Reinvestigation of Some Iron Dinitrosyl Complexes with Thio-ligands

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The complexes formed when thio-ligands react with $[Fe(NO)_2X]_2$ have been reinvestigated. E.s.r. and Mössbauer evidence are presented which show that the complexes should be formulated as $Fe(NO)_2LX$ rather than $[Fe(NO)_2L]^+X^-$ as originally proposed.

FROM both chemical and biochemical points of view, transition-metal complexes containing the nitric oxide ligand have aroused much interest and their structures and properties have been extensively reviewed.[1,2] E.s.r. studies of aqueous solutions of Fe^{II} salts in contact with nitric oxide have been reported.[3,4] The structures of the complexes formed in solution were inferred, from electron-nuclear hyperfine interactions, to have the formulation $Fe(NO)_2L_2$, where L represents a unidentate ligand. Other workers have carried out Mössbauer studies on related compounds such as $Fe(NO)_2(CO)_2$,[5] $Fe(NO)_2(Ph_3P)_2$, $Fe(NO)_2(Ph_3P)Br$, *etc.*[6] Iron nitrosyl bis-dithiolates [7] and bis-dithiocarbamates [8] have also been investigated by Mössbauer spectroscopy. These latter complexes have a square pyramidal geometry with the dithiolate and dithiocarbamate ligands forming five- and four-membered chelating rings, respectively with the Fe: the four sulphur atoms form the base of the pyramid with the nitrosyl group at the apex.

Recently, Hieber and Kaiser [9] reported that $[Fe(NO)_2Br]_2$ reacted with thioamides and other ligands to form paramagnetic complexes which were formulated as $[(ON)_2FeL]^+Br^-$, where L behaves as a bidentate ligand and completes the tetrahedral arrangement about the iron. Our interest in these complexes lay in the fact that they were apparently the first examples of a thioamide functioning in a bidentate fashion. In such complexes, delocalisation of the metal electrons over the four membered $\overline{\mathrm{Fe{\cdot}S{:}C{\cdot}N}}$ ring is possible and it was of interest to see how such a delocalisation would compete against the NO ligand which can behave as a very strong π-acceptor. Since Mössbauer spectroscopy is an extremely useful probe for obtaining information about the immediate iron environment,[10] and because e.s.r. has been invaluable in providing structural information on paramagnetic iron nitrosyl complexes,[3,4,6] we have reinvestigated Hieber and Kaiser's complexes [9] with these techniques.

On the basis of our results, we conclude that these compounds have been incorrectly formulated [9] and do not contain a bidentate thioamide group. The complexes are, however, examples of iron tetrahedrally co-ordinated by two nitrosyl groups, a thioamide (unidentate) and a halogen.

EXPERIMENTAL

The complexes were prepared according to the procedures of Hieber and Kaiser [9] and analytical and i.r. data indicated that the compounds were identical to those reported by these authors.

Mössbauer spectra were recorded on equipment previously described.[11] The system was calibrated with sodium nitroprusside as a standard and all shifts are referred to this as having zero isomer shift. Samples contained 10 mg Fe/cm^2 and all spectra were computer fitted to Lorentzian line shapes.

I.r. spectra in the 400—4000 cm^{-1} range were recorded using a Perkin-Elmer 337 or Beckman IR5. Spectra in the 200—400 cm^{-1} region were recorded using a Beckman IR12. Samples were prepared as mulls or as solutions in tetrahydrofuran.

E.s.r. spectra were recorded using a JES-3B5-X spectrometer at *X*-band frequency with 100 KHz/s field modulation, and the spectra were calibrated using an external standard of Mn^{2+} in MgO.

RESULTS AND DISCUSSION

Hieber and Kaiser [9] have concluded that the complexes of the type $Fe(NO)_2XL$, where X = Br or I, and L = thioamide (ta), have the thioamide functioning as a chelating ligand. The evidence for this formulation was based largely on a comparison of the i.r. bands in the 400—4000 cm^{-1} region of the free and complexed ligand. Spectra which we have obtained in this region confirm the general formulation for these complexes. Although we, like the previous workers,[9] find a shift in $\nu_{C=S}$ on complex formation indicating that the thioamide is co-ordinated through sulphur, we found no shift in the ν_{NH} or δ_{NH_2} vibrations on going from the free ligand to the complex. We take this to mean that the amide nitrogen is not co-ordinated to the metal. However, it should be pointed out that, our data were obtained in solution rather than in the solid state and the structures of the complexes could be different in solution, with a solvent molecule occupying the site formerly taken by the $:NH_2^-$ group in the solid state.

