NOVEL NEUTRAL IRON(II) ISOCYANIDE MALEONITRILE DITHIOLATE [Fe(S$_2$C$_2$(CN)$_2$)(*t*-BuNC)$_4$] COMPOUND

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NOVEL NEUTRAL IRON(II) ISOCYANIDE MALEONITRILE DITHIOLATE [Fe(S$_2$C$_2$(CN)$_2$)(*t*-BuNC)$_4$] COMPOUND. FeBr$_2$ reacts with the S$_2$C$_2$(CN)$_2^{2-}$ ion (1:1 ratio) in the presence of an excess of *t*-BuNC in THF to give the mixed ligand [Fe(S$_2$C$_2$(CN)$_2$)(*t*-BuNC)$_4$] compound. This neutral product with a formal oxidation state of two for the iron atom was characterized by conductivity measurements, and, i.r., Mössbauer, ^{13}C and ^{1}H n.m.r. spectroscopy. There is a Fe-C π back-donation strengthened towards isocyanide ligands, according to the data of ^{13}C, ^{1}H n.m.r. and Mössbauer spectroscopy.

Keywords: iron (II); isocyanide; dithiolate.

INTRODUCTION

The chemistry of iron mononuclear[1-8], polynuclear[9-16], dithiolates, and iven incipient mixed dithiolate-isocyanide iron derivatives[17], is usually restricted to formal iron(III) and iron(IV) compounds[3,13,18]. Since isocyanide ligand has both donor-acceptor proprieties, it is inherent that the covalent bonding character and the delocalization of the electron density into dithiolate transition iron compounds will be enhanced in their presence[19,20]. Hence, metal centers are also stabilized in both low and high oxidation states by isocyanides. Stable dithiolate-isocyanide iron(II) derivatives are an opened research field. In this paper, therefore, the synthesis and the characterization of dithiolate-isocyanide iron(II) species are described.

EXPERIMENTAL PART

Experiments were performed under argon atmosphere, using standard Schlenk techniques to avoid oxidation of the products. The solvents were dried and distilled under O$_2$-free argon prior to use. The compounds *t*-BuNC[21], FeBr$_2$[22] and Na$_2$(S$_2$C$_2$(CN)$_2$)[23], were prepared as previously described.

I.r. spectra were obtained on Midac Prospect IR FT-IR instruments, using KBr pellets or Nujol mulls. ^{1}H and ^{13}C n.m.r. spectra were recorded upon either BRÜKER AC300P (^{1}H 300.13, ^{13}C 75.47) Fourier-transform machine in CDCl$_3$ unless otherwise stated. ^{1}H and ^{13}C spectra were referenced to internal SiMe$_4$. Melting points were recorded on a Büchi 510 apparatus and are uncorrected. Elemental analyses (C, H, N) were performed on a Perkin Elmer 2400 microanalytical instrument. Iron was determined by 1,10-phenantroline method, using a Varian Cary 1 spectrophotometer. Conductivities were measured at 25 ºC using a HANNA Instruments HI 8033 conductivity bridge and standard cell. For the Mössbauer measurements, the usual transmission geometry was employed, with an Ortec multichannel system PC board, using 512 channels, as the

data counting. The source was a nominal 10 mCi ^{57}Co in a Pd or Rh matrix and the results are quoted relative to standard metallic Fe. Thermogravimetric (TG) curves were recorded using a Shimadzu TGA-50H thermal analyser system. The samples (with initial mass around 12 mg) were heated in alumina crucible under either argon or oxygen flow (20.0 cm^3/min) at a heating rate of 2.0 ºC/min. The differential thermogravimetric (DTG) curves were computationally derived from the TG curves.

Preparation of [Fe(S$_2$C$_2$(CN)$_2$)(*t*-BuNC)$_4$]

Small portions of Na$_2$(S$_2$C$_2$(CN)$_2$) (0.320 g, 1.72 mmol) were added to a stirred solution of FeBr$_2$ (0.316 g, 1.46 mmol) in THF (20 cm^3). The stirring mixture was refluxed for 1h at 70 ºC and added *t*-BuNC (0.90 cm^3, 7.3 mmol). After 1h, THF was removed under reduced pressure and the resulting solid was dissolved in CHCl$_3$ (20 cm^3), and filtered through a column of Florisil (1 cm). The solvent was removed *in vacuo* and the residue dissolved in THF (8 cm^3). Concentration to ca. 4 cm^3 and dropwise addition of Et$_2$O (10 cm^3) gave a dark red precipitate, which was washed with Et$_2$O/PhH (1:1) (3 x 2 cm^3 portions), and vacuum-dried. Yield 95 %. M.p. 180.5 ºC, dec. (Found: C, 54.0; H, 6.8; Fe, 11.1; N, 15.4. C$_{24}$H$_{36}$S$_2$FeN$_6$ calcd.: C, 54.5; H, 6.9; Fe, 10.6; N, 15.9%).

