The Mössbauer Effect and Chemistry. Part 8.[1] The Spectra of Some Bis(*NN*-dialkyldithiocarbamato)halogeno(nitrosyl)iron Complexes

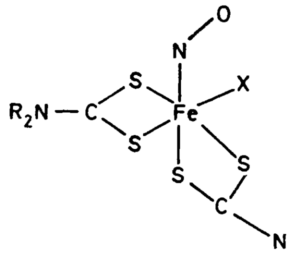
By **Brian W. Fitzsimmons** * and **Allan R. Hume**, Department of Chemistry, Birkbeck College, Malet Street, London WC1E 7HX

A number of bis(*NN*-dialkyldithiocarbamato)halogeno(nitrosyl)iron complexes has been prepared by standard and new methods. These compounds have been characterised by magnetic susceptibility measurements, and by Mössbauer and i.r. spectroscopy. The application of magnetically perturbed Mössbauer spectroscopy to one example, $[Fe(S_2CNEt_2)_2(NO)I]$, has revealed a *cis*-octahedral geometry. Other examples have similar quadrupole splittings and hence have this geometry also.

BÜTTNER and FELTHAM[2] prepared two examples of a series of octahedral iron(II) complexes having the formula $[Fe(S_2CNR_2)_2(NO)X]$ (X = halogen, S_2CNR_2 = *NN*-dialkyldithiocarbamate) by oxidative addition of the appropriate halogen to the well known square-pyramidal bis(*NN*-dialkyldithiocarbamato)nitrosyliron complexes[3] (Scheme 1). The stereochemistry in solution of these halogeno(nitrosyl) complexes was investigated by ^1H n.m.r. and they were assigned as *cis*-octahedral complexes on the basis of spectra which were consistent with two protonic environments (I). Since they show these well resolved n.m.r. spectra, these complexes are diamagnetic in solution at least and are thus examples of low-spin octahedral iron(II) complexes.

$$[Fe(S_2CNR_2)_2(NO)] + \tfrac{1}{2}X_2 \longrightarrow [Fe(S_2CNR_2)_2(NO)X]$$

SCHEME 1



(I)

We wished to study this family further for a number of reasons, three of which can be listed. First, a study of the Mössbauer spectra of the solid complexes seemed appropriate since we have long been interested in the Mössbauer parameters of low-spin iron(II) complexes.[4] Secondly, it has been revealed in several studies[5] that the overall physical properties of metal dithiocarbamate complexes are very sensitive to the nature of the substituent R in the S_2CNR_2 chelate, and thirdly, we wished to determine the sign of the principal component of the electric-field-gradient tensor and to use the magnitude of the asymmetry parameter as a guide to the structure of the solid complexes.

EXPERIMENTAL

Preparation of Compounds.—Sodium dithiocarbamates. The sodium salts of the dithiocarbamates were prepared following the procedure of Gleu and Schwab:[6]

$$NRR'H + CS_2 + Na[OH] \longrightarrow Na[S_2CNRR'] + H_2O$$

Bis(NN-*disubstituted dithiocarbamato*)*iron nitrosyls*, $[Fe(S_2CNR_2)_2(NO)]$. With minor modifications, the straightforward procedure described by Adams and Raynor[7] was adopted for the preparation of these compounds:

$$[Fe(OH_2)_6]^{2+}(aq) + 2[H_3O]^{+}(aq) + [NO_2]^{-}(aq) + 2[S_2CNR_2]^{-}(aq) \longrightarrow [Fe(S_2CNR_2)_2(NO)]\,(c) + 9H_2O$$

An aqueous solution of sodium nitrite (5.2 g, 0.075 mol in 30 cm^3 of water) was mixed with an acidic solution of iron(II) sulphate (13.9 g $Fe[SO_4]\cdot 7H_2O$, 0.05 mol in 100 cm^3 of 0.5 mol dm^{-3} sulphuric acid). This was followed immediately by the addition to the mixture of an aqueous solution of the appropriate sodium dithiocarbamate salt (0.1 mol in 100 cm^3 water). Vigorous stirring was maintained for 3 min. The product was extracted into dichloromethane (2 × 50 cm^3), and the brown extracts were filtered and mixed with an equal volume of methanol. After allowing this mixture to stand in a solid CO_2–acetone bath for 2 h, the crude brown product was filtered off. Recrystallisation, using the same solvent system, provided moderate yields (45% of the diethyl derivative, 13% of the morpholinyl one) of the desired dark green crystalline products.