Far-i.r. spectra were recorded in an attempt to obtain information about the metal–ligand linkages. The spectra of these complexes, together with those of $[Fe(NO)_2Br]_2$ and $[Fe(NO)_2I]_2$ are summarised in the

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[2] W. P. Griffith, *Adv. Organometallic Chem.*, 1960, **7**, 211.

[3] C. C. McDonald, W. D. Phillips, and H. F. Mower, *J. Amer. Chem. Soc.*, 1965, **87**, 3319.

[4] L. Burlamacchi, G. Martini, and E. Tiezzi, *Inorg. Chem.*, 1969, **8**, 2021.

[5] P. A. Mazak and R. L. Collins, *J. Chem. Phys.*, 1969, **51**, 3220.

[6] J. P. Crow, W. R. Cullen, F. G. Herring, J. R. Sams, and R. L. Tapping, *Inorg. Chem.*, 1971, **10**, 1616.

[7] T. Birchall and N. N. Greenwood, *J. Chem. Soc.* (*A*), 1969, 286.

[8] C. F. Johnson, R. Richards, and H. A. O. Hill, *J. Chem. Phys.*, 1969, **50**, 2394.

[9] W. Hieber and K. Kaiser, *Z. anorg. Chem.*, 1968, **358**, 271.

[10] N. N. Greenwood and T. C. Gibb, 'Mössbauer Spectroscopy,' Chapman and Hall, London, 1971.

[11] T. Birchall, *Canad. J. Chem.*, 1964, **47**, 1351.

Table. All the compounds show bands in the region of 300 cm^{-1} which are attributed to Fe–NO vibrations. These bands are generally weak and broad and are observed in both the mull and solution spectra: for $[Fe(NO)_2I]_2$ no bands were visible in this region in the mull spectrum. The compounds all show absorption at 200—250 cm^{-1} which is the region normally expected for Fe–S or Fe–Cl(Br) vibrations, and since these vibrations usually are very strongly coupled[12,13] it is not possible to assign the bands specifically. The Fe–I stretch should occur at much lower frequency than 200 cm^{-1} and hence less interaction would be expected with the vibrations in the 200—250 cm^{-1} region and simpler spectra should result. This is observed for $[Fe(NO)_2Br]_2$ and $[Fe(NO)_2I]_2$ and for $Fe(NO)_2(tu)Br$ and $Fe(NO)_2(tu)I$ (tu = thiourea) with the iodo complexes having simpler spectra in the 200—250 cm^{-1} region. All the complexes except those involving *o*-aminothiophenol (atp) have a band in the solution spectra at *ca.* 400 cm^{-1}, which is not present in the mull spectra. This could well arise from an interaction between the complex and the solvent and indeed such an interaction in the case of the $[Fe(NO)_2X]_2$ compounds is supported by the e.s.r. evidence.[6] On the basis of the data in the Table, it is not possible to ascertain whether the amide ligands are co-ordinated to iron through both the S and the N, but the data do seem to suggest that the halogen may well be co-ordinated. This throws considerable doubt on the proposed structures.[9]

