Y$	CONDUCTANCE: Non-electrolytes in nitromethane. Evidences of the existence of the species $LnCl^{2+}$, $LnCl_2^+$ and $LnCl_3$ in DMA. ELECTRONIC SPECTRA: Molar absorptivities determined. Spectra and intensities are extremely dependent of the Cl^- concentration. (Nd) ;The parameters β, $b^{1/2}$, δ, and P in nitromethane were determined.	D_3 Trigonal prismatic (polymeric)	49 51 47 48 45
$Ln(NCS)_3(DMA)_n$ $n = 5$ $Ln = La-Nd$ $n = 4$ $Ln = Sm-Lu, Y$	IR: NCS^- — bonded through the nitrogen. CONDUCTANCE: Non-electrolytes in nitromethane; 1 : 1 in DMA. Condutometric titrations give evidences of the $Ln(NCS)^{2+}$, $Ln(NCS)_2^+$ and $Ln(NCS)_3$ in DMA. ELECTRONIC SPECTRA (Nd) : The parameters β, $b^{1/2}$, δ, and P in nitromethane were determined.	C_{3v} Monocapped trigonal prism	49 53 45
$Ln(ReO_4)_2(DMA)_n$ ReO_4 $n = 5$ $Ln = La$ $n = 4$ $Ln = Ce-Eu, Dy-Er, Y$	IR: Lowering of the Td symmetry ReO_4^-. CONDUCTANCE: 1 : 2 electrolytes in DMA. TG: Loose DMA, giving mainly anhydrous perrhenates, which decompose giving ReO_2. ELECTRONIC SPECTRA (Nd) : The parameters β, $b^{1/2}$, δ, were determined.	S_4 Dodecahedral	49 54 45
$LnBr_3.5DMA.nH_2O$ $n = 0$ $Ln = La-Dy$ $n = 3$ $Ln = Ho-Lu, Y$	CONDUCTANCE: Non-electrolytes in nitromethane. The hydrated adducts are 1 : 1 electrolytes in nitromethane. In DMA close to 1 : 2. Condutometric titrations give evidences of the existence of species $LnBr^{2+}$, $LnBr_2^+$ and $LnBr_3$ in DMA. ELECTRONIC SPECTRA (Nd) : The parameters β, $b^{1/2}$, δ and P in nitromethane were determined.	C_{2v} Bicapped trigonal prism	48 45 52
$Ln(DMA)_n (PF_6)_3$ $n = 7$ $Ln = La-Ho$ $n = 6$ $Ln = Er-Lu, Y$	IR: PF_6^- maintain it's Oh symmetry and is not coordinated. CONDUCTANCE: 1 : 3 electrolytes in nitromethane and acetonitrile. Equivalent conductance in acetonitrile indicate behaviour of weak electrolytes, with formation of ion pairs. X-RAY: Three isomorphous series: a) La; b) Ce-Ho; c) Er-Lu, Y. ELECTRONIC SPECTRA: The shape is not modified at different concentrations. (Nd) : The parameters β, $b^{1/2}$, δ, and P in nitromethane were determined.	C_{3v} Monocapped trigonal prism	55 45
$Ln(N_3)^{2+}$ $Ln(N_3)_2^+$ $Ln(N_3)_3$, $Ln(N_3)_5^{2-}$	Conductometric titrations and the spectrophotometric molar ratio method give evidence of the several species.		56
$Ln(DMA)_n (H_2O)_2 I_3$ $n = 6, x = 4$ $Ln = La-Er, Y$ $n = 4, x = 3$ $Ln = Tm-Lu$	IR: ν Ln–O at ~480 cm^{-1}. CONDUCTANCE: Close to 1 : 3 electrolytes ($n = 6, x = 4$) and 1 : 2 electrolytes ($n = 4$, $x = 3$) in acetonitrile. Close to 1 : 3 electrolytes in nitromethane. Equivalente conductance data indicate a behaviour of weak electrolytes in DMA and acetonitrile. X-RAY: Two isomorphous series corresponding to the different compositions. ELECTRONIC SPECTRA (Nd) : Determined at different concentrations in DMA and acetonitrile.	C_{3v}	57 45

I Ln(DMA)$_n$(H$_2$O)$_6$ I(CF$_3$SO$_3$)$_3$ [a] n = 3 Ln = La–Tb n = 2 Ln = Dy–Lu, Y I Ln(DMA)$_m$(H$_2$O)$_6$ I(CF$_3$SO$_3$)$_3$ [b] m = 3 Ln = La–Eu m = 2 Ln = Eu–Lu, Y	a) Obtained from DMA; b) obtained from CHCl$_3$. CONDUCTANCE: 1 : 1 electrolytes in nitromethane and 1 : 2 in acetonitrile. X-RAY: Two isomorphous series corresponding to the different compositions. ELECTRONIC SPECTRA (Nd) : the parameters β, b$^{1/2}$, δ and P in nitromethane were determined.	n = m = 3 D$_{3h}$ Tricapped trigonal prism n = m = 2 D$_{3h}$ Bicapped trigonal prism	58

TABLE 7

N,N,N', N'-TETRAMETHYLMALONAMIDE (TMMA)

FORMULAS	PROPERTIES	SIMMETRY AND GEOMETRY (Eu)	REF.
I Ln(TMMA)$_4$ I(ClO$_4$)$_3$ Ln = La–Lu, Y	IR: Split of ν CO – ClO$_4^-$ not coordinated. CONDUCTANCE: 1 : 3 electrolytes in nitromethane. X-RAY: Three different types of patterns: a) La; b) Ce–Ho; c) Er–Lu, Y. ELECTRONIC SPECTRA (Nd) : The parameters β, b$^{1/2}$, δ and P in nitromethane were determined.	D$_{2d}$ or S$_4$ Distorted dodecahedron	59 60 61
I Ln(NO$_3$)$_3$(TMMA)$_2$ I Ln = La–Lu, Y	IR: NO$_3^-$ – coordinated. CONDUCTANCE: Non-electrolytes in nitromethane, Ho–Lu near to 1 : 1. X-RAY: Five types of patterns: a) La–Pr, Sm; b) Nd–Dy; c) Y, Ho; d) Tm, Yb; e) Er–Lu. ELECTRONIC SPECTRA (Nd): The parameters β, b$^{1/2}$, δ and P in nitromethane were determined.	D$_{2d}$ (distorted)	59 60 61
i LnCl$_3$ (TMMA)$_2$ I Ln = La–Lu, Y (except Tm)	IR: Splitting of ν CO band is observed. CONDUCTANCE: 1 : 2 electrolytes in methanol. X-RAY: Five different types of patterns: a) La; b) Ce; c) Pr–Er, Y; d) Yb; e) Lu. ELECTRONIC SPECTRA (Nd): The parameters β, b$^{1/2}$, δ were determined.	C$_{2v}$ Monocapped trigonal prism	62 61
I Ln(NCS)$_2$(TMMA)$_3$ ISCN La = La–Yb, Y I Lu(NCS)$_3$(TMMA)$_2$ I	IR: NCS – bonded through the nitrogen. CONDUCTANCE: 1 : 1 electrolytes in methanol and nitromethane, Lu – non- -electrolytes in nitromethane. X-RAY Two different types of patterns: a) La–Yb, Y; b) Lu. ELECTRONIC SPECTRA (Nd) : The parameters β, b$^{1/2}$, δ and P in nitromethane were determined.		62 61
I Ln(TMMA)$_n$ I(PF$_6$)$_3$ n = 5 Ln = La n = 4 Ln = Ce–Lu, Y	IR: Splitting of ν CO band. PF$_6^-$ not coordinated (Raman an IR). CONDUCTANCE: 1 : 3 electrolytes in acetonitrile, nitromethane and nitrobenzane. X-RAY: Three different types of patterns: a) La; b) Ce-Tb; d) Dy-Lu, Y. ELECTRONIC SPECTRA (Pr, Nd, Ho, Er) : Molar absorptivities and spectral parameters were determined. The oscillator strenght in nitromethane was determined. TG and DTA: Residues are oxides.	D$_{2d}$	63 61

I Ln(TMMA)ₙ I I₃ n = 5 Ln = La, Ce n = 4 Ln = Pr, Lu, Y	IR: Splitting of ν CO band. CONDUCTANCE: 1 : 3 electrolytes in nitromethane, acetonitrile and methanol. X-RAY: Four different types of patterns: a) La, Ce; b) Pr–Dy; c) Ho; d) Er–Lu, Y. ELECTRONIC SPECTRA (Nd) : The parameters β, $b^{1/2}$, δ were determined.	D_{2d} Dodecahedron	64 61
I Ln(TMMA)ₙ I (CF₃SO₃)₃ n = 5 Ln = La, Ce n = 4 Ln = Pr–Lu, Y	IR: Splitting of ν CO band. $CF_3SO_3^-$ not coordinated. CONDUCTANCE: 1 : 3 electrolytes in nitromethane and acetonitrile. X-RAY: Four different types of patterns: a) La, Ce; b) Nd, Eu; c) Pr, Sm, Gd–Yb, Y; d) Lu. ELECTRONIC SPECTRA (Pr, Nd, Ho, Er): The parameters β, $b^{1/2}$, δ and P in nitromethane were determined.	(La) D_{2d} Dodecahedral (Eu) C_{4v} Monocapped square antyprism (Lu) D_{2d} Dodecahedral	65

TABLE 8

N, N, N', N'–TETRAMETHYLUREA (TMU)

