CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
THE PENNSYLVANIA STATE UNIVERSITY, UNIVERSITY PARK, PENNSYLVANIA 16802

The Crystal and Molecular Structure of an Iron Complex Containing both 1,1-Dithiolato and 1,2-Dithiolene Ligands, Bis(*N*,*N*-diethyldithiocarbamato) [*cis*-1,2-bis(trifluoromethyl)-ethylene-1,2-dithiolato]iron

BY DONALD L. JOHNSTON,[1] WAYNE L. ROHRBAUGH, AND WILLIAM DEW. HORROCKS, JR.*

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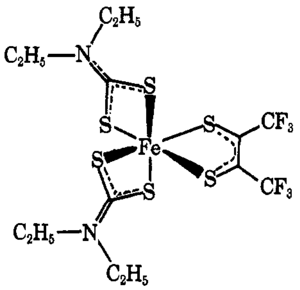
The crystal structure of bis(*N*,*N*-diethyldithiocarbamato)[*cis*-1,2-bis(trifluoromethyl)ethylene-1,2-dithiolato]iron, $Fe[S_2CN(C_2H_5)_2]_2[S_2C_2(CF_3)_2]$, has been determined from three-dimensional single-crystal X-ray diffraction data collected by automatic counter methods. The structure was refined by least-squares methods to a conventional R factor of 0.064 and a weighted R of 0.084 based on 1376 "observed" reflections. The compound crystallizes in the monoclinic space group $C2/c$ with cell dimensions (measured at 17°) of $a = 17.131$ (8) Å, $b = 10.320$ (6) Å, $c = 15.472$ (8) Å, and $\beta = 121.15$ (3)°. The density calculated for $Z = 4$ is 1.641 (6) g/cm^3 and the measured density is 1.63 (3) g/cm^3. The structure consists of discrete molecules with the iron atom lying on a twofold axis surrounded by a 1,2-dithiolene (tfd) ligand and two dithiocarbamate (dtc) ligands. The coordination of the six sulfur atoms about the iron atom can be described as an octahedron distorted toward trigonal-prismatic geometry. Average bond lengths (Å) are as follows: for dtc, Fe–S = 2.310 (3), S–C = 1.718 (8), C–N = 1.302 (10); for tfd, Fe–S = 2.195 (3), S–C = 1.702 (9), C–C (in the chelate ring) 1.360 (17).

Introduction

Pignolet and Holm have recently reported[2] an oxidative addition reaction of bis(perfluoromethyl)-1,2-dithietene, $S_2C_2(CF_3)_2$, with *N*,*N*-diethyldithiocarbamatoiron(II) to yield the product $Fe[S_2CN(C_2H_5)_2]_2(S_2C_2(CF_3)_2]$, **1**, hereafter designated as $Fe((C_2H_5)_2dtc)_2(tfd)$. This complex is of interest in that it combines in the same molecular species (i) a singlet–triplet spin-state equilibrium in the solid and in solution, (ii) redox properties indicative of a three-membered electron-transfer series with the $0 \rightleftarrows -1$ interconversion being electrochemically reversible, and (iii) stereochemical mobility of a ligand structural portion (restricted rotation about the C–N bonds) and overall molecular configuration (interconversion of Δ and Λ enantiomeric forms[3]), which may be studied by nmr owing to the large isotropic shifts in the paramagnetic form.



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$Fe((C_2H_5)_2dtc)_2(tfd)$ contains an $M-S_6$ core, which for some transition metals has been found to possess a trigonal-prismatic coordination geometry.[4] Furthermore it has recently been shown[5] conclusively that the related molecule $Fe(CH_3C_6H_5dtc)_2(tfd)$ undergoes $\Delta \rightleftarrows \Lambda$ inversion *via* a trigonal or Bailar twist mechanism. This twist takes place about the pseudo-C_3 axis, the transition state for which involves approximate trigonal-prismatic geometry.

The present molecule represents perhaps the only example of a molecule whose structure has been determined under conditions in which a significant number of molecules in the same single crystal are present in different spin states. In the present case approximately 50% of the molecules are in the triplet state at the temperature of the X-ray determination (20°). In addition, the present structure is the first determination of a complex involving both 1,1-dithiolate and 1,2-dithiolene ligands. It was hoped that the unusual electronic structure of this complex, as evidenced by its unique magnetic properties, could be elucidated by the present structural study, particularly with regard to a determination of the effective oxidation level of the 1,2-dithiolene ligand.