All the complexes studied, except the dinitrosyl iron halide dimers, are paramagnetic in the solid state. Solutions of $[Fe(NO)_2X]_2$ are also paramagnetic and were shown to exhibit e.s.r. signals with hyperfine interaction between the electron and the halogen, and we confirm these results.[6] In polar solvents, such as tetrahydrofuran, it is likely that the species present is $Fe(NO)_2X(thf)$ (thf = tetrahydrofuran) but for solutions of $[Fe(NO)_2Br]_2$ in CCl_4 the apparent seven-line pattern obtained cannot be simply interpreted and further investigation of these species is required. Solutions of the thio-complexes all give strong e.s.r. signals with hyperfine coupling, four lines for the bromo- and six lines for the iodo-complexes. The e.s.r. data for all the complexes are reported in the Table. The *g* values for the bromo-complexes are *ca.* 2·045 while the iodo-complexes are somewhat higher at 2·060. There is no apparent trend in the hyperfine splittings. It is clear that the unpaired electron in these complexes is coupled to the halogen indicating that the halogen is covalently bound to the metal. These complexes cannot, therefore, be formulated as ionic species as Hieber and Kaiser have suggested.[9] This also suggests that perhaps the amide ligand is not acting in a chelating fashion but is only co-ordinated to the iron through the sulphur. Further resolution of the spectra to reveal coupling to ^{14}N could solve this problem but unfortunately the rather large line widths did not allow any additional hyperfine structure to be seen. In this respect the spectra are similar to those reported by Burlamacchi *et al.*[4] and Crow *et al.*,[6] neither group reporting any hyperfine coupling to ^{14}NO in dinitrosyl iron complexes. Hyperfine coupling to ^{14}N has been observed in some $(NO)_2FeL_2$ complexes by McDonald *et al.*,[3] with splitting constants being generally *ca.* 2 gauss. In contrast Fe(NO)(dithiol)$_2$ complexes (dithiol = maleonitriledithiol, benzene-1,2-dithiol, 2,2-dicyanoethylene-1,1-dithiol,[3] and *NN*-dimethyldithiocarbamate[15]) showed coupling to ^{14}N ranging from 12·7 to 15·5 gauss, indicating that considerable electron spin density is delocalised onto the NO ligand. This is no doubt due to the favourable stereochemical position of the NO in these five-co-ordinate complexes. It seems reasonable

Spectral data for the complexes $Fe(NO)_2LX$

Complex *	I.r. spectra in the range 400—200 cm^{-1}					E.s.r. data				Mössbauer data		
		ν_{Fe-N}	ν_{Fe-S}	ν_{Fe-X}	Other band	Solvent	*g* Value	a_X/gauss †	Γ/gauss	Temp./K	Isomer shift mm s^{-1}	Quadrupole splitting mm s^{-1}
$[Fe(NO)_2Br]_2$	THF	283w	(235vs,b)		400m	CCl_4	2·053	23·1(7)	12·2	77	0·69	1·85
	Mull	304sh, 292m	(235vs,b)			$CCl_4 + Me_2CO$	2·048	15·3(4)	7·8			
						CH_2Cl_2	2·048	16·1(4)	5·6			
						$CHCl_3$	2·047	16·0(4)	7·8			
						$(CH_3)_2CO$	2·048	(1)	38·0			
						THF	2·046	(1)	39·8			
						THF	2·047	16·7(4)	8·9			
$[Fe(NO)_2I]_2$	THF	200w	250m		395m	CCl_4	2·062	15·5(6)	7·8	77	0·60	1·62
	Mull		229s			$CCl_4 + Me_2CO$	2·063	(1)	42·7			
						THF	2·062	(1)	42·7			
						THF	2·062	19·4(6)	7·8			
$Fe(NO)_2(tu)Br$	THF	305w, 292m	(240w, 220w)		413s	THF	2·044	16·4(4)	7·7	77	0·59	1·31
	Mull	275m, 262	(238m, 224m)							298	0·51	1·18
$Fe(NO)_2(tu)I$	THF	288vb	212w		423s	THF	2·061	19·0(6)	9·0	77	0·58	1·22
	Mull	314w, 270bm	240w, 220w							298	0·48	1·18
$Fe(NO)_2(ta)Br$	THF	313w, 272m	(240m, 222m)		413m	THF	2·048	16·8(4)	7·9	77	0·58	1·25
	Mull	337m, 265m	(243m, 222m)							298	0·50	1·17
$Fe(NO)_2(tb)Br$	THF	290vb	(255m, 230m, 210m)		417m	THF	2·045	15·3(4)	7·7	77	0·58	1·21
										298	0·53	1·13
$Fe(NO)_2(atp)Br$	THF	288vb	(254w, 247w, 227sh)			THF	2·046	15·3(4)	7·7	77	0·46	1·20
	Mull	395w, 373m	(240w)							298	0·38	1·17
$Fe(NO)_2(atp)_2Br$	Mull	463s, 393m, 370s 299w, 288s	(234m, 211m)			THF	2·041	20·8(4)	10·9	77 298	0·49 0·38	1·25 1·15
$Fe(NO)_2(tb)I$						THF	2·056	16·0(6)	6·0			
$Fe(NO)_2(dptu)Br$						THF	2·042	16·4(4)	8·8	77	0·59	1·31
										298	0·65	0·78