RESULTS AND DISCUSSION

The dithiolate-isocyanide iron(II) [Fe(S$_2$C$_2$(CN)$_2$)(*t*-BuNC)$_4$] complex was prepared from iron(II) bromide, as illustrated in Scheme 1.

$$FeBr_2 + Na_2S_2C_2(CN)_2 + 4 \; t\text{-BuNC} \longrightarrow$$
$$[Fe(S_2C_2(CN)_2)(t\text{-BuNC})_4] + 2 \; NaBr$$
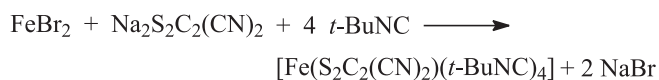
Scheme 1. *Reaction in THF at 70 ºC*

The product was reasonably air-stable in solid state at room temperature. However, it decomposes slowly in acetone and THF solutions. However due to its insolubility in hydrocarbon solvents it

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was well crystallized as intense colored solids in these solvents. The thermogravimetric results in Table 1 suggest that occur a fragmentation process, in accord to Scheme 2.

Table 1. TG data of the product

Step	Temperature (°C) Initial - final	Lost Mass (calcd.) (mg)	Lost residue
1	152.5 – 217.6	2.24 (2.23)	$4t$-BuNC-7/4O$_2$[a]
2	217.6 – 631.6	1.30 (1.29)	$CS_2 + N_2 + 2CO$
3	900	0.72 (0.74)	Fe_2O_3C[b]

[a]acquired element; [b]residue at 900 °C

The isocyanide ligands are initially displaced during the initial fragmentation process. This behavior reflects the great abundance and a weak covalency of the isocyanides with the metallic center. In the temperature set between 152.5 – 217.6 °C, the iron atom is probable oxidized by oxygen molecule.

The i.r. spectral data together the attempts of the attributions in the stretching frequency region for the product are listed in Table 2. The $\nu(CN)$ positions were observed near those observed in $S_2C_2(CN)_2^{2-}$ precursor (2195 cm^{-1}) and in free isocyanide (2134 cm^{-1})[2]. Since both sulfur and carbon bonded atoms of the dithiolate and isocyanide ligands are strong donor toward iron center. Therefore, the net charge will be compensated by an increasing in the π back-donation towards these ligands. A weak shoulder observed around 2060 cm^{-1} can be attributed to the usual combination effect[24]. A strong band at 1371 cm^{-1} observed in a lower region was assigned to a perturbed C=C (w_1) stretching vibration[1], owing to the electron delocalization upon dithiolate coordination with the iron atom. However, other small bands (w_2 and w_3) in the 1240-600 cm^{-1} region

were not attributed, because they were obscured by skeleton vibration of t-BuNC molecule.
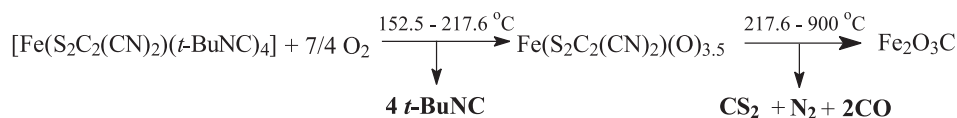
The ^{13}C n.m.r. spectral data are listed in Table 3, and the spectra in Figure 1. Although ^{13}C n.m.r. spectra of isocyanides is problematic[27], the most of all expected ^{13}C resonances of t-BuNC were detected and assigned, including the very weak carbon quaternary Fe-$\underline{C}$ signals. The most significant spectral feature is a downfield shift for the $\underline{C}N$ resonance (ca. 5 ppm) of t-BuNC after the coordination. The decrease in shielding observed correlates with the increase in iron-isocyanide π back-donation. The presence of two duplet signals for each carbon 1 and 2 in the spectrum (Figure 1) is compatible with occupation of axial and equatorial position relative to the dithiolate moiety.

The ^1H n.m.r. spectral data of the product are presented in the Table 3. The spectrum has shown a singlet downfield resonance referenced to the free ligand, as it was observed in the ^{13}C n.m.r. spectrum.

The conductivity data in acetone presented in Table 2 are typical of non-electrolyte compound, which assures a neutral identity for the product.

The ^{57}Fe-Mössbauer spectra obtained for the compound are shown in Figure 2. The isomer shifts (δ) and quadrupole splittings (ΔE_Q) parameters are presented in Table 2.

The isomer shift value observed for the product is ca. 0.0 mm s^{-1}, in contrast to that value observed for the iron(II) bromide precursor in its Mössbauer spectrum. Such results demonstrate, as expected, a higher s-electron density in the iron atom after dithiolate and isocyanide coordinations[29]. Moreover, this result is consistent with a back-donation increment from the iron(II) in the product relative to the iron(II) bromide precursor. Finally, the ΔE_Q similar values for the product and for the $FeBr_2$ are an indication that both compounds have a near octahedral configuration around the iron site. The product

$$[Fe(S_2C_2(CN)_2)(t\text{-BuNC})_4] + 7/4\ O_2 \xrightarrow{152.5\ -\ 217.6\ ^{\circ}C} Fe(S_2C_2(CN)_2)(O)_{3.5} \xrightarrow{217.6\ -\ 900\ ^{\circ}C} Fe_2O_3C$$

$$\textbf{4}\ \textit{t}\textbf{-BuNC} \qquad\qquad \mathbf{CS_2 + N_2 + 2CO}$$

Scheme 2. Thermal decomposition for [Fe(S$_2$C$_2$(CN)$_2$)(t-BuNC)$_4$]

