Inorganica Chimica Acta, 40 (1980) 37–42
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Single Crystal Electron Paramagnetic Resonance Studies of $\{FeNO\}^7$-Bis(dimethyldithiocarbamate)

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Received September 3, 1979

The single crystal EPR spectrum of $Fe(NO)(S_2CN(CH_3)_2)_2$ *(1%) in* $Co(NO)(S_2CN(CH_3)_2)_2$ *was measured at room temperature at X-band. Both the g and* A_N *tensors have rhombic symmetry with* $g_z = 2.028$, $g_x = 2.046$, $g_y = 2.039$, $A_N(z) = 14.9$, $A_N(x) = 12.6$, *and* $A_N(y) = 12.2$ *Oe. The features of the g and* A_N *tensors are related to the geometry of the Fe-NO moiety and to the description of its electronic structure.*

Introduction

Low-spin derivatives of the $\{FeNO\}^7$ group [1] have been of both practical and theoretical interest to inorganic chemists and biochemists. Two spectroscopic properties of these iron–nitrosyl complexes, their visible–u.v. [2, 3] and their EPR spectra [4–7], have proven to be particularly useful for probing the ligand environment around the iron atom. Indeed, there have been at least 26 reports of the EPR features of nitrosyl derivatives of heme and non-heme iron proteins since 1971. These studies have primarily involved the use of EPR spectra of nitrosyl derivatives to probe the number and type of axial ligands attached to the iron atom in heme complexes [8]. Moreover, because low-spin paramagnetic $\{FeNO\}^7$ complexes have EPR spectra which are normally observable at room temperature in liquid solutions, a rather large number of reports on the EPR spectra of structurally well characterized $\{FeNO\}^7$ complexes have also appeared. However, there have been just two single crystal studies of $\{FeNO\}^7$ complexes [9, 10], of which only one had been structurally characterized by X-ray crystallography [10]. It was for these several reasons that we report the research described below.

Experimental

All operations involving solutions of the nitrosyl complexes were carried out under an atmosphere of N_2. The compounds, $Fe(NO)(DMDTC)_2$ and $Co(NO)(DMDTC)_2$, were prepared as described in the literature [1, 2]. Each compound was fully characterized by elemental analyses, infrared spectroscopy, and X-ray crystallography.

Single crystals of $Co(NO)(DMDTC)_2$ containing $Fe(NO)(DMDTC)_2$ as an impurity were grown from a CH_2Cl_2 solution containing $Fe(NO)(DMDTC)_2$ and $CoNO(DMDTC)_2$ in a ratio of approximately 1:99 by slow crystallization (72 hr) at –10 °C. The faces of two of these crystals were identified as {011}, {100}, and {111} using a Picker FACS I diffractometer. The cartesian coordinate axes adopted are shown in Fig. 1.

The EPR spectra of these single crystals were obtained at X-band and ambient temperature using a Varian E-3 EPR spectrometer equipped with a goniometer accurate to 0.1° or better. The E-3 spectrometer was calibrated using an Hewllit-Packard frequency meter, a gaussmeter, and DPPH (g = 2.0034). The estimated errors in g and A_N values are indicated in the Tables.

Results and Discussion

$Fe(NO(DMDTC)_2/Co(NO)(DMDTC)_2$

The crystal structure of the diamagnetic host, $Co(NO)(DMDTC)_2$, was originally determined by Owston and co-workers [11] on a twinned crystal, and was later redetermined by Enemark and Feltham [12]. The compound crystallizes in the monoclinic space group $P2_1/C$. The molecule has rectangular-based pyramidal geometry with the NO group occupying the axial position, and provides a site of C_1 symmetry for the iron complex. The $\{CoNO\}^8$ group is disordered and strongly bent (134.5° and 135.7°). The oxygen atom occupies positions over each of the Co–S vectors of one dithiocarbamate ligand (Fig. 1). The relationships between the crystal and molecular axes are also shown in Fig. 1. Since the molecule has only C_1 symmetry, the choice of molecular axes is not unique. However, for comparison with other compounds, the Co–N vector was