Finally the present structural determination was necessary in order to permit the interpretation of single-crystal epr[6] and magnetic susceptibility anisotropy[7] experiments on this substance. These latter studies are necessary for the evaluation of the dipolar contribution to the observed isotropic nmr shifts.[8]

In summary, the present X-ray determination was undertaken to (i) determine the overall coordination geometry, (ii) assess the degree of oxidation of the dithiolene moiety, (iii) discover any effects of the spin-state equilibrium on the X-ray structural parameters, and (iv) enable the interpretation of single-crystal physical studies on this substance.

Experimental Section

Collection and Reduction of Intensity Data.—Black prismatic crystals of $Fe[S_2CN(C_2H_5)_2]_2[S_2C_2(CF_3)_2]$ were supplied by Dr. L. H. Pignolet and prepared as described elsewhere.[2,5] Preliminary Weissenberg photographs of the $h0l$, $h1l$, and $h2l$ layers showed systematic extinctions: $00l$, $l \neq 2n$; hkl, $h + k \neq 2n$, consistent with the space groups $C2/c$ or Cc. A crystal of ap-

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[1] Petroleum Research Fund predoctoral fellow, 1969–1970.

[2] L. H. Pignolet and R. H. Holm, *J. Amer. Chem. Soc.*, **92**, 1791 (1970).

[3] *Inorg. Chem.*, **9**, 1 (1970).

[4] (a) H. B. Gray, R. Eisenberg, and E. I. Steifel, *Advan. Chem. Ser.*, **No. 62**, 641 (1967); (b) J. A. McCleverty, *Progr. Inorg. Chem. Radiochem.*, **10**, 49 (1968); (c) G. N. Schrauzer, *Accounts Chem. Res.*, **2**, 72 (1969); (d) G. N. Schrauzer, *Transition Metal Chem.*, **4**, 299 (1968).

[5] L. H. Pignolet, R. A. Lewis, and R. H. Holm, *J. Amer. Chem. Soc.*, **93**, 360 (1971).

[6] L. H. Pignolet and R. H. Holm, unpublished results.

[7] W. D. Horrocks, Jr., L. H. Pignolet, and R. H. Holm, research in progress.

[8] W. D. Horrocks, Jr., *Inorg. Chem.*, **9**, 690 (1970).

proximate dimensions 0.12 × 0.29 × 0.086 mm was chosen for cell dimension and intensity measurements. This crystal was mounted on a glass fiber with the b axis of the monoclinic cell (coinciding with the longest crystal dimension) parallel to the spindle axis (φ) of the instrument. Cell dimension and intensity measurements were made using a four-circle Syntex computer controlled automatic diffractometer equipped with a scintillation counter and pulse height analyzer. Zirconium-filtered (at the source) molybdenum radiation was employed (λ(Mo Kα) 0.709261 Å). Unit cell dimensions were determined from a least-squares refinement[9] of 14 well-centered, high-2θ reflections measured at 17°; these are a = 17.131 (8) Å, b = 10.320 (6) Å, c = 15.472 (8) Å, β = 121.15 (3)°, and V = 2341.0 (9) Å^3. Standard deviations of the least significant figure(s) here and elsewhere are given in parentheses. The density calculated for four formula units per unit cell is ρ_{calcd} = 1.641 (6) g/cm^3. The measured density, determined by flotation in a mixture of dibromomethane and 1-butanol, is ρ_{calcd} = 1.63 (2) g/cm^3. With four molecules per unit cell no symmetry restrictions are placed on the molecule for space group Cc while $C2/c$ requires that the iron atom lie at a fourfold special position with either $\bar{1}$ or 2 symmetry. The former is eliminated on chemical grounds so the position of 2 symmetry (Wyckoff) was chosen for the iron: 0, y, $^1/_4$. For space group Cc the x and z coordinates of the iron may be arbitrarily specified to fix the origin so the above choice of iron coordinates is consistent with either space group. The final choice of the space group $C2/c$ was verified by the successful refinement of the structure.