Both the distilled water and the sulphuric acid used in the preparation of the solutions were boiled and cooled in an atmosphere of nitrogen prior to their use. Analytical data are listed in Table 1.

Bis(NN-*disubstituted dithiocarbamato*)*iodo*(*nitrosyl*)*iron complexes*, $[Fe(S_2CNR_2)_2(NO)I]$. These compounds were prepared following the procedure due to Büttner and Feltham:[2]

$$[Fe(S_2CNR_2)_2(NO)] + \tfrac{1}{2}I_2 \xrightarrow{\text{ethanol}} [Fe(S_2CNR_2)_2(NO)I]$$

Attempted recrystallisation of the products from benzene–diethyl ether mixtures, as described in ref. 2, tended to yield oily materials which required extended periods of vacuum desiccation before solid products could be recovered. Dissolving the crude products in boiling ethanol, filtration, then addition of water until the onset of precipitation, followed by cooling and slow evaporation of the solvent into the air, was found to yield crops of well formed crystals. The recrystallised products were washed with water (2 × 25 cm^3) and dried under vacuum at room temperature. Analytical data and yields based on parent nitrosyl complexes are listed in Table 2.

Bromobis(NN-*disubstituted dithiocarbamato*)*nitrosyliron complexes*, $[Fe(S_2CNR_2)_2(NO)Br]$. The procedure given in ref. 2 was found to yield products which gave excessively high halogen analyses. The following procedure was found to yield greater quantities of purer product.

A methanolic suspension of the bis(dithiocarbamato)-nitrosyliron parent complex (0.01 mol in 200 cm^3) was stirred vigorously in an open beaker for 2 h with 20 cm^3 of

TABLE 1

Analytical, Mössbauer spectral, magnetic susceptibility, and infrared spectral results for the compounds $[Fe(S_2CNR_2)_2(NO)]$

R_2	Yield (%)	Analysis (%) [a]				Mössbauer parameters [b]		10^{-6} Paramagnetic susceptibility [c]	$\mu_{eff.}$ (20 °C)	$\tilde{\nu}$(N–O)/cm^{-1}
		C	H	N	S	ΔE	δ_{Fe}			
Me_2	44	22.15 (22.1)	3.65 (3.70)	12.5 (12.9)	40.1 (39.25)	1.04	0.52	1 538 (1 525)	1.92 (1.89)	1 688
Et_2	45	31.3 (31.4)	5.30 (5.25)	10.9 (11.0)	33.65 (33.5)	0.85	0.41	1 315 (1 476)	1.95 (1.87)	1 685
Pr^n_2	47	38.25 (38.35)	6.45 (6.45)	9.30 (9.60)	29.1 (29.25)	0.75	0.37	1 297	1.91	1 680
Pr^i_2	51	37.85 (38.35)	6.45 (6.45)	9.30 (9.60)	29.15 (29.25)	0.75	0.38	1 199	1.89	1 690
Bu^n_2	29	44.2 (43.7)	7.25 (7.30)	8.20 (8.50)	26.55 (25.9)	0.72	0.34	1 808	2.07	1 705
$[CH_2]_4$	32	31.6 (31.75)	4.35 (4.25)	10.9 (11.1)	34.25 (33.85)	0.97	0.43			1 693
$[CH_2]_5$	21	35.85 (35.45)	5.05 (4.95)	9.80 (10.35)	32.3 (31.55)	0.87	0.42	(1 377)	1.81	1 694
$CHMe[CH_2]_4$	38	39.45 (38.7)	5.45 (5.55)	9.10 (9.70)	30.4 (29.5)	0.85	0.35	1 525	1.90	1 695
$CHMe[CH_2]_3CHMe$	22	41.65 (41.55)	6.20 (6.05)	8.70 (9.10)	27.3 (27.7)	1.00	0.45	2 520	2.45	1 695
$[CH_2]_2O[CH_2]_2$	13	29.1 (29.25)	4.00 (3.9)	10.3 (10.25)	30.3 (31.2)	0.74	0.44	1 686	2.01	1 712
$(C_6H_{11})_2$	30	51.35 (52.15)	7.40 (7.35)	6.80 (7.00)	22.25 (21.4)	0.73	0.35	1 577	1.93	1 702
$(CH_2Ph)_2$	28	58.25 (57.15)	4.50 (4.45)	6.40 (6.65)	21.0 (20.3)	0.58	0.35	2 335	2.35	1 720
PhMe	23	42.4 (42.65)	3.25 (3.55)	9.55 (9.35)	29.05 (28.45)	0.89	0.44	1 580 (1 720)	1 94 (2.05)	1 710

[a] Calculated values are given in parentheses. [b] Spectra measured at 77 K. ΔE and δ are in mm s^{-1} and δ is relative to natural ion. Values are accurate to ±0.02 mm s^{-1}. [c] Values in parentheses are those of L. Cambi and L. Szego, *Chem. Ber.*, 1931, **64**, 2591.