Table 2. I.r. spectral data[a], Mössbauer spectral parameter[b] and molar conductivity[c]

Compound	$[S_2C_2(CN)_2]^{2-}$ $\nu(CN)$, cm^{-1}	t-BuNC $\nu(CN)$, cm^{-1}	$[S_2C_2(CN)_2]^{2-}$ $\nu(C=C)$, cm^{-1}	δ	ΔE_Q	Γ	T (K)	Λ	Ref.
$[Fe(S_2C_2(CN)_2)(t\text{-BuNC})_4]$	2200 w sh, 2182s	2140vs br	1371s	0.070	0.684	0.31	12	0.76	
$Na_2(S_2C_2(CN)_2)$	2195s		1438s						
t-BuNC		2134s							25
$[Fe(S_2C_2(CN)_2)]$[d]				0,333	2.710	0.30	84		
$FeBr_2$				1,34	1,043		78		26

[a]Recorded on KBr pellets; [b]All data in mm s^{-1}, relative to room temperature natural-abundance α-Fe foil; [c]All data in Ω^{-1}cm^2 mol^{-1} on Me$_2$CO solutions (ca. 10^{-3} M), 25 °C; [d]unpublished results.

Table 3. ^{13}C and ^1H n.m.r. spectral data for $[Fe(S_2C_2(CN)_2)(t\text{-BuNC})_4]$ and t-BuNC in CDCl$_3$ solution

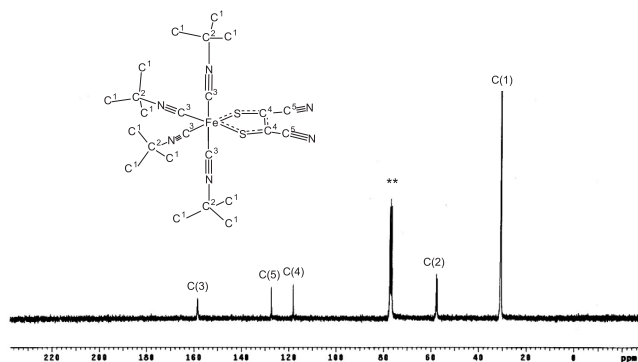| Compound	Assignment, δ/p.p.m.(intensity)						Ref.
	CNC($\underline{C}H_3)_3$	CN$\underline{C}$(CH$_3)_3$	$\underline{C}$NC(CH$_3)_3$	$S_2\underline{C}_2$(CN)$_2$	$S_2C_2(\underline{C}N)_2$	CNC(C$\underline{H}_3)_3$	
$[Fe(S_2C_2(CN)_2)(t\text{-BuNC})_4]$	30.56	57.33	158.51	118.15	127.93	1.44	
	30.82	57.77					
t-BuNC	30.3	54.1	153.2			1.17	28

Figure 1. *¹³C n.m.r. spectrum for [Fe(S₂C₂(CN)₂)(t-BuNC)₄]. All hydrogen atoms have been omitted for clarity*
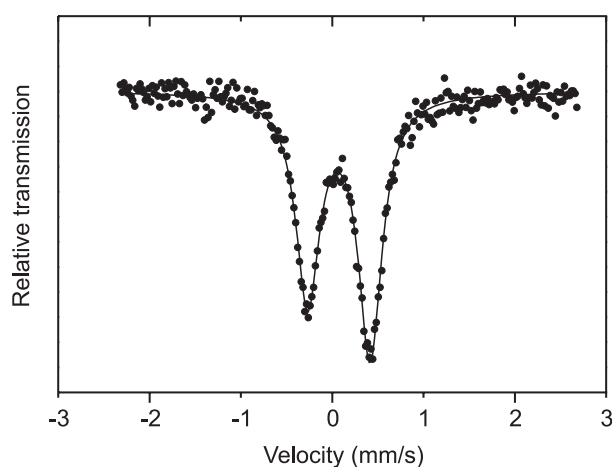
Figure 2. *Mössbauer spectra at 12 K for [Fe(S₂C₂(CN)₂)(t-BuNC)₄]*

exhibits a small spectral asymmetry in the intensity (Figure 2). This asymmetry can be resulted from the solid state effect, due to slightly distinct iron sites in the molecules.

CONCLUSION

A novel iron(II) compound, $[Fe(S_2C_2(CN)_2)(t\text{-}BuNC)_4]$ was obtained from the reaction of $FeBr_2$ with $Na_2S_2C_2(CN)_2$ in excess of t-BuNC in THF. The π-acceptor nature of the dithiolate and isocyanide ligands was studied by the n.m.r. (¹³C and ¹H) and Mössbauer spectroscopy, owing to an increase of the chemical shift and a decrease of the isomer shift, respectively.

ACKNOWLEDGMENTS

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