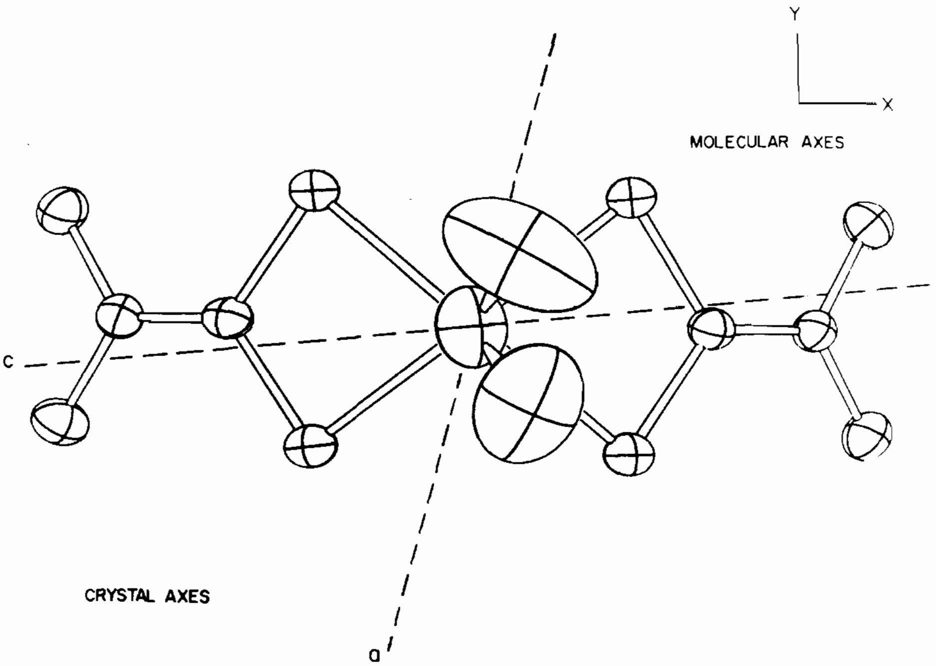

Fig. 1. Relationship between molecular cartesian coordinates and crystal axes for Co(NO)(DMDTC)$_2$.

TABLE I. Comparison of the Bond Distances and Bond Angles of Fe(NO)(DMDTC)$_2$ and Co(NO)(DMDTC)$_2$.

	Co[a]	Fe[b]
M–N	1.764	1.720
N–O (avg.)	1.121	1.102
M–N–O (avg.)	134.9°	170.4°
M–S (avg.)	2.263	2.299
M–S$_4$ plane	0.52	0.63

[a]Reference 12. [b]Reference 14.

selected as the molecular z axis, and the bisector of the –CS$_2$ angle was taken as x.

The structure of Fe(NO)(DMDTC)$_2$ has been determined by Owston and co-workers [13, 14] at 20 °C and –80 °C. The structure of this $\{FeNO\}^7$ complex at both temperatures is very similar to that of the $\{CoNO\}^8$ complex described above. The iron compound crystallizes in the same space group, $P2_1/C$. The molecule has rectangular pyramidal geometry with an axial nitrosyl group. The average Fe–S distance is 0.036 Å longer than that of the cobalt complex, while the Fe–N distance is slightly shorter (0.044 Å). Each metal atom is displaced from the mean S$_4$-plane with the displacement of the iron atom being 0.11 Å greater than that of Co. However, the shorter Fe–N and N–O distances compensate for the additional displacement of the iron atom. Thus, the only major structural difference between these two complexes resides in the MNO bond angles which are *ca.* 170° and 135° for the iron and cobalt complexes respectively (Table I). Because Fe(NO)(DMDTC)$_2$ is five-coordinate and has a very low FeNO bending frequency, possible distortion of its molecular geometry by the cobalt host lattice was of some concern. In order to explore further the suitability of Co(NO)(DMDTC)$_2$ as a host for Fe(NO)(DMDTC)$_2$, the intermolecular contacts between the oxygen atom and the atoms of the other molecules in the cobalt lattice were calculated assuming a linear Co–N–O group. None of these contacts was found to be less than the sum of the respective van der Waals radii. Consequently, the iron compound was expected to enter the cobalt lattice without significant alteration of its molecular structure, an expectation borne out by the EPR results described below.

EPR spectra of two different crystals of Co(NO)(DMDTC)$_2$ containing *ca.* 1% Fe(NO)(DMDTC)$_2$ were obtained every 10° in two orthogonal planes. In each orientation, the spectrum consisted of a well-resolved triplet. The individual components of the triplet were of equal intensity with a separation of 12–14 Oe, which clearly identifies them as the hyperfine components of the $^{14}N(O)$ nucleus. The linewidths (4–9 OeFWHM) and low concentrations of the other magnetic nuclei (^{57}Fe, ^{13}C) precluded observation of additional hyperfine lines. The

TABLE II. EPR Data for Fe(NO)(DMDTC)$_2$.