49% hydrobromic acid. The resulting brown solution was filtered and slowly mixed with an equal volume of water. The light brown microcrystalline product was collected by suction filtration, washed with water (3 × 100 cm^3), and vacuum desiccated at room temperature over silica gel. The yield of the bromobis(*NN*-diethyldithiocarbamato)-nitrosyliron complex prepared in this way was 48% based on the parent complex.

Attempted preparation of chlorobis(NN-*disubstituted dithiocarbamato*)*nitrosyliron complexes.* The substitution of concentrated hydrochloric acid for hydrobromic acid in the procedure described for the preparation of the bromine analogues of these compounds resulted in the formation of brown methanolic solutions, from which, by careful addition of water, light brown solid materials could be precipitated. However, on standing in air, or being subjected to vacuum desiccation at room temperature, these compounds, invariably, rapidly became oily. Subjecting these oils to extended periods of vacuum desiccation, recrystallisation attempts from a variety of different solvent systems, and cooling to 78 K all proved to be useless in promoting crystallisation.

TABLE 2

Analytical, Mössbauer spectral, magnetic susceptibility, and infrared spectral results for the compounds $[Fe(S_2CNR_2)_2(NO)X]$

X	R_2	Analysis (%) [a]				Mössbauer parameters [b]		$10^{-6}\chi_M$/c.g.s. units	$\mu_{eff.}$ (20 °C)	$\tilde{\nu}$(N–O)/cm^{-1}
		C	H	N	S	ΔE	δ			
I	Me_2	16.4 (15.9)	2.75 (2.65)	9.05 (9.25)	29.4 (28.25)	1.23	0.23	358	0.92	1 829
Br	Et_2	26.1 (25.95)	4.40 (4.35)	8.95 (9.10)	27.8 (27.7)	1.25	0.20	129	0.56	1 813
I	Et_2	23.1 (23.6)	4.05 (3.95)	8.05 (8.25)	26.05 (25.15)	1.23	0.23	247	0.77	1 805
I	Pr^n_2	29.35 (29.75)	5.00 (4.95)	7.05 (7.45)	22.5 (22.65)	1.31	0.25	182	0.66	1 814
I	Pr^i_2	29.35 (29.75)	5.00 (4.95)	7.05 (7.45)	22.5 (22.65)	1.18	0.27	82	0.44	1 810
I	$[CH_2]_4$	23.05 (23.75)	3.40 (3.15)	7.70 (8.30)	25.4 (25.35)	1.16	0.29	264	0.80	1 804
I	$[CH_2]_5$	27.15 (27.0)	3.90 (3.75)	7.70 (7.90)	23.35 (24.0)	1.21	0.24	522	1.12	1 812
I	$CHMe[CH_2]_3CHMe$	32.65 (32.6)	4.55 (4.75)	6.90 (7.15)	21.4 (21.75)	1.17	0.23			1 814
I	$(C_6H_{11})_2$	43.1 (43.05)	6.00 (6.05)	5.15 (5.80)	16.9 (17.65)	1.21	0.23	292	0.83	1 812
I	$(CH_2Ph)_2$	48.1 (47.55)	3.55 (3.70)	5.05 (5.55)	17.8 (16.9)	1.21	0.26	339	0.98	1 818

[a] Calculated values are given in parentheses. [b] Values are in mm s^{-1} and spectra were measured at 77 K. δ is relative to natural iron.

Instrumental Techniques.—Mössbauer spectra were measured using an Elcint function generator in conjunction with a Meda 1024-channel multichannel analyser. The detector used was a Harwell Research proportional counter and the ^{57}Co(Pd) source was provided by the Radiochemical Centre, Amersham. The magnetically perturbed Mössbauer spectra were obtained at 4.2 K using a B.O.C. SCM4 helium cryostat fitted with a superconducting magnet. Spectral data were processed using the London University CDC 6600 and University College, London, IBM 360 computers. The programs used included one written by Lang and Dale [8] for fitting the magnetically perturbed spectra. Infrared spectra were recorded as Nujol mulls using a Perkin-Elmer 457 grating spectrometer. Magnetic moments were measured at room temperature using the Guoy method. The equipment consisted of a modified Oertling laboratory analytical balance and a Mullard type EE 1002 electromagnet fitted with 4-in diameter pole pieces; Hg[Co(CNS)$_4$] was used as a calibrant and the diamagnetic corrections used in the calculations of $\mu_{\text{eff.}}$ were those given in ref. 9.