FORMULAS	PROPERTIES	SYMMETRY AND GEOMETRY (Eu)	REF.
I LnCl₃(TMU)ₙ I n = 3.5 Ln = La n = 3 Ln = Ce–Lu, Y	IR: Splitting of νCO band. CONDUCTANCE: Non-electrolytes in nitromethane.		66
I Ln(NO₃)₃(TMU)₃ I Ln = La–Lu, Y	IR: NO_3^- bonded to central ions. CONDUCTANCE: Non-electrolytes in nitromethane.		67
I Ln(TMU)₆ I Cl0₄)₃ Ln = La–Lu, Y	TG–DTA: The compounds gradually loose TMU, giving LnCl₃ as residue.		68 69
Ln(ReO₄)₃ 5(TMU) Ln = La–Sm I Ln(TMU)₆ I (ReO₄)₃ Ln = Eu–Lu, Y	IR: In the pentakis complexes ReO_4^- are partially coordinated and in the hexakis they are not coordinated. CONDUCTANCE: 1 : 1 electrolytes in nitromethane.		70
I Ln(ReO₄)₂(TMU)₂ I ReO₄ Ln = La–Sm	IR: ReO_4 – ionic (Td) and bidentate (C_{2v}). CONDUCTANCE: 1 : 1 electrolytes in methanol. X-RAY: a) La, Ce; b) Pr; c) Nd, Sm.		71
I Ln(NCS)₃(TMU)ₙ I n = 5 Ln = La–Nd n = 4 Ln = Sm–Er, Y n = 3 Ln = Tm–Lu	IR: NCS⁻ coordinated through the nitrogen. CONDUCTANCE: practically non-electrolytes in nitromethane and nitrobenzene. X-RAY: Four types of patterns: a) La–Nd; b) Sm–Dy; c) Ho–Er, Y; d) 3TMU.		72
I LnBr₃(TMU)ₙ I n = 7 Ln = La n = 3 Ln = Pr–Er n = 4 Ln = Tm–Lu, Y	CONDUCTANCE: Non-electrolytes in acetonitrile, 1 : 2 in methanol. X-RAY: Three types of patterns: a) La; b) Ce–Er; c) Tm–Lu, Y. ELECTRONIC SPECTRA: Molar absorptivities in acetonitrile and methanol.		73

FORMULAS	PROPERTIES	SYMMETRY AND GEOMETRY	REF.
Ln(TMU)₆ (Ph₄B)₃ Ln = Nd–Er, Y	IR: ν Ln–O at ~210 cm⁻¹. CONDUCTANCE: Close to 1 : 3 electrolytes in nitromethane. TG–DTA curves.	(Nd^{3+}) Octahedral	74 69
Ln(CF₃–SO₃)₃ 5TMU Ln = La-Nd Ln(TMU)₆ (CF₃SO₃)₃ Ln = Sm–Lu, Y	IR: CF₃–SO₃ (La–Nd) in part coordinated; (Sm–Lu, Y) not coordinated. CONDUCTANCE: La–Nd – 1 : 1 electrolytes, Sm–Lu, Y – 1 : 2 electrolytes in nitromethane, 1 : 2 electrolytes in acetonitrile. X-RAY: Different paterns for compounds from La–Sm. Compounds from Eu–Lu, Y, form an isomorphous series. ELECTRONIC SPECTRA (Nd): Central ion not involved in a cubic site. The parameters β, $b^{1/2}$, δ and P in acetonitrile, nitromethane and TMU were determined.	O_h Octahedral	75
Ln(TMU)₆ (PF₆)₃ Ln = La, Pr–Gd, Dy, Er, Y	IR: PF₆⁻ not coordinated; ν Ln–O at ~185 cm⁻¹. CONDUCTANCE: 1 : 3 electrolytes in acetonitrile and nitromethane. ELECTRONIC SPECTRA (Nd) : Central ion in a cubic site. Crystal field parameter $B_0^2 = 107$ cm⁻¹. TG: They decompose giving LnF₃ + 6TMU + 3PF₆.		76 69

TABLE 9

N,N–DIMETHYLACETOACETAMIDE (DMAA)

FORMULAS	PROPERTIES	SYMMETRY AND GEOMETRY (Eu)	REF.
Ln(DMAA)₄ (ClO₄)₃ Ln = La–Lu, Y	IR: ClO₄⁻ not coordinated. ν Ln–O doublet 575-565 cm⁻¹. CONDUCTANCE: 2 : 3 electrolytes in nitromethane. X-RAY: Two types of patterns: a) La–Yb, Y; b) Lu. ELECTRONIC SPECTRA (Nd) : The parameters β, $b^{1/2}$, δ and P in acetonitrile and nitromethane were determined.	D_{2d} Dodecahedron	77 78

TABLE 10

N, N, N', N'–TETRAMETHYLADIPAMIDE (TMAA)

FORMULAS	PROPERTIES	SYMMETRY AND GEOMETRY (Eu)	REF.
Ln(TMAA)ₙ (ClO₄)₃ n = 4 Ln = La–Nd n = 3 Ln = Sm–Lu, Y	IR: ClO₄⁻ not coordinated. ν Ln–O at ~460 cm⁻¹. CONDUCTANCE: 1 : 3 electrolytes in acetonitrile and nitromethane. X-RAY: Two isomorphous series corresponding to the different compositions.	D_{3h}	79 80
La(NO₃)₃(TMAA)₂ Ln₂(NO₃)₆(TMAA)₃ Ln = Ce–Lu, Y	IR: NO₃⁻ coordinated – bidentate (IR + Raman). CONDUCTANCE: La – non-electrolyte in nitromethane, acetonitrile, nitrobenzene and 1 : 1 in methanol; Ce–Lu, Y – 1 : 1 in acetonitrile, nitromethane, nitrobenzene, and 1 : 2 in methanol. X-RAY: Four types of patterns: a) La; b) Ce–Er; c) Tm, Lu; d) Y, Yb. MOLECULAR WEIGHT: cryoscopic in nitrobenzene: La – monomeric; others – dimeric.		81

l Ln(TMAA)$_n$ l(PF$_6$)$_3$ n = 4 Ln = La–Nd n = 3 Ln = Sm–Lu, Y	IR: PF$_6^-$ presents O$_h$ symmetry, is not coordinated. ν Ln–O at ~460 and 350 cm^{-1}. CONDUCTANCE: 1 : 3 electrolytes in acetonitrile and nitromethane. Equivalent conductance in acetonitrile show a behaviour of weak electrolytes. ELECTRONIC SPECTRA (Pr, Nd, Ho, Er): the molar absorptivities were determined.	D$_{3h}$	80
l Ln(NCS)$_2$(TMAA)$_2$ l NCS Ln = La–Lu	IR: NCS – bonded through the nitrogen. ν Ln–O at~430, 330 cm^{-1} and ν Ln–N at~405 cm^{-1}. CONDUCTANCE: Lower than 1 : 1 electrolytes in acetonitrile and 1 : 1 in methanol. X-RAY: Two different types of patterns: a) La; b) Ce–Lu. ELECTRONIC SPECTRA (Nd): The parameters β, b$^{1/2}$, δ were determined.	C$_{4v}$ Octahedral	82

TABLE 11

PHTALIC ACID TETRAMETHYLAMIDE (TMPA)

FORMULAS	PROPERTIES	SYMMETRY AND GEOMETRY (Eu)	REF.
l Ln(TMPA)$_4$ l(ClO$_4$)$_3$ Ln = La–Lu, Y	IR: ClO$_4^-$ not coordinated. CONDUCTANCE: 1 : 3 electrolytes in nitromethane. X-RAY: Four types of patterns: a) La–Nd; b) Sm–Er, Y; c) Tm–Yb; d) Lu. ELECTRONIC SPECTRA (Pr, Nd) : In solid state and methanol.		83

TABLE 12

N, N–DIMETHYLBENZAMIDE (DMBA)

FORMULAS	PROPERTIES	SYMMETRY AND GEOMETRY (Eu)	REF.
l Ln(DMBA)$_6$ l(ClO$_4$)$_3$ Ln = La–Lu, Y	IR: ClO$_4^-$ not coordinated. CONDUCTANCE: 1 : 3 electrolytes in acetonitrile. Between 1 : 2 and 1 : 3 in nitromethane. X-RAY: Three types of patterns: a) La–Pr; b) Sm–Er, Y; c) Tm–Lu.		84
l Ln(NO$_3$)$_3$(DMBA)$_3$ l Ln = La–Lu, Y	IR: NO$_3^-$ coordinated. CONDUCTANCE: Non-electrolytes in nitromethane and acetonitrile. X-RAY: a) La–Sm – are isomorphous; b) others – not grouped.		84

TABLE 13

N, N–DIMETHYLFORMAMIDE (DMF)

FORMULAS	PROPERTIES	SYMMETRY AND GEOMETRY (Eu)	REF.
l Ln(NCS)$_3$(DMF)$_4$ l Ln = Dy–Lu, Y	IR: NCS$^-$ coordinated through the nitrogen. CONDUCTANCE: Non-electrolytes in nitromethane; 1 : 2 in DMF.		85

I Ln(DMF)$_8$ I(PF$_6$)$_3$ Ln = La—Lu, Y	IR: PF$_6^-$ not coordinated (also confirmed by Raman). CONDUCTANCE: 1 : 3 electrolytes in nitromethane. X-RAY: Six types of patterns: a) La; b) Ce—Pr; c) Nd, Sm, Dy—Er, Y; d) Eu; e) Gd, Tb; f) Lu. ELECTRONIC SPECTRA (Nd): The central ion is not envolved in a cubic site. The parameters β, b$^{1/2}$, δ and P in nitromethane were determined.	D$_{2d}$ Dodecahedral	86