Host Material	g_z	g_x	g_y	A_z	A_x	A_y	Temp. (K)
Fe(NO)DMDTC)$_2$^{a}	2.0277(4)	2.0461(5)	2.0379(5)	–	–	–	300
Co(NO)(DMDTC)$_2$^{b}	2.028(1)	2.046(1)	2.039(1)	14.9(2)	12.6(2)	12.2(2)	300
EPA glass^c	2.027	2.042	2.038	14.5	12.8	11.1	100

^{a}Undiluted single crystal; Ref. 18. ^{b}Dilute single crystal; this work. ^{c}2:5:5 ethanol–isopentane–diethylether: Q-band data; Ref. 20.

observed g factors had values ranging between 2.03 and 2.05. Both g and A_N tensors were found to have rhombic symmetry and the $\cos^2\theta$ dependence expected for Fe(NO)(DMDTC)$_2$ molecules occupying the lattice sites provided by the Co(NO)(DMDTC)$_2$ host (Fig. 2). Since the principal axes of the molecule do not correspond to any of the rotational directions of the crystal, the g values were obtained using the expression:

$$g^2(\theta, \phi) = g_x^2\sin^2\theta\cos^2\phi + g_y^2\sin^2\theta\sin^2\phi + g_z^2\cos^2\theta.$$

Within experimental error (+ 5°), the principal values of the g and A_N tensors are colinear and lie along the molecular x, y, and z axes (Fig. 1). It should be emphasized that g tensors with rhombic symmetry are not required to lie along two-fold or pseudo two-fold axes such as those shown in Fig. 1. as evidenced by several well established examples of rhombic Cu^{2+} and low-spin Co^{2+} complexes [15–17].

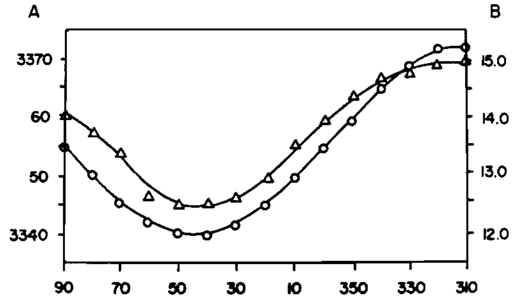

Fig. 2. The angular dependence of g (curve A, ○) and A_N (curve B, △) upon rotation about the a axis of Co(NO)(DMDTC)$_2$ doped with ~1% Fe(NO)(DMDTC)$_2$.

The present results are compared with those obtained by Gibson [18] for an undiluted single crystal of Fe(NO)(DMDTC)$_2$ (Table II). Gibson did not report the principal values of A_N for the

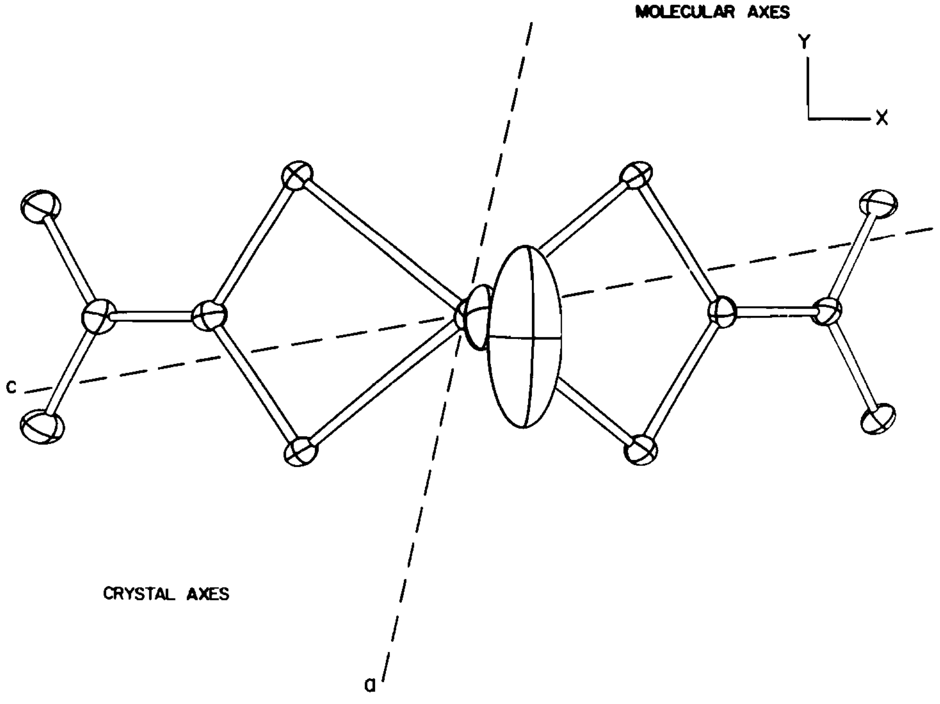

Fig. 3. Projection down the Z axis of Fe(NO)DMDTC)$_2$ (room temperature structure).