RESULTS AND DISCUSSION

Using standard methods we prepared a wide range of the parent five-co-ordinate square-pyramidal nitrosyls.[3] Although a definitive study of the Mössbauer spectra of one example {[Fe(S$_2$CNEt$_2$)$_2$(NO)]} has been carried out,[10] the parameters for such a range have not been collected together before. These parameters, together with some i.r. spectral data and magnetic susceptibility results, are in Table 1. Although the chemical isomer shifts fall into a narrow range, the quadrupole splittings vary somewhat with the hydrocarbon groups attached to the nitrogen atom. This is not unexpected since the overall V_{zz} is a difference between the lattice and valence contribution. Whilst the former contribution can be assumed to dominate in this stereochemistry, the latter will be sensitive to orbital splittings and hence to the nature of the attached chelate.

The products obtained by oxidative addition of halogen to the parent nitrosyls are listed in Table 2. Although the iodides [Fe(S$_2$CNR$_2$)$_2$(NO)I] could be prepared in reasonable yield by direct addition of iodine (Scheme 1), the bromides analysed badly and gave very high bromine figures. Mössbauer spectroscopy indicated that these impure products contained the tetrabromoferrate(III) ion. A milder oxidising system was selected on the basis of electrochemical considerations and this gave good yields in the case of the diethyl derivative. The overall reaction is depicted in Scheme 2. In all, some nine iodides and one bromide were prepared. Some of these compounds showed a tendency to crystallise as 1 : 1 solvates with benzene; this is a feature of dithiocarbamate chemistry,[11] but here solvent-free samples could be readily prepared without any accompanying decomposition. The magnetic susceptibility measurements reveal that all these iron complexes are diamagnetic as the Bohr magneton numbers lie in the range 0.44—1.12. Low-spin d^6 compounds are expected to show some temperature-independent paramagnetism: this gives rise to a small susceptibility of $\sim 100 \times 10^{-6}$ c.g.s. units.[12] Here, small amounts of impurity may have raised the observed moments.

$$2[\mathrm{Fe(S_2CNR_2)_2(NO)}] + 2[\mathrm{H_3O}]^+ + 2\mathrm{Br}^- + \tfrac{1}{2}\mathrm{O_2} \longrightarrow 2[\mathrm{Fe(S_2CNR_2)_2(NO)Br}] + 3\,\mathrm{H_2O}$$

SCHEME 2

The i.r. stretching frequencies of the N–O group in the halogeno-complexes is some 100—120 cm^{-1} to higher wavenumbers than in the parent nitrosyls: this is to be expected as there will be a reduction in Fe–NO π back bonding in the oxidised complexes as the number of d electrons is reduced.

Inspection of the Mössbauer spectral parameters reveals that the oxidation process is associated with a significant reduction in chemical isomer shift. The results presented here refer to an Fe$^{\mathrm{I}}$–Fe$^{\mathrm{II}}$ family: they indicate that the change in configuration from $3d^7$ to $3d^6$ reduces δ by an average of 0.22 mm s^{-1}.

Turning attention to the observed quadrupole splittings, it is immediately clear that a family of uniform stereochemistry is under observation. Changes in either halogen or in alkyl or aryl group in the chelate have no effect on the overall geometry of the [Fe(S$_2$CNR$_2$)(NO)X] complexes. The most direct evidence as to the nature of the stereochemistry comes from the magnetically perturbed Mössbauer spectra. The Figure shows such a spectrum for the iodo-derivative with the S$_2$CNEt$_2$ ligands. The solid line is the theoretical spectrum calculated assuming a Hamiltonian of the form: [8]

$$\mathscr{H} = \mathscr{H}_0 + \frac{eQV_{zz}}{4}\left[\hat{I}_z{}^2 - \frac{5}{4} + \frac{\eta}{3}(\hat{I}_x{}^2 - \hat{I}_y{}^2)\right] - g\mu_{\mathrm{N}}I \,.\, B$$

where Q is the electric quadrupole moment of the $I = \frac{3}{2}$ state of ^{57}Fe, η is the asymmetry parameter given by $(V_{xx} - V_{yy})/V_{zz}$, I is the spin quantum number, μ is the nuclear magneton, g the nuclear g factor, and B the magnetic flux density. The details of the best fit for the spectrum shown in the Figure are as follows:

B	ΔE	δ	$\Gamma_{\frac{1}{2}}$	η
2.52	+1.2 mm s^{-1}	0.25 mm s^{-1}	0.27 mm s^{-1}	0.82

The high value for the asymmetry parameter is the most immediately useful result since this establishes a *cis* stereochemistry for this complex. A *trans* structure would be expected to have an almost axially symmetric electric field gradient with an essentially zero asymmetry parameter. Since ΔE is fairly constant throughout the series it is clear that this stereochemistry is uniform. The high asymmetry parameter, of itself, proves that NO and halogen are quite different in their quadrupole-splitting strength and that these strengths are themselves different from that exerted by the sulphur atoms. Nothing further about these relative quadrupole-splitting strengths can be adduced but the *cis* structure is now firmly established for the solid complexes.

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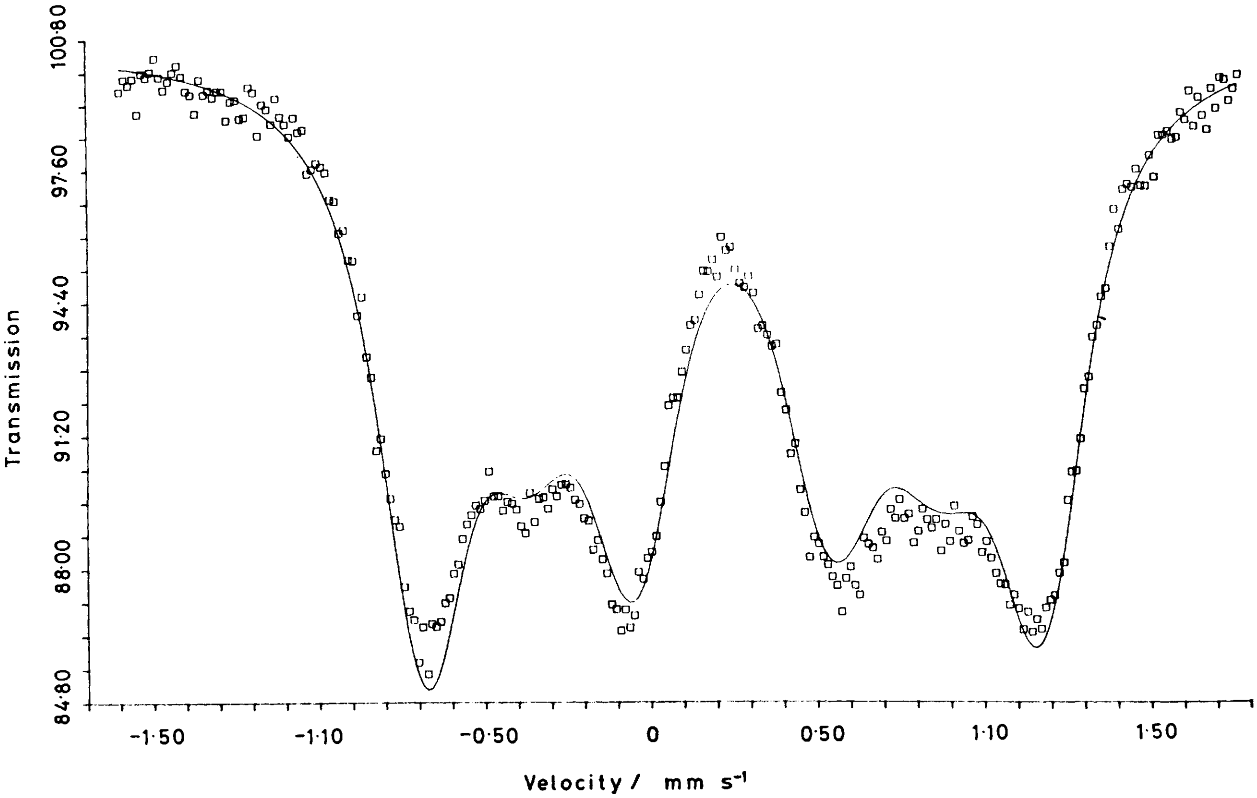

Mössbauer spectrum of [$Fe(S_2CNEt_2)_2(NO)I$] at 4.2 K in an applied magnetic field with a flux of 2.52 T. The solid line is calculated using the parameters listed in the text

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