TABLE 14

ISONICOTINIC ACID HYDRAZIDE (ISONIAZIDE) (INH)

FORMULAS	PROPERTIES	SYMMETRY AND GEOMETRY (Eu)	REF.
I Ln(INH)$_5$ I(ClO$_4$)$_3$ Ln = La, Pr—Gd	IR: Shifts of ν NH, ν CO and ν NH$_2$ to lower frequencies. ClO$_4^-$ not coordinated (also confirmed by Raman). CONDUCTANCE: 1 : 2 electrolytes in methanol (ion pairs). X-RAY: All compounds are isomorphous. TG—DTA curves. Compounds give the anhydrous perchlorate, than decompose giving LnOCl. ELECTRONIC SPECTRA (Nd) : The parameters β, b$^{1/2}$, δ were determined. The absorption spectrum of Eu^{3+} was also determined.	D$_{4d}$	87
LnCl$_3$.2INH.2H$_2$O Ln = La—Sm, Gd, Dy, Ho, Er, Yb	CONDUCTANCE: 1 : 1 electrolytes in methanol. X-RAY: All compounds are isomorphous.		88
I Ln(INH)$_5$ I$_3$ Ln = La, Nd, Eu, Tb, Ho, Y	IR: ν CO and ν NH$_2$ shift to lower frequencies. Bonding through CO and NH$_2$. CONDUCTANCE: 1 : 2 electrolytes in methanol. ELECTRONIC SPECTRA (Nd) : Nd^{3+} not involved in a cubic site. The parameters β, b$^{1/2}$, δ were determined.	D$_{4d}$	89
I Ln(INH)$_3$(H$_2$O)$_3$ I(NO$_3$)$_3$ Ln = La, Nd, Sm, Gd, Ho, Yb	IR: Coordination through CO and NH$_2$. STRUCTURE: Tricapped trigonal prism with the three water molecules forming the caps.	Tricapped trigonal prism	90

TABLE 15

2,5—PIPERAZINEDIONE (pdo)

FORMULAS	PROPERTIES	SYMMETRY AND GEOMETRY (Eu)	REF.
Ln(ClO$_4$)$_3$.4pdo Ln = La—Er, Y	IR: ClO$_4^-$ (C$_{3v}$ symmetry) — coordination to central ions. δ NH shifts to lower frequencies. X-RAY: All compounds are isomorphous. ELECTRONIC SPECTRA (Nd) : The parameters β, b$^{1/2}$, δ were determined.	D$_4$	91 92
LnI$_3$.4pdo Ln = La—Nd, Eu, Tb, Dy, Y	X-RAY: All compounds are isomorphous. δ NH shifts to higher and δ NH to lower frequencies. ELECTRONIC SPECTRA (Nd) : The parameters β, b$^{1/2}$, δ were determined.	D$_4$	92

TABLE 16

HEXAMETHYL PHOSPHORAMIDE (HMPA)

FORMULAS	PROPERTIES	SIMMETRY AND GEOMETRY (Eu)	REF.
I Ln(HMPA)$_6$ I(ClO$_4$)$_3$ Ln = La–Lu, Y	IR: Small shift of ν PO to lower frequencies. CONDUCTANCE: The values are between that of 1 : 2 and 1 : 3 electrolytes in nitromethane. X-RAY: All compounds are isomorphous.		93
I Ln(HMPA)$_6$ I(Ph$_4$B)$_3$ Ln = Ce, Nd, Eu, Ho, Lu, Y	IR: ν Ln–O is observed at $\approx$ 200 cm^{-1}. CONDUCTANCE: Behaviour close to that of 1 : 3 electrolytes. ELECTRONIC SPECTRA: Nd^{3+} ions are localized in a cubic site.		94 74
I Ln(HMPA)$_6$ I(F$_3$C–SO$_3$)$_3$ Ln = La–Eu I Ln(F$_3$C–SO$_3$)$_2$(HMPA)$_4$ I F$_3$C–SO$_3$ Ln = Nd, Sm–Lu, Y	IR: Compounds with 6 HMPA – F$_3$C–SO$_3$ not coordinated. Tetrakis compounds – two F$_3$C–SO$_3$ bidentate and one not coordinated. CONDUCTANCE: Hexakis complexes: 1 : 3 electrolytes in acetonitrile and 1 : 2 in nitromethane. Tetrakis complexes: 1 : 2 electrolytes in acetonitrile and 1 : 1 in nitromethane. X-RAY: The hexakis complexes form one isomorphous series and the tetrakis a different series. ELECTRONIC SPECTRA (Nd^{3+}) : Hexakis complexes: involved in a nearly cubic site. Tetrakis complexes: similar spectra. The parameters β, b$^{1/2}$, δ and P in acetonitrile and nitromethane were determined.	Hexakis C$_{4v}$ Tetrakis D$_{2d}$	95
I Ln(H$_3$C–SO$_3$)$_3$(HMPA)$_n$ I n = 2 Ln = La–Eu, Y n = 3 Ln = Sm–Lu	CONDUCTANCE: Non electrolytes in methanol. X-RAY: Three isomorphous series: a) La–Eu; b) Y; c) Sm–Lu. ELECTRONIC SPECTRA (Nd): The parameters β, b$^{1/2}$, δ and P in methanol were determined. (Nd) : ions not involved in a cubic site.	2HMPA C$_{3v}$ 3HMPA C$_3$	96

TABLE 17

DIPHENYLPHOSPHINAMIDE (DPPA)

FORMULAS	PROPERTIES	SIMMETRY AND GEOMETRY (Eu)	REF.
I Ln(DPPA)$_6$ IClO$_4$)$_3$ Ln = La–Lu, Y	IR: ClO$_4^-$ not coordinated. CONDUCTANCE: 1 : 3 electrolytes in nitromethane; 1 : 2 in nitrobenzene. X-RAY: Three isomorphous series: a) La, Ce; b) Pr––Eu; c) Gd–Lu, Y. ELECTRONIC SPECTRA (Nd) : The parameters β, b$^{1/2}$, δ and P in nitromethane and acetonitrile were determined. Compounds with hexafluorophosphates present the same shape and P in nitromethane.	O$_h$ – C$_{4v}$ Octaedral	97 98

I Ln Cl$_3$(DPPA)$_n$ I n = 5 Ln = La–Nd n = 4 Ln = Sm–Lu, Y	IR: ν as and ν s NH$_2$ are shifted. Splitting of ν PO is observed. ELECTRONIC SPECTRA (Nd) : The parameters β, b$^{1/2}$ and δ were determined. The central ion is not involved in a cubic site.	C$_{3v}$ monocapped octaedral (polymeric)	99 98
I Ln(NO$_3$)$_3$(DPPA)$_3$ I Ln = La–Ho Ln(NO$_3$)$_3$(DPPA)$_4$ Ln = Er–Lu, Y	IR: NO$_3^-$ coordinated to central ions. CONDUCTANCE: Non-electrolytes in nitrobenzene. La–Ho non--electrolytes in nitromethane. Er–Lu, Y: close to 1 : 1 in nitromethane. ELECTRONIC SPECTRA (Nd) : The parameters β, b$^{1/2}$, δ and P in nitromethane and acetonitrile were determined.	C$_{3v}$ tricapped trigonal prism	99 98
I Ln(DPPA)$_6$ I(PF$_6$)$_3$ Ln = La–Lu, Y	IR: PF$_6^-$ not coordinated. Shifts of ν as and ν s NH$_2$ in accordance with oxygen bonding. CONDUCTANCE: 1 : 3 electrolytes in nitromethane and acetonitrile. X-RAY: Only one serie of isomorphous substances. ELECTRONIC SPECTRA: Molar absorptivities of the compounds of Pr, Nd, Ho, Er in nitromethane and acetonitrile. (Nd) : The central ions are localized in a cubic site. The parameters β, b$^{1/2}$, δ and P in nitromethane and acetonitrile were determined.	C$_{4v}$ octaedral	100 98
I LnBr$_2$(DPPA)$_5$ I Br Ln = La–Lu, Y	IR: Shifts of ν as and ν vs NH$_2$ in accordance with bonding through the oxygen. CONDUCTANCE: Values lower than 1 : 1 electrolytes in nitromethane and acetonitrile and 1 : 2 electrolytes in methanol. X-RAY: Two isomorphous series: a) La, Ce; b) Pr–Lu, Y. ELECTRONIC SPECTRA (Nd) : Central ions not involved in a cubic site. The parameters β, b$^{1/2}$ and δ were determined.	C$_{2v}$	101

TABLE 18

N, N–DIMETHYL–DIPHENYLPHOSPHINAMIDE (DDPA)

FORMULAS	PROPERTIES	SYMMETRY AND GEOMETRY (Eu)	REF.
I Ln(NO$_3$)$_3$ (DDPA)$_3$ I Ln = La, Pr, Nd, Sm, Eu, Er, Y	IR: NO$_3^-$ coordinated. CONDUCTANCE: Non--electrolytes in nitrobenzene. X-RAY: Three different patterns: a) La; b) Pr; c) Sm, Eu, Y. ELECTRONIC SPECTRA (Nd) : The parameters β, b$^{1/2}$, δ and P in acetonitrile were determined.	D$_{3h}$ tricapped trigonal prism	102 103
I Ln(ClO$_4$)$_2$(DDPA)$_4$ IClO$_4$ Ln = La–Lu, Y	IR: ClO$_4^-$ ionic and bidentate. CONDUCTANCE: 1 : 1 electrolytes in nitrobenzene; 1 : 1 (La–Sm); 1 : 2 (Eu–Dy); 1 : 3 (Er–Lu) in nitromethane. X-RAY: Six different types of patterns: a) La–Sm; b) Eu, Gd; c) Tb, Er, Y; d) Tm; e) Yb; f) Lu. ELECTRONIC SPECTRA (Nd) : The parameters β, b$^{1/2}$, δ and P in nitromethane and acetonitrile were determined.	D$_{2d}$ dodecahedron	104 103