Intensity data were collected by the θ–2θ scan technique scanning 1.1° on each side of the calculated 2θ peak position at a speed of 1°/min. Background was measured by a 15-sec stationary count at each end of the scan. The raw intensity I was calculated by $I = S - \alpha(B_1 + B_2)$ and the square of the standard deviation of the intensity was calculated as $\sigma^2(I) = S + \alpha^2 \cdot (B_1 + B_2) + (dS)^2$ where S is the total accumulated scan count, B_1 and B_2 are the initial and final background counts, α is the ratio of the scan time to the total background time, and d is an empirical constant here taken as 0.04. Three check reflections were measured every 105 measurements and showed a random variation during data collection of ±6% in I at I = 13,000 and ±4.5% at I = 3000. A total of 2074 reflections were measured. The $1\bar{1}1$ and $1\bar{1}0$ reflections occur at very low 2θ values and showed evidence of beam-stop interference and were deleted from the final data set. In addition the 002 and 200 reflections of very high intensity exhibited an error of 10% in F_o which may be attributed to extinction. These were not used in the final least-squares refinements. Of the remaining reflections, 1376 had $I \geq 4\sigma(I)$ and these were used in the final refinement.

φ rotation at χ = 90° for the $0\bar{2}0$ reflection showed $I^{1/2}$ to vary between 90 and 100 on a relative scale. The φ values where the absorption was minimized correspond to those of the $(0,0,n)$ and $(0,0,\bar{n})$ reflections. Transmission coefficients of 0.87, 0.70, and 0.86 are obtained for passage of the X-ray beam through each of the crystal dimensions, respectively. No absorption correction (μ_{Mo} = 12.0 cm^{-1}) was applied to the data. The data were corrected for Lorentz (L) and polarization (p) effects with the observed structure factors computed by $F_o = [I/Lp]^{1/2}$. The standard deviation of this quantity is given by $\sigma(F_o) = \sigma(I)[ILp]^{-1/2}/2$.

Solution and Refinement of the Structure.—A three-dimensional Patterson map disclosed the positions of the iron atom and two of the sulfur atoms. Three cycles of least-squares refinement[10] of the positions of these atoms yielded R_1 = 0.475.[11] A Fourier synthesis,[9] phased from the results of the above refinement, revealed the additional sulfur atom, three carbon atoms, and the nitrogen atom. (In space group $C2/c$ the asymmetric unit is comprised of half of the molecule, the other half being generated by a twofold rotation.) Three cycles of least-squares refinement of the positional and isotropic thermal parameters of these atoms reduced R_1 to 0.280. The remaining nonhydrogen atoms were revealed by a Fourier synthesis at this point and three further cycles of least-squares refinement yielded R_1 = 0.121 and R_2 = 0.150. Using anisotropic temperature factors for all atoms three cycles of least-squares refinement converged to final values of R_1 = 0.064 and R_2 = 0.084. The standard deviation in an observation of unit weight at the end was 2.21. The maximum shift in any parameter during the final cycle was less than 0.2 of its standard deviation. A final difference Fourier map had a maximum peak height of 0.351 e$^-$/Å^3 which may be compared with 2.28 e$^-$/Å^3 for a fluorine atom on the previous difference map. Several peaks appeared in reasonable positions for hydrogen atoms bonded to carbons, but many spurious peaks of nearly the same magnitude also were present. The hydrogen atoms were not included in the refinement. Throughout the refinements scattering factors were taken from ref 12 as were the dispersion correction factors $\Delta f'$ and $\Delta f''$ for iron and sulfur which were included in the final refinements.

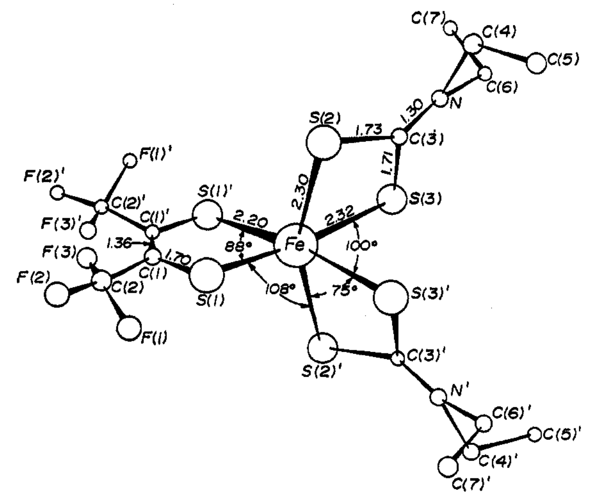

Figure 1.—Atom-labeling scheme for the $Fe[S_2CN(C_2H_5)_2]_2$-$[S_2C_2(CF_3)_2]$ molecule.