* THF = Tetrahydrofuran, tu = thiourea, ta = thioacetamide, tb = thiobenzamide, atp = *o*-aminothiophenol, dptu = diphenylthiourea. † ^{79}Br and ^{81}Br coupling was not resolved. Γ Line width.

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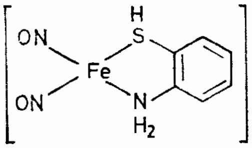
[12] C. D. Flint and M. Goodgame, *J. Chem. Soc.* (*A*), 1968, 750.

[13] T. Birchall and M. Morris, *Canad. J. Chem.*, 1972, **50**, 211.

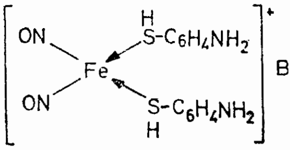
[14] L. F. Dahl, E. R. deGil, and R. D. Feltham, *J. Amer. Chem. Soc.*, 1969, **91**, 1653.

[15] J. F. Gibson, *Nature*, 1962, **196**, 64.

to suppose that the thioamide complexes reported here have tetrahedral structures in view of the similarity of our e.s.r. spectra to those of other workers.[3,4,6] However, in solution a five- or six-co-ordinate structure with solvent molecules occupying the other sites cannot be ruled out. The structures of $Fe(NO)_2(atp)Br$ and $Fe(NO)_2(atp)_2Br$ are much less certain but in the light of the e.s.r. evidence presented above, they cannot be formulated as (1) and (II).[9] It is tempting to suggest that $Fe(NO)_2(atp)Br$ has a similar structure to the amide complexes with a unidentate atp ligand bonded through sulphur, but the Mössbauer data reported below suggest that this may not be so. The structure of the $Fe(NO)(atp)_2Br$ is even less clear but this molecule also has a bromine atom covalently bound to iron.



(I)



(II)

Mössbauer data obtained for these complexes are summarised in the Table. Our data for $[Fe(NO)_2X]_2$ are in reasonable agreement with those reported previously.[6] The thioamide and thiourea complexes have smaller isomer shifts compared to the nitrosyl halide dimers, indicating a higher *s* electron density at the iron. Since the $Fe(NO)_2XL$ complexes may be described as d^9 systems, as opposed to d^{10} for $[Fe(NO)_2X]_2$, this shift is not unexpected: one fewer *d* electron results in less shielding of the *s* electrons from the nucleus and hence a higher *s* electron density. Crow *et al.*[6] have reported data for similar d^9 complexes involving ligands of Group V elements and, apart from the case where $L = C_5H_{11}N$, the isomer shifts are somewhat lower than those reported here. Where this is the case, the changes can be attributed to the π bonding capabilities of the ligand: back donation from *d* orbitals to empty ligand orbitals would result in an increased *s* electron density. The parameters reported here for the thioamide and thiourea complexes are independent of the nature of the ligand L, or the halogen, and suggest that it is the NO ligand which is the dominant factor in determining the Mössbauer parameters.

Both atp complexes have significantly lower isomer shifts than the amide complexes. In the case of $Fe(NO)_2(atp)Br$ this increased *s* electron density means either that the atp ligand is a much better π acceptor than the amides, which does not seem very likely, or that this complex has quite a different structure. Both atp complexes have similar Mössbauer parameters and therefore probably have structures which are closely related. $Fe(NO)_2(atp)_2Br$ contains five ligands, assuming atp to be unidentate, and can clearly not contain four-co-ordinate iron. By inference, we suggest that the $Fe(NO)_2(atp)Br$ also has at least five co-ordinate iron.

We are currently attempting crystallographic analyses of some of these materials in order to confirm the structures of these thioamide complexes in the solid state and to ascertain the exact nature of the atp complexes.

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