FORMULAS	PROPERTIES	SYMMETRY AND GEOMETRY (Eu)	REF.
$\vert Ln(NCS)_3(DDPA)_n \vert$ n = 4 Ln = La–Gd n = 3 Ln = Tb–Lu, Y	IR: NCS⁻ bonded through the nitrogen. CONDUCTANCE: Non-electrolytes in nitromethane and acetonitrile. X-RAY: two series of isomorphism: a) n = 4; b) n = 3. ELECTRONIC SPECTRA (Nd) : The parameters β, $b^{1/2}$, δ and P in acetonitrile were determined.	C_{3v} monocapped trigonal prism or octaedral monocapped	105 103
$\vert Ln(DDPA)_n \vert (PF_6)_3$ n = 6 Ln = La–Nd n = 5 Ln = Sm–Gd	IR: PF_6^- maintains its O_h symmetry, is not coordinated. CONDUCTANCE: 1 : 3 electrolytes in acetonitrile, nitromethane and methanol. X-ray: two types of patterns: a) La–Nd; b) Sm–Gd, ELECTRONIC SPECTRA : The parameters β, $b^{1/2}$, δ and P in acetonitrile and nitromethane were determined.	C_{2v} retangular pyramide (polymeric)	106 103
$\vert Ln(ReO_4)_2(DDPA)_n \vert ReO_4$ n = 2 Ln = La–Tb n = 3 Ln = Dy–Lu, Y	IR: ReO_4^- ionic and bidentade. Ln–O at 445 cm⁻¹. CONDUCTANCE: 1 : 1 electrolytes in acetone and 1 : 2 in methanol. X-RAY: Two series of isomorphism; a) La–Tb; b) Dy–Lu, Y. ELECTRONIC SPECTRA (Nd): Central ion is not located in a cubic site. The parameters β, $b^{1/2}$, and δ were determined.	C_{4v} distorted to C_{2v} distorted bipyramide	107
$\vert LnBr_2(DDPA)_4 \vert Br$ Ln = La–Lu, Y	CONDUCTANCE: values lower to that of 1 : 1 electrolytes in acetonitrile and nitromethane; 1 : 2 in methanol. X-RAY: Three different types of difratograms: a) La–Eu; b) Gd–Dy, Er; c) Ho, Tm–Lu, Y. ELECTRONIC SPECTRA (Nd) : Ln not located in a cubic site.	C_{2v}	108

TABLE 19

TRIPHENYL-PHOSPHINE-OXIDE (TPPO)

FORMULAS	PROPERTIES	SYMMETRY AND GEOMETRY (Eu)	REF.
$Ln(ClO_4)_2(TPPO)_4 \vert ClO_4$	IR: ClO_4^- partially coordinated. CONDUCTANCE: < 1 : 1 electrolytes in nitromethane. ELECTRONIC SPECTRUM (Nd)		109

TABLE 20

DIPHENYL-MONOBENZYL-PHOSPHINE-OXIDE (DPMBPO)

FORMULAS	PROPERTIES	SYMMETRY AND GEOMETRY (Eu)	REF.
$\vert Nd(ClO_4)_2(DPMBPO)_4 \vert ClO_4$	IR: ClO_4^- partially coordinated. CONDUCTANCE: < 1 : 1 electrolytes in nitromethane. ELECTRONIC SPECTRUM (Nd)		109

TABLE 21

MONOPHENYL-DIBENZYL-PHOSPHINE-OXIDE (MPDPPO)

FORMULAS	PROPERTIES	SIMMETRY AND GEOMETRY (Eu)	REF.
I Nd(ClO$_4$)$_2$(MPDPPO)$_4$ IClO$_4$	IR: ClO$_4^-$ partially coordinated. CONDUCTANCE: < 1 : 1 electrolytes in nitromethane. ELECTRONIC SPECTRUM (Nd)		109

TABLE 22

TRIBENZYL-PHOSPHINE-OXIDE (TBPO)

FORMULAS	PROPERTIES	SIMMETRY AND GEOMETRY (Eu)	REF.
I Nd(ClO$_4$)$_2$(TBPO)$_4$ IClO$_4$	IR: ClO$_4^-$ partially coordinated. CONDUCTANCE: < 1 : 1 electrolytes in nitromethane. ELECTRONIC SPECTRUM (Nd)		109

TABLE 23

DIPHENYL-PHOSPHYNIL-MORPHOLIDE (DPPM)

FORMULAS	PROPERTIES	SYMMETRY AND geometry (Eu)	REF.
I Ln(NO$_3$)$_3$(DPPM)$_3$ I Ln = La–Lu, Y	IR: splittings of ν PO and ν PN are observed. NO$_3^-$ coordinated to central ions. ν Ln–O at ~450 cm^{-1}. CONDUCTANCE: non electrolytes in nitromethane and nitrobenzene. X-RAY: only one isomorphous series. ELECTRONIC SPECTRA (Nd): central ion not involved in a cubic site. The parameters β, b$^{1/2}$, δ were determined.	D$_{3h}$ tricapped trigonal prism	110 111
I Ln(NCS)$_3$(DPPM)$_n$ I n = 4 Ln = La–Nd n = 3 Ln = Sm–Lu, Y	IR: splittings of ν PO is observed. NCS$^-$ is bonded through the nitrogen. CONDUCTANCE: non-electrolytes in nitromethane and nitrobenzene. X-RAY: two isomorphous series are observed: a) La–Nd; b) Sm–Lu, Y. ELECTRONIC SPECTRA (Nd) : the parameters β, b$^{1/2}$, δ were determined. Nd^{3+} are not located in a cubic site.	C$_{3v}$ octahedral with distortion	110 111
I Ln(ClO$_4$)$_2$(DPPM)$_4$ I Ln = La–Lu, Y	IR: ClO$_4^-$ partially coordinated. ν Ln–O at~445 cm^{-1}. CONDUCTANCE: 1 : 3 electrolytes in acetonitrile. La, Ce 2 : 1 electrolytes; Pr–Gd between 1 : 1 and 1 : 2 and Tb–Lu, Y 1 : 2 in nitromethane. X-RAY: only one isomorphous series. ELECTRONIC SPECTRA (Nd): the parameter β, b$^{1/2}$, δ were determined. Nd^{3+} not located in a cubic site.	D$_{2d}$	112 111

I LnCl₃(DPPM)₃ I Ln = La—Lu, Y	CONDUCTANCE: non-electrolytes in nitromethane; 1 : 1 in methanol. X-RAY: one isomorphous series. ELECTRONIC SPECTRA (Nd) : the parameters β, $b^{1/2}$, δ were determined. Nd^{3+} : octahedral site with distortion.	C_{3v} octahedral	113 111
I LnBr₃(DPPM)₃ I Ln = La—Tb I LnBr₂(DPPM)₄ I Br Ln = Dy—Lu, Y	CONDUCTANCE: n = 3, non-electrolytes in nitromethane; n = 4, 1 : 1, 1 : 2 electrolytes in methanol; n = 3, non- electrolytes in acetonitrile; n = 4, 1 : 1 in acetonitrile. X-RAY: two isomorphous series: a) La—Tb; b) Dy—Lu, Y. ELECTRONIC SPECTRA (Nd): the parameters β, $b^{1/2}$, δ were determined. Nd^{3+} not located in a cubic site.	C_{3v} trigonal prismatic	113 111

TABLE 24

TRIS (1,2-METHYL) AZIRIDINYL PHOSPHINE OXIDE (TMAPO)

FORMULAS	PROPERTIES	SIMMETRY AND GEOMETRY (Eu)	REF.
I Ln(ClO₄)₂(TMAPO)₄ IClO₄ Ln = La—Tb I Ln(TMAPO)₆ I(ClO₄)₃ Ln = Dy—Lu, Y	IR: ClO_4^- partially coordinated (La—Tb) and not coordinated Dy—Lu, Y; ν Ln—O at ⁻460 cm⁻¹. CONDUCTANCE: 1 : 3 electrolytes in acetonitrile. La—Tb 1 : 2 electrolytes and Dy—Lu, Y 1 : 3 in nitromethane. X-RAY: two isomorphous series: a) La—Tb; b) Dy—Lu, Y. ELECTRONIC SPECTRA: Nd, Ho, Er: molar absorptivities. Nd^{3+} not involved in cubic site. The parameters β, $b^{1/2}$, δ were determined.	C_{4v}	114

TABLE 25

TRIMETHYLPHOSPHINE OXIDE (tmpo)

FORMULAS	PROPERTIES	SYMETRY AND GEOMETRY (Eu)	REF.
I Ln(tmpo)₆ I(ClO₄)₃ Ln = La, Gd, Eu, Lu	IR: ClO_4^- not coordinated. CONDUCTANCE: 1 : 3 electrolytes in nitromethane (Eu). X-RAY; all compouns are isomorphous. ELECTRONIC SPECTRA: the crystal field parameters B_0^4 = 1640 cm⁻¹ and B_4^4 = = 982 cm⁻¹	octahedral symmetry	115
I Ln(tmpo)₆ I(PF₆)₃ Ln = La, Gd, Eu, Lu	IR: PF_6^- not coordinated.		115