undiluted single crystal, presumably because of excessive line widths due to dipolar broadening. However, the principal g values reported by Gibson and the present results are the same within experimental error. This close agreement between the data obtained from the diluted and undiluted single crystals is taken to indicate that the molecular structure of $Fe(NO)(DMDTC)_2$ has not been significantly altered by the cobalt host lattice.

The EPR spectra of several $\{FeNO\}^7$ complexes have been studied in a variety of frozen and liquid solutions by several different research groups [18–23]. These investigations show that both g_{avg} and $A_{N(iso)}$ are solvent and temperature dependent. For example, Symons and co-workers [19] have examined the EPR spectrum of $Fe(NO)(DEDTC)_2$ in 25 different solvents over the temperature range from 100–300 K. They found that the changes in g_{avg} and $A_{N(iso)}$ as well as in ν_{NO} induced by the solvent and temperature correlate with the E_T values for these solvents. From these observations, Guzy *et al.* [19] concluded that $Fe(NO)(DEDTC)_2$ maintained square pyramidal geometry in solution and that the solvent molecules were interacting with the complex at the vacant coordination site *trans* to the NO group. Goodman, Raynor and Symons [20] studied the EPR spectrum of $Fe(NO)(DEDTC)_2$ at S-, Q-, and X-band frequencies in an EPA glass, and obtained principal values for the g, A_N, and A_{Fe} tensors.

Kooser [24] has examined the EPR spectrum of the closely related dithiooxalate derivative of $\{FeNO\}^7$ in many of these same solvents. From measurements of the linewidths of $[Fe(NO)(DTOX)_2]^{2-}$ as a function of temperature in $CHCl_3$, CH_2Cl_2, and CH_3OH, Kooser concluded that an equilibrium exists between five-coordinate $[Fe(NO)(DTOX)_2]^{2-}$ and a six-coordinate species with solvent molecules occupying the sixth coordination site.

Subsequent to the reports of Kooser [24] and of Symons and co-workers [19, 20], five-coordinate complexes of $\{FeNO\}^7$ with both linear and bent FeNO groups in square pyramidal geometry have been isolated and structurally characterized [3, 25–29]. Thus, a variety of structural isomers for solutions of these $\{FeNO\}^7$ complexes are possible: square pyramidal with either a linear or bent FeNO group; trigonal bipyramidal with either a linear or bent FeNO group; and six-coordinate with a bent FeNO group. Although the marked changes of g_{avg} and A_N with solvent and temperature may indicate the presence of more than one geometric form of $Fe(NO)(DEDTC)_2$ in solution, it seems unlikely that solvents such as benzene, chloroform and cyclohexane will form six-coordinate complexes of $Fe(NO)(DEDTC)_2$ when six-coordinate complexes of $Fe(NO)(DMDTC)_2$ with even the best donor ligands have not as yet been isolated. An alternative explanation of the effects of weakly donating solvents is that two (or more) geometric forms of the five-coordinate complex co-exist in solution, and that the equilibrium(a) between them is both solvent and temperature dependent. However, since only one EPR signal is observed, these species must be interconverting rapidly or must have very similar values of g_{avg} and A_N. For good donors such as pyridine or alcohols, six-coordinate complexes may also be present. In any case, it is clear that $Fe(NO)(DEDTC)_2$ is of uncertain geometry in solution and that comparison of solution properties with those obtained from single crystals must be viewed with caution.

Bearing these complications in mind, the results obtained by Simons and co-workers [19, 20] are compared with those of Gibson [18], and with those from the present work (Table II). Although there is reasonable agreement between the solution and single crystal values for two of the three g values, the value of g_x observed by Goodman *et al.* [20] at X-band differs significantly from the single crystal data. Again, except for g_x, the principal values of both the g and A_N tensors obtained by Goodman *et al.* at Q-band agree well those obtained in the present study. Although not definitive for the reasons cited above, no major changes in the molecular geometry of $Fe(NO)(DMDTC)_2$ appear to have been generated by dissolution in $Co(NO)(DMDTC)_2$ or in EPA. Consequently, the g values obtained from these solutions have been assigned to $Fe(NO)(DMDTC)_2$ with rectangular pyramidal geometry and an FeNO angle of 170 ± 10°.

g Tensors of $Fe(NO)(DMDTC)_2$

Qualitatively, the principal components of the g tensor of $Fe(NO)(DMDTC)_2$ resemble those found for a wide range of five-coordinate Co(II) complexes [30–37].