TABLE 26

TETRAMETHYLENE-SULFOXIDE (TMSO)

FORMULAS	PROPERTIES	SYMMETRY AND GEOMETRY (Eu)	REF.
$\mid$ Ln(TMSO)$_n$ $\mid$ (ClO$_4$)$_3$ n = 8 Ln = La—Gd n = 7.5 Ln = Tb—Er, Y n = 7 Ln = Tm, Lu	IR: ClO$_4^-$ maintains its T$_d$ symmetry — not coordinated. CONDUCTANCE: 1 : 3 electrolytes in nitromethane. ELECTRONIC SPECTRA (Nd) : The parameters β, b$^{1/2}$, δ were determined. Spectra in nitromethane and solid very similar. Values of P were determined.	D$_{3d}$ bicapped octahedral or bicapped trigonal antiprism	116 117 118
$\mid$ Ln(NO$_3$)$_3$ (TMSO)$_n$ $\mid$ n = 4 Ln = La, Ce n = 3.5 Ln = Pr—Eu n = 3 Ln = Gd—Lu, Y	IR: The number of bands indicate that NO$_3^-$ ions are coordinated. CONDUCTANCE: non-electrolytes in nitromethane. X-RAY: five different patterns were observed: a) La, Ce; b) Pr—Eu; c) Gd—Dy; d) Ho, Y; e) Er—Lu. ELECTRONIC SPECTRA: molar absorptivities in nitromethane (Pr, Nd, Sm, Ho, Er, Tm). Parameters β, b$^{1 \cdot 2}$ and δ and P in nitromethane were recorded (Nd^{3+}).	D$_{3h}$ tricapped trigonal prism (dimer)	119 118
$\mid$ Ln(NCS)$_3$(TMSO)$_4$ $\mid$ Ln = Sm—Lu, Y	IR: NCS$^-$ coordinated through the nitrogen. CONDUCTANCE: non electrolytes in nitromethane. X-RAY: two series of patters: a) Sm—Tm; Y; b) Yb, Lu. C.N.: apparent: 7. ELECTRONIC SPECTRA (Nd) : The parameters β, b$^{1/2}$, and δ were determined.	C$_{3v}$ monocapped trigonal prism	120 118
$\mid$ LnCl$_3$(TMSO)$_n$ $\mid$ n = 2 Ln = La—Nd n = 3 Ln = Sm—Lu, Y	CONDUCTANCE: non eletrolytes in nitromethane (except La—Nd); 1 : 1 eletrolytes in methanol due to dissociative properties of the solvent. Equivalent conductance indicate a behavior of weak electrolytes in methanol. X-RAY: three different isomorphous series: a) La; b) Ce—Nd; c) Sm—Lu, Y. ELECTRONIC SPECTRA (Nd): Parameters β, b$^{1/2}$ and δ were determined.	C$_{3v}$ trigonal prism	121 118
$\mid$ Ln(TMSO)$_{7.5}$ $\mid$ (PF$_6$)$_3$ Ln = La—Lu, Y	IR: PF$_6^-$ maintains its O$_h$ symmetry and is not coordinated. CONDUCTANCE: 1 : 3 electrolytes in nitromethane. X-RAY: two isomorphous series: a) La—Pr; b) Nd—Lu, Y. ELECTRONIC SPECTRA (Nd) : parameters β, b$^{1/2}$ and δ determined and also P in nitromethane.	D$_{3d}$ bicapped octahedral	122 118
$\mid$ LnBr$_2$(TMSO)$_n$ $\mid$ Br n = 7 Ln = La—Yb, Y n = 6 Ln = Lu	CONDUCTANCE: 1 : 1 electrolytes in nitromethane and acetonitrile; 1 : 2 electrolytes in methanol. X-RAY: three isomorphous series: a) La—Ce; b) Pr—Er, Y; c) Tm—Lu. C.N. : apparent: 9 for n = 7 and 8 for n = 6. ELECTRONIC SPECTRA (Nd) : the parameters β, b$^{1/2}$ and were determined.	D$_{3d}$ bicapped octahedral	123 118

FORMULAS	PROPERTIES	SYMMETRY AND GEOMETRY	REF.
$\mid Ln(TMSO)_{7.5} \mid (ReO_4)_3$ Ln = La–Lu, Y	IR: ReO_4 mantains its T_d symmetry – not coordinated. CONDUCTANCE: 1 : 1 electrolytes in nitromethane and acetonitrile due to the existence of ion pairs. X-RAY: three isomorphous series: a) La; b) Ce–Nd; c) Sm–Lu, Y. DSG/TG. ~580°C all ligands are lost; above 570°C sublimation of ReO_7 is observed; ~900°C residues are oxydes.		124
$\mid LnI (TMSO)_5(H_2O)_3 \mid I_2$ Ln = La–Lu, Y	IR: splittings of SO band into two or three bands. CONDUCTANCE: 1 : 2 electrolytes in acetonitrile and nitromethane. X-RAY: only one isomorphous series. C.N.: apparent : 9.	C_3 or C_2	125
$\mid Ln(TMSO)_n \mid I_3$ n = 8 Ln = La–Nd n = 7.5 Ln = Sm–Lu, Y	IR: splittings of SO band are observed in some cases. CONDUCTANCE: close to 1 : 3 electrolytes in nitromethane and acetonitrile. X-RAY: two isomorphous series: a) La–Nd; b) Sm–Lu, Y. C.N.: apparent: 8.	D_{3d} identical to perrhenate and hexafluoro- phosphate	126
$\mid Ln(H_3C–SO_3)_3(TMSO)_3 \mid$ Ln = La–Lu, Y	IR: $H_3C–SO_3$ – lowering of the C_{3v} symmetry- coordinated as bidentade. CONDUCTANCE: non- electrolytes in methanol. X-RAY: five different patters: a) La; b) Ce–Nd; c) Sm–Eu; d) Gd, Tb; f) Er–Lu, Y. TG: loose TMSO given $Ln(H_3C–SO_3)_3 \xrightarrow[-340°C]{N_2} Ln_2S_3$ (part is oxydized to SO_4^{2-}). ELECTRONIC SPECTRA: (Nd) : the parameters β, $b^{1/2}$ and δ were determined. Nd^{3+} is not involved in a cubic site; spectrum in methanol is different from the solid.	D_{3h} distorted tricapped trigonal prism	127 137
$\mid Ln(TMSO)_{7.5} \mid (CF_3\text{-}SO_3)_3$ Ln = La–Lu, Y	IR: $F_3C–SO_3$ mantains its C_{3v} symmetry and is not coordinated. CONDUCTANCE: 1 : 2 eletrolytes in acetonitrile and nitromethane, due to ion-pairs. X-RAY: one isomorphous series. ELECTRONIC SPECTRA (Nd) : the parameters β, $b^{1/2}$ and δ were determined. Spectra in nitromethane and acetonitrile identical to solid; P was determined. OBS:: $\mid Ln(TMSO)_{7.5} \mid X_3$ $X = ClO_4^-$, PF_6^-, I^-, $CF_3SO_3^-$ present the same geometry (probably dimer with one ligand acting as bridge).	bicapped octahedral or bicapped antiprism	117

TABLE 27

THIOXANE-OXIDE (TSO)

FORMULAS	PROPERTIES	SYMMETRY AND GEOMETRY (Eu)	REF.
$\mid Ln(NO_3)_3(TSO)_n \mid$ n = 4 Ln = La–Nd n = 3 Ln = Sm–Lu, Y	IR: splitting of ν SO band. NO_3^- ions coordinated. CONDUCTANCE: non-eletrolytes in nitromethane. C.N.: apparent: 9. ELECTRONIC SPECTRA (Nd) : the parameters β, $b^{1/2}$ and P in nitromethane were determined. Nd^{3+} not involved in a cubic site.	D_{3h} tricapped trigonal prism	128 129

|LnCl$_3$(TSO)$_n$| n = 6 Ln = La–Nd n = 4.5 Ln = Sm–Gd n = 3.5 Ln = Tb–Lu, Y	IR: splitting of ν SO band. CONDUCTANCE: 1 : 1 electrolytes in methanol, due to dissociative properties of the solvent. ELECTRONIC SPECTRA (Nd) : the parameters β, b$^{1/2}$, δ were determined. Nd^{3+} is not in a cubic site.	C_{3v} bicapped trigonal prism (dimer)	128 129
|Ln(ClO$_4$)$_3$(TSO)$_n$| n = 9 Ln = La–Nd n = 8.5 Ln = Sm n = 8 Ln = Eu–Er n = 7 Ln = Tm–Lu, Y	IR: splitting of ν SO band. ClO$_4^-$ mantains its T$_d$ symmetry and are not coordinated. CONDUCTANCE: 1 : 2 electrolytes in nitromethane due to existence of ion-pairs. X-RAY: three types of patterns: a) La–Sm; b) Eu–Er; c) Tm–Lu. ELECTRONIC SPECTRA (Nd): the parameters β, b$^{1/2}$, δ abd P in nitromethane were determined. Nd^{3+} is not involved in cubic site. C.N.: apparent: 8.	D_{3h} bicapped octahedral	130 129
|Ln(NCS)$_3$(TSO)$_n$| n = 5 Ln = La–Dy n = 4 Ln = Ho–Lu, Y	IR: NCS$^-$ is coordinated through the nitrogen. CONDUCTANCE: non-eletrolytes in nitromethane. X-RAY: three isomorphous series: a) La–Dy; b) Ho, Y; c) Yb–Lu. C.N.: apparent: 8 or 7. ELECTRONIC SPECTRA (Nd): the parameters β, b$^{1/2}$, δ and P in nitromethane were determined. Nd^{3+} is not involved in a cubic site.	C_{3v} bicapped trigonal prism	131 129
|Ln(TSO)$_{7.5}$|(PF$_6$)$_3$ Ln = La–Lu, Y	IR: PF$_6^-$ mantains its O$_h$ symmetry and are not coordinated. CONDUCTANCE: 1 : 3 electrolytes in acetonitrile and nitromethane. X-RAY: all adducts are isomorphous. ELECTRONIC SPECTRA (Nd) : the parameters β, b$^{1/2}$, δ and P in nitromethane were determined. Nd^{3+} is not involved in a cubic site.	D_{3d} bicapped octahedral	132 129
|Ln(TSO)$_8$|(PF$_6$)$_3$ Ln = La–Lu, Y	IR: Raman : PF$_6^-$ not coordinated. Ln–O at $\sim$220 cm^{-1}. X-RAY: all compounds are isomorphous. ELECTRONIC SPECTRA: (Nd) : solid and nitromethane solution.		133
|LnBr$_2$(TSO)$_6$|Br Ln = La–Lu, Y	IR: splitting of ν SO band. CONDUCTANCE: 1 : 1 electrolytes in nitromethane and acetonitrile; 1 : 2 in methanol. X-RAY: three different types of patterns: a) La–Tb; b) Dy–Lu; c) Y. ELECTRONIC SPECTRA (Nd): the parameters β, b$^{1/2}$, δ were determined, Nd^{3+} is not involved in a cubic site.	C_{2v} bicapped trigonal prism	123 129
|Ln(ReO$_4$)$_2$(TSO)$_4$|ReO$_4$ Ln = La–Lu, Y	IR: splitting of ν SO band. ReO$_4^-$ are in part coordinated. CONDUCTANCE: 1 : 1 electrolytes in methanol. X-RAY: three different types of patterns: a) La–Pr; b) Nd–Tm, Lu; c) Yb, Y. ELECTRONIC SPECTRA (Nd) : the parameters β, b$^{1/2}$, δ were determined. Nd^{3+} is not involved in a cubic site.	C_{2v} bicapped trigonal prism	134 129

Formula	Properties	Symmetry and Geometry	Ref.
$\lvert Ln(TSO)_n \rvert I_3$ $n = 8.5 \quad Ln = La-Nd$ $n = 7.5 \quad Ln = Sm-Lu, Y$	IR: splitting of SO band. CONDUCTANCE: 1 : 2 electrolytes in acetonitrile and methanol; 1 : 1 in nitromethane (ion-pairs). Equivalent conductance in methanol — behavior of weak electrolytes. X-RAY: existence of two isomorphous series: a) La–Nd; b) Sm–Lu, Y. ELECTRONIC SPECTRA (Nd) : the parameters $\beta, b^{1/2}, \quad \delta$ were determined. Nd^{3+} not involved in a cubic site.	D_{3d} bicapped octahedral	135 129
$\lvert Ln(F_3C-COO)_3(TSO)_3 \rvert$ $Ln = La-Lu, Y$	IR: two types of bonding are proposed: monodentate and bridge. CONDUCTANCE: non-electrolytes in acetonitrile and nitromethane. X-RAY: all isomorphous. ELECTRONIC SPECTRA (Nd) : the parameters $\beta, b^{1/2}, \delta$ were determined. Nd^{3+} not involved in a cubic site.	D_{2d} dodecahedral	136
$\lvert Ln(H_3C-SO_3)_3(TSO)_3 \rvert$ $Ln = La-Lu, Y$	IR: $H_3C-SO_3^-$: more than one type of bonding is suggested. CONDUCTANCE: non electrolytes in methanol. X-RAY: three different patters: a) La–Gd; b) Tb, Dy; c) Ho–Lu, Y. ELECTRONIC SPECTRA (Nd) : the parameters $\beta, b^{1/2}, \delta$ and P in methanol were determined. Nd^{3+} not involved in a cubic site. Spectra in methanol identical to $Nd(CH_3SO_3)_3 . 3H_2O$ and $Nd(CH_3SO_3)_3$.	D_{2d} or trigonal point groups	137

TABLE 28

TRANS-1, 4-DITHIANE-1, 4-DIOXIDE (TDTD)

FORMULAS	PROPERTIES	SYMMETRY AND GEOMETRY (Eu)	REF.
$\lvert La(TDTD)_5(H_2O)_5 \rvert (ClO_4)_3$ $\lvert Ln(TDTD)_6(H_2O)_3 \rvert (ClO_4)_3$ $Ln = Nd, Tb, Er, Lu, Y$	IR: splitting of ν SO. ClO_4^- mantains its T_d symmetry and is not coordinated. X-RAY: two types of patterns: a) La; b) Nd, Tb, Er, Lu, Y.		138
$\lvert Ln(TDTD)_4(H_2O)_4 \rvert (PF_6)_3$ $Ln = La-Lu, Y$	IR: PF_6^- mantains its O_h symmetry and is not coordinated, CONDUCTANCE: 1 : 3 electrolytes in water. X-RAY: all compounds are isomorphous.		139

TABLE 29

DIPHENYL-SULFOXIDE (dpso)

FORMULAS	PROPERTIES	SYMMETRY AND GEOMMETRY (Eu)	REF.
$\lvert Ln(dpso)_7 \rvert (ClO_4)_3$ $Ln = Sm, Eu, Yb.$	IR: ClO_4^- mantains its T_d symmetry and is not coordinated. C.N.: apparent : 7.	C_{3v} except for $^5D_0 \rightarrow {}^7F_0$	140

I Eu(dpso)₇ I (PF₆)₃	IR: PF₆⁻ not coordinated. (O_h symmetry). C.N. : apparent : 7.	C_{3v} except for $$^5D_0 \rightarrow {}^7F_0$$	140

TABLE 30

1,4-DITHIANE-MONOSULFOXIDE (DTMSO)

FORMULAS	PROPERTIES	SYMMETRY AND GEOMETRY (Eu)	REF.
I Ln(DTMSO)₈ I(ClO₄)₃ Ln = La, Nd I Ln(DTMSO)₇(H₂O)₂ I(ClO₄)₃ Ln = Tb, Er, Yb, Y	IR: ClO₄⁻ not coordinated; T_d symmetry. ν Ln−O at ~500 cm⁻¹. CONDUCTANCE: La, Nd, Tb, Y: 1 : 2 electrolytes; Er, Yb close to 1 : 3 in nitromethane. Low values attributed to ion-pairs. X-RAY: two types of diagrams: a) La, Nd; b) Tb, Er, Yb, Y.		141
I Ln(DTMSO)ₙ I (PF₆)₃ n = 8 Ln = La−Nd, Y n = 7.5 Ln = Sm−Tm n = 6.5 Ln = Yb−Lu	IR: PF₆⁻ not coordinated (O_h symmetry). ν Ln−O at ~500 cm⁻¹. CONDUCTANCE: 1 : 3 electrolytes in nitrometane and acetonitrile. DTA: curves are presented. Melting points and decomposition temperature. ELECTRONIC SPECTRA (Nd) : the parameters β, $b^{1/2}$, δ are presented. Nd^{3+} not involved in a cubic site.	D_{3d} distorted bicapped octahedral (dimer)	142

TABLE 31

DIMETHYLSULFOXIDE (DMSO)

FORMULAS	PROPERTIES	SYMMETRY AND GEOMETRY (Eu)	REF.
I Ln(DMSO)ₙ I(PF₆)₃ n =~7.5 Ln = La−Gd n =~7 Ln = Tb, Dy, Y	IR: PF₆⁻ ionic (O_h symmetry) CONDUCTANCE: 1 : 3 electrolytes in nitromethane.		143
I Ln(NO₃)₃ (DMSO)ₙ I n = 4 Ln = La, Nd n = 3 Ln = Er, Yb, Lu also dmso d₆	IR: NO₃⁻ bidentate ligand, according to several criteria. ν Ln−O: between 230−180 cm⁻¹.		144
I Ln(DMSO)₈ I (ReO₄)₃ Ln = La−Lu, Y	IR + Raman: ReO₄⁻ is not coordinated (T_d symmetry). CONDUCTANCE: 1 : 1 in intromethane − interaction with solvent. Obs. Comparative Study − capacity of coordination ReO⁻₄>ClO⁻₄>PF⁻₆		145

TABLE 32

DI-N-BUTYL-SULFOXIDE (Bu₂SO)

FORMULAS	PROPERTIES	SYMMETRY AND GEOMETRY (Eu)	REF.
I Ln(Bu₂SO)₆ I(ClO₄)₃ Ln = La–Lu, Y	IR: ClO₄⁻ not coordinate (T$_d$ symmetry with small distortion). CONDUCTANCE: between 1 : 2 and 1 : 3 electrolytes in nitromethane; 1 : 3 electrolytes in acetonitrile. X-RAY: two types of patterns: a) La; b) Ce–Lu, Y		146

TABLE 33

PENTAMETHYLENESULFOXIDE (pmso)