The square pyramidal Co(II) complexes generally have the three principal g values greater than 2.0023 with $g_x, g_y > g_z \cong 2.0023$. Although some controversy has surrounded the assignment of ground states for square pyramidal low-spin Co(II) complexes, there now seems to be general agreement that most have a $^2A_1$ ground state with a $(d_{xz})^2(d_{yz})^2(d_{x^2-y^2})^2(d_{z^2})^{\pm}$ configuration in which the unpaired electron resides in an orbital principally comprised of d_{z^2}. Expressions for the principal values of the g tensor for rhombic and tetragonal Co(II) complexes with $^2A_1(d_{z^2})$, $^2B_1(d_{xz})$, or $^2B_2(d_{yz})$ ground states using third order perturbation theory have been developed by McGarvey [38].

These expressions show that $g_z = 2.0023$ without configuration interaction mixing with $d_{x^2-y^2}$ and without second and third order coupling with the quartet states of Co(II). Coupling with the quartet states results in $g_z > 2.0023$, while configuration interaction mixing of d_{z^2} with $d_{x^2-y^2}$ results in $g_z < 2.0023$. Both g_x and g_y are greater than g_z while their relative magnitudes are determined by the energy separation between $^2A_1$ and $^2B_1(d_{xz})$ and $^2B_2(d_{yz})$.

The several groups of workers who have previously investigated the EPR spectra of $Fe(NO)(DMDTC)_2$ have concluded that its electronic properties can best be described in terms of a $^2A_1(d_{z^2})$ ground term. The results of the present study are in general agreement with this assignment, and are consistent with the molecular orbital diagram in Fig. 12 of Ref. 1. The expressions obtained by McGarvey [38] can also be used to explain the g tensor of $Fe(NO)(DMDTC)_2$ provided coupling with the excited states 3^2B_1 and 3^2B_2 are included. The effect of including coupling with the $3b_1$ and $3b_2$ orbitals is to reduce the values of g_x and g_y as was pointed out by Gray *et al.* [21] but to first order does not affect g_z. Consequently, we expect to find $g_x \cong g_y > g_z \cong 2.0023$, but with g_x, g_y less than the values of 2.2–2.3 found for the Co(II) complexes. As in the case of the Co(II) complexes, coupling with the low lying quartet states will cause g_z to be greater than the free electron value. For $Fe(NO)(DMDTC)_2$ the fact that $g_z > 2.0023$ is consistent with the presence of low-lying quartet states. Several square pyramidal complexes of $\{FeNO\}^7$ with quartet ground states have been isolated. Thus the quartet states are even accessible as ground states and therefore must be rather low-lying excited states in $Fe(NO)(DMDTC)_2$ as suggested by the EPR data.

A_N *Tensors of* $Fe(NO)(DMDTC)_2$

The g and A_N tensors of $Fe(NO)(DMDTC)_2$ are co-linear within experimental error (±5°) and each tensor component lies along the principal axes of the complex, even though the molecule is in a lattice site with only C_1 symmetry. After corrections for dipolar coupling, the resultant anisotropic ^{14}N hyperfine tensor has contributions from two sources. The first tensor is symmetric about the Z axis and represents the contribution of $2p_{z(N)}$ to the ground state $|1.26(z), -0.63(x), -0.63(y)|$. The second is symmetric about the X molecular axis and represents the contribution of $2p_{x(N)}$ to the ground state wave function $|-0.16(z), 0.33(x), -0.16(y)|$. Thus, the slight bending (10°) of the NO group in the XZ plane has introduced a $2p_{x(NO)}$ component to the ground state wave function. The direction cosines calculated from the observed anisotropy in the ^{14}N tensor correspond to the direction cosines of the projection of the bent NO group onto the XY plane of the $Fe(NO)(DMDTC)_2$ molecule. Although such close agreement between the molecular structure and these EPR results may well be fortuitous, considering the rather large uncertainties in both the structural data and the EPR data, these relationships suggest that they may prove useful for deducing the geometry of the $\{FeNO\}^7$ group in complexes with rhombic symmetry.

Acknowledgements

The autors thank Dr. J. H. Enemark and Dr. S. Kukolich for helpful discussions and acknowledge the National Institutes of Health, the National Science Foundation and the University of Arizona for support of this research.

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