FORMULAS	PROPERTIES	SYMMETRY AND GEOMETRY (Eu)	REF.
I Ln(pmso)₇ I(ClO₄)₃ Ln = La–Lu	IR: ClO₄⁻ not coordinated (T$_d$ symmetry). ν Ln – ligand ~230–306 cm⁻¹. CONDUCTANCE: 1 : 3 electrolytes in acetonitrile between 1 : 2 and 1 : 3 in nitromethane. X-RAY: three isomorphous series: a) La, Ce; b) Tb, Dy, Ho, Er, Y; c) Tm–Lu. The others presented different patterns. ELECTRONIC SPECTRA (Nd, Er).		147

TABLE 34

PYRAZINE-N-OXIDE (pyzNO)

FORMULAS	PROPERTIES	SYMMETRY AND GEOMETRY (Eu)	REF.
I La(pyzNO)₇(H₂O)₂ IClO₄)₃ I Ln(pyzNO)₈ I(ClO₄)₃ Ln = Pr, Eu, Er, Y	IR: ClO₄⁻ not coordinated (Td symmetry). CONDUCTANCE: 1 : 3 electrolytes in acetonitrile, 1 : 2 in nitromethane (ion-pairs). ELECTRONIC SPECTRA (Nd): The parameters β, $b^{1/2}$, δ and P in acetonitrile were determined. The central ion is not involved in a cubic side.	D$_{3d}$ Bicapped octahedral	148 149
I LnCl₃(pyzNO)ₙ I n = 2 Ln = La n = 2.5 Ln = Pr, Eu n = 3 Ln = Er, Y	IR: (La) single ν NO band, the others present splittings. CONDUCTANCE: 1 : 1 electrolytes in methanol (dissociative properties). X-RAY: Three types of patterns: a) La; b) Pr, Eu; c) Er, Y. ELECTRONIC SPECTRA (Nd) : The central ion is not involved in a cubic site. The parameters β, $b^{1/2}$, δ were determined.	C$_{2v}$ C$_2$ or C$_s$	150 149
I Ln(pyzNO)₈ I(PF₆)₃ Ln = La, Pr, Eu, Er, Y	IR: Splitting ν NO band is observed. PF₆⁻ (small distortion due to solid state, not coordinated). CONDUCTANCE: 1 : 3 electrolytes in acetonitrile and nitromethane. X-RAY: All compounds are isomorphous. ELECTRONIC SPECTRA (Nd) : The central ion is not involved in a cubic site. The parameters β, $b^{1/2}$, δ and P in acetonitrile were determined.	D$_{3d}$ Bicapped octahedral	150 149

$LnI_3 \cdot 3pyzNO \cdot 8H_2O$ Ln = Ce, Nd, Eu, Tb, Yb, Y	CONDUCTANCE: 1 : 2 electrolytes in acetonitrile and methanol. X-RAY: All compounds are isomorphous. ELECTRONIC SPECTRA (Nd) : The central ion is not involved in a cubic site. The parameters β, $b^{1/2}$, δ were determined.	D_{2d} distorted	151
$|Ln(NO_3)_3(pyzNO)_3|$ Ln = La–Lu, Y	IR: NO_3^- – bidentate. CONDUCTANCE: Non-electrolytes in nitromethane and acetonitrile. X-RAY: Three types of patterns: a) La–Eu; b) Gd–Tm; c) Yb, Lu. ELECTRONIC SPECTRA (Nd) : The central ion is not involved in a cubic site. The parameters β, $b^{1/2}$, δ and P in acetonitrile were determined.	D_{3h} Tricapped trigonal prism	152 149
$|Ln(NCS)_3(pyzNO)_4|$ Ln = La–Lu, Y	IR: NCS^- – coordinated through the nitrogen. CONDUCTANCE: Non electrolytes in acetonitrile. ELECTRONIC SPECTRA (Nd) : The central ion is not involved in a cubic site. The parameters β, $b^{1/2}$, δ and P in acetonitrile were determined.	C_{3v} Monocapped trigonal prism	153 149
$|Ln(pyzNO)_6(H_2O)_3|(CF_3SO_3)_3$ Ln = La, Ce, Nd, Sm, Eu, Tb, Er, Tm, Y	IR: The anion is not coordinated. CONDUCTANCE: Non-eletrolites in nitromethane, 1 : 2 in acetonitrile (ion-pairs). X-RAY: Two types of patterns: a) La, Ce; b) Nd, Sm, Eu, Tb, Er, Y. ELECTRONIC SPECTRA (Nd): The central ion is not envolved in a cubic site. The parameters β, $b^{1/2}$, δ and P in acetonitrile and nitromethane were determined.	C_{3v} Tricapped trigonal prism	154

TABLE 35

PYRAZINE-1,4-DIOXIDE (pyzdo)

FORMULAS	PROPERTIES	SYMMETRY AND GEOMETRY (Eu)	REF.
$|Ln(pyzdo)_4|(ClO_4)_3$ Ln = La, Pr, Eu, Er, Y	IR: ClO_4^- not coordinated (Td symmetry). Polymeric species. X-RAY: All compounds are isomorphous.		155

TABLE 36

2,6-LUTIDINE-N-OXIDE (2,6-LNO)

FORMULAS	PROPERTIES	SYMMETRY AND GEOMETRY (Eu)	REF.
$|Ln(NO_3)_3(2,6-LNO)_4|$ Ln = Y, La, Nd, Gd, Er	IR: Splitting of ν NO band. NO_3^- are coordinated. ν Ln–O at ~490 cm^{-1}. CONDUCTANCE: Non-electrolytes in nitromethane and acetonitrile, 1 : 1 in methanol. X-RAY: Three types of patterns: a) La; b) Nd, Gd; c) Er, Y.		156

$\vert Ln(2,6\text{-}LNO)_8 \vert (ClO_4)_3$ Nd = Y, La, Nd, Gd, Er	IR: Splittings of ν NO band. ClO_4^- not coordinated $(T_d$ symmetry). ν Ln–O at ~490 cm^{-1}. CONDUCTANCE: 1 : 3 electrolytes in nitromethane and acetonitrile, 1 : 2 in methanol (ion-pairs). X-RAY: Two types of patterns: a) La, Nd; b) Gd, Er, Y.	156
$\vert LnCl_3(2,6\text{-}LNO)_3 \vert$ Ln = Y, La, Nd, Gd, Er	IR: Splitting of ν NO band. ν Ln–O at ~490 cm^{-1}. CONDUCTANCE: 1 : 1 electrolytes in methanol. X-RAY: Two types of patterns: a) La, Nd; b) Gd, Er, Y.	156

TABLE 37

TRIETHYLENEDIAMINE-N-OXIDE (TEDANO)
1,4-diaza-bicyclo ı 2,2,2 ı octane-N-oxide

FORMULAS	PROPERTIERS	SYMMETRY AND GEOMETRY (Eu)	REF.
$\vert Ln(TEDANO)_n \vert (ClO_4)_3$ n = 7 Ln = La–Nd n = 6 Ln = Sm–Lu, Y	IR: ν NO – small shift to higher frequencies in relation to the hydrated ligand. ν CN – practically unaltered. ClO_4^- not coordinated. CONDUCTANCE: 1 : 3 electrolytes in acetonitrile. X-RAY: All compounds are isomorphous.		157
$\vert Ln(TEDANO)_n \vert (PF_6)_3$ n = 5 Ln = La–Tb, Y n = 4.5 Ln = Dy–Er n = 4 Ln = Tm, Lu	IR: ν NO – small shift to higher frequencies; ν CN practically unaffected. PF_6^- – not coordinated. CONDUCTANCE: 1 : 3 electrolytes in acetonitrile and nitromethane. X-RAY: Three types of patterns: a) La–Tb, Y; b) Dy–Er; c) Tm, Lu.		157

TABLE 38

TRIETHYLENEDIAMINE-DIOXIDE (TEDADO)
1,4-diaza-bicyclo ı 2,2,2 ı octane-1,4-dioxide

FORMULAS	PROPERTIES	SYMMETRY AND GEOMETRY (Eu)	REF.
$\iota Ln(TEDADO)_3(H_2O)_3 \iota (ClO_4)_3$ Ln = La, Pr–Lu, Y	IR: ν NO practically unaffected. ClO_4^- not coordinated (Td symmetry). CONDUCTANCE: 1 : 3 in water. X-RAY: All compounds are isomorphous.		158
$\vert Ln(TEDADO)_{2.6}(H_2O)_2 \vert (PF_6)_3$ Ln = La–Lu, Y	IR: ν NO practically unaffected. PF_6^- not coordinated (Oh symmetry). CONDUCTANCE: 1 : 3 in water. X-RAY: Very poorly crystalline.		159

TABLE 39

2-PICOLINE-N-OXIDE (2-picNO)

FORMULAS	PROPERTIES	SYMMETRY AND GEOMETRY (Eu)	REF.

Compound	Properties	Geometry	Ref
$\|Ln(2\text{-picNO})_7(H_2O)_n\|(ClO_4)_3$ $n = 3$ Ln = La–Tm, Y $n = 2$ Ln = Yb, Lu	IR: ClO_4^- not coordinated (Td symmetry). CONDUCTANCE: 1 : 3 electrolytes in acetonitrile. X-RAY: Two isomorphous series: a) La–Tm, Y; b) Yb, Lu. ELECTRONIC SPECTRA (Nd): The parameters β, $b^{1/2}$, δ and P in nitromethane were determined.	C_{3v} Monocapped trigonal prism	160 161
$\|Ln(NO_3)_3(2\text{-picNO})_3\|$ Ln = La–Lu, Y	IR: NO_3^- bidentate (confirmed by Raman). CONDUCTANCE: Non electrolytes in acetonitrile and nitromethane. X-RAY: Four types of patterns: a) La; b) Pr, Nd (two crystalline forms); c) Ce–Lu, Y; d) Ho, Yb (two forms). ELECTRONIC SPECTRA (Nd): The parameters β, $b^{1/2}$, δ and P in nitromethane were determined.	D_{3h} Tricapped trigonal prism	162 161
$\|LnCl_3(2\text{-picNO})_3(H_2O)_2\|$ Ln = La, Pr, Nd, Eu–Ho	IR: Splittings of ν NO band attributed to solid effects. CONDUCTANCE: 1 : 1 electrolytes in methanol. X-RAY: Two types of patterns: a) Nd, Tb ; b) La, Pr, Eu, Gd, Dy, Ho. ELECTRONIC SPECTRA (Nd) : The central ion is not involved in a cubic site. The parameters β, $b^{1/2}$, δ were determined.	C_3 or C_{3v} Bicapped trigonal prism	163 161
$\|Ln(NCS)_3(2\text{-picNO})_n\|$ $n = 5$ Ln = La–Pr $n = 4$ Ln = Nd–Eu $n = 3$ Ln = Eu–Lu, Y	IR: Splittings of ν NO band are observed in some cases. NCS$^-$ — coordinated through the nitrogen. CONDUCTANCE: Non electrolytes in acetonitrile. X-RAY: Three types of patterns: a) La–Pr; b) Nd–Eu; c) Eu–Lu, Y. ELECTRONIC SPECTRA (Nd) : The central ion is not involved in a cubic site. The parameters β, $b^{1/2}$, δ and P in nitromethane were determined.	C_{3v} Monocapped trigonal prism	164 161
$\|Ln(2\text{-picNO})_n\|(PF_6)_3$ $n = 7$ Ln = La–Sm $n = 6$ Ln = Sm–Lu, Y	IR: PF_6^- not coordinated (Oh symmetry). CONDUCTANCE: 1 : 3 electrolytes in acetonitrile and nitromethane. X-RAY: Two isomorphous series: a) La–Sm; b) Sm–Lu, Y. ELECTRONIC SPECTRA (Nd) : The central ion is not involved in a cubic site. The parameters β, $b^{1/2}$, δ and P in nitromethane were determined.	D_{2h} Rhombic	165
$\|NdBr_3(2\text{-picNO})_5\|$ $\|NdI_3(2\text{-picNO})_5\|$	ELECTRONIC SPECTRA (Nd): the parameters β, $b^{1/2}$, δ were determined. The central ion is not involved in a cubic site in both cases.	C_{3v} Bicapped trigonal prism	161
$\|Ln(ReO_4)_3(2\text{-picNO})_n\|$ $n = 5$ Ln = La, Nd, Eu $n = 4$ Ln = Tb, Er, Y $n = 3$ Ln = Nd, Eu	IR: ReO_4^- bands at 905, 870 and 285 cm^{-1}. X-RAY: Three isomorphous series: a) La, Nd, Eu; b) Tb, Er, Y; c) Nd, Eu. ELECTRONIC SPECTRA (Nd) : The central ion is not involved in a cubic site. The parameters β, $b^{1/2}$, δ were determined.	5(2-picNO) C_{3v}-Bicapped trigonal prism 3(2–picNO) C_{3v}–Trigonal prism	166

	$H_3C-SO_3^-$ – a lowering of the C_{3v} symmetry is	C_3	167
I Ln(H$_3$C–SO$_3$)$_3$(2-picNO)$_n$ I n = 2 Ln = Ce–Sm n = 4 Ln = La, Lu, Y	observed; the anion is coordinated. CONDUCTANCE: Non-electrolytes in methanol. X-RAY: n = 2 one isomorphous series; n = 4 four types of patterns: a) La; b) Ce–Tb; c) Dy–Yb; d) Lu. ELECTRONIC SPECTRA (Nd) : Central ion is not involved in a cubic site. The parameters β, $b^{1/2}$, δ were determined. The spectrum is modified in methanol.	Tetracapped trigonal prism	

TABLE 40

3-PICOLINE-N-OXIDE (3-picNO)

FORMULAS	PROPERTIES	SYMMETRY AND GEOMETRY (Eu)	REF.
⊣Ln(3-picNO)$_8$ I(PF$_6$)$_3$ Ln = La–Lu, Y	IR: PF$_6^-$ not coordinated (Oh symmetry). CONDUCTANCE: 1 : 3 electrolytes in nitromethane and acetonitrile. Equivalent conductance – weak electrolyte behaviour (ion pairs in concentrated solutions). X-RAY: All compounds are isomorphous. ELECTRONIC SPECTRA (Nd) : The central ion is not involved in a cubic site. The parameters β, $b^{1/2}$, δ were determined. The molar absorptivities in nitromethane and acetonitrile are the same at different concentrations.	D_{2d} with distortion to D_{4d}	168

TABLE 41

ELECTROCHEMICAL STUDIES

SPECIES	RESULTS	REF.
Eu(III)/Eu(II)	The Eu(III)/Eu(II) in aqueous formamide solutions, by current reversal chrono potentiometry at a mercury pool electrode, in 1M NaClO$_4$ was investigated. Double layer effects must be considered rather than in solvation effects when explaining the influence of formamide on the Eu(III)/Eu(II) electrode reactions.	169
	The influence of the temperature of the diffusion coeficient of Eu(III) in aqueous formamide solutions was studied. The solution viscosity is the main reason for the changes of the diffusion coeficient. The values of solvodinamic radii and activation evergy for diffusion are also determined.	170
	The electrochemical behavious in aqueous ethyleneglycol was investigated at several temperatures. Kinetic parameters for the charge transfer reaction and activation energies for diffusion and visosity were determined.	171
Yb(III)	The electrochemical behaviour of Yb(III) in perchlorate media was studied by cyclic voltametry and current reversal chronopotentiometry at several temperatures. The results show that the reversible electrochemical reduction of Yb^{3+} is followed by homogeneous reactions. Diffusion coeficients and activation energy were determined.	172

Eu(III)
Sm(III)
Yb(III)

Electrochemical reduction in propylene carbonate by cyclic voltametry
was investigated. Reaction proceed in two stages due to the formation
of divalent ions. The influence of the water content in the stability of
Sm^{2+} is analysed, since Sm^{2+} is partly oxidised by water. The stability
of the divalent species decreases in the order $Eu^{2+} > Yb^{2+} > Sm^{2+}$.

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CONTRIBUIÇÃO AO ESTUDO DA ESTRUTURA, REATIVIDADE E QUÍMICA BIOINORGÂNICA DO FERRO

Henrique Eisi Toma
Instituto de Química
Universidade de São Paulo
Caixa Postal 20780, São Paulo, SP

1. Introdução

Nas últimas décadas tem sido notável o desenvolvimento da química inorgânica, particularmente nas áreas de bioinorgânica, reatividade e catálise. Esse desenvolvimento se fez sentir em nosso país, com o aparecimento de novos grupos e a dinamização do intercâmbio científico com outras nações. Na USP, o estudo da reatividade de compostos inorgânicos teve grande impulso, sob supervisão de Henry Taube, ao longo dos sete anos de duração do programa NAS-CNPq. Coube a John Malin, em 1970, a missão de implantar no Instituto de Química da USP, o primeiro laboratório de cinética rápida do país, trazendo da Universidade de Stanford, a pesquisa fundamental que notabilizou Henry Taube. Nos três anos em que permaneceu no Brasil, Malin nucleou um pequeno grupo, formado por Toma, Pereira e Coelho. Na segunda metade do programa NAS-CNPq a interação de pesquisadores brasileiros com a escola de Taube foi igualmente importante e produtiva. Essa interação possibilitou a consolidação do laboratório de reações inorgânicas na USP, e a formação de novos grupos, atualmente localizados em São Carlos, Araraquara, Ribeirão Preto e Fortaleza.

O presente artigo é dedicado ao cinquentenário da USP. Nele procuramos focalizar alguns aspectos da química inorgânica e biológica do ferro, numa tentativa de compor uma visão integrada dos nossos trabalhos nesse campo, nos últimos dez anos de atividade. Em seu espírito imbuímos uma singela homenagem a Henry Taube, Prêmio Nobel de Química de 1983. [1]

2. Interações π em complexos – A química dos cianoferratos

O desenvolvimento da química de coordenação separou naturalmente os compostos considerados clássicos dos compostos organometálicos. Na primeira classe o metal apresenta características típicas de ácidos de Lewis, e interage preferencialmente com ligantes doadores de pares eletrônicos. Nos compostos organometálicos, o caráter de base de Lewis do íon metálico é acentuado em função do abaixamento do estado de oxidação, aumentando a afinidade por ligantes insaturados. Ions metálicos com características intermediárias entre as dessas duas classes eram relativamente pouco estudados até o final da década de 60. Explorando de forma sistemática a química das aminas de rutênio, Taube foi pioneiro na química de fronteira entre os compostos clássicos e os organometálicos. [3] Em 1967, Taube surpreendia a comunidade científica relatando a formação direta de complexos com nitrogênio molecular, espécie considerada inerte até então. [4,5] Seus trabalhos mais expressivos nesse campo concentraram-se inicialmente na química de complexos de rutênio [6-8] com ligantes nitrogenados e insaturados, expandindo-se gradualmente para a química do ósmio. [9]

Apesar do ferro ser um elemento extremamente importante, nosso interesse pelos seus compostos somente veio a ser despertado com os trabalhos com rutênio, iniciados na USP em 1970. Nessa época, um dos temas em investi-