The observed and calculated structure factors are given in Table I. On the same scale $F_o(000)$ = 550. The final atomic positional parameters and the components of the anisotropic thermal tensors are given in Table II.

Description and Discussion of the Structure

Overall Structure and Coordination Polyhedron.—The crystal structure consists of discrete $Fe((C_2H_5)_2$-$dtc)_2(tfd)$ molecules of C_2 symmetry, which is crystallographically required. The C_2 axis passes through the iron atom and bisects the C–C bond of the 1,2-dithiolene chelate ring. The iron is bonded to six sulfur ligand atoms which form a distorted octahedral coordination polyhedron. The octahedron is distorted toward idealized trigonal-prismatic geometry. The iron atom lies very nearly in each of the three planes defined by the three chelate rings with the largest deviation being 0.06 Å. The closest intermolecular contact is a F(1)–S(1) approach of 2.78 Å which is slightly less than the sum of van der Waals radii (3.07 Å). The nearest iron–iron approach in the crystal is 7.85 Å, while the nearest intermolecular sulfur–sulfur contact is 4.64 Å. The molecule and the atom-labeling scheme are illustrated in Figure 1. Table III gives selected interatomic distances and angles. A stereoview of the molecule viewed down the pseudo-C_3 axis common to idealized octahedral and trigonal prismatic structures is presented in Figure 2.

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(9) Computations were performed on an IBM 360-67 at the Computation Center of The Pennsylvania State University. The following programs were used for operations indicated: refinement of cell dimensions—Hope's CELDIM; conversion of papertape diffractometer output to IBM cards—Stanko's PTAPE; Lp corrections—Prewitt's ACAC; Patterson function and Fourier synthesis—Zalkin's FORDAP; least-squares refinement—the Brown University version of Busing and Levy's ORFLS; interatomic distance and angle computation—Zalkin's DISTAN; calculation of least-squares planes—Chu's LSPLAN; preparation of Table I—Zalkin's LIST; stereoview—Johnson's ORTEP.

(10) The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where F_o and F_c are the observed and calculated structure factors and w is the weight taken as $[\sigma(F_o)]^{-2}$.

(11) Conventional residual $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and weighted residual $R_2 = [\Sigma w(||F_o| - |F_c||)^2/\Sigma wF_o^2]^{1/2}$.

(12) "International Tables for X-Ray Crystallography, Kynoch Press, Birmingham, England, 1962, p 201 ff.

TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $Fe[S_2CN(C_2H_5)_2]_2[S_2C_2(CF_3)_2]$[a]

L	FOR	FCA
H,K=	0,	-12
-3	9	7*
-2	12	9
-1	8	5*
0	12	10
1	7	5*
2	11	9*
3	6	7*
H,K=	0,	-10
-9	13	11
-8	4	0*
-7	9	8*
-6	16	15
-5	31	29
-4	21	19
-3	17	17
-2	9	4
-1	15	14
0	5	1*
1	14	14
2	6	4*
3	17	17
4	21	19
5	24	29
6	15	15
7	10	8
8	4	0*
9	10	11*
H,K=	0,	-8
-11	9	8*
-10	5	10*
-9	10	2
-8	19	19
-7	12	10
-6	17	18
-5	10	9
-4	19	18
-3	8	6*
-2	18	14
-1	8	6*
0	26	25
1	4	6*
2	16	14
3	4	6*
4	18	18
5	9	9*
6	17	18
7	11	10
8	19	19
9	3	2*
10	12	10
11	5	8*
H,K=	0,	-6
-13	5	5*
-12	12	12
-11	15	16
-10	16	16
-9	19	18
-8	12	9
-7	14	14
-6	0	1*
-5	19	19
-4	20	20
-3	18	16
-2	24	24
-1	67	65
0	28	29
1	66	65
2	23	24
3	19	16
4	20	20
5	18	19
6	0	1*
7	11	14
8	12	9
9	20	18
10	16	16
11	15	16
12	11	12
13	9	5*
H,K=	0,	-4
-14	12	14
-13	18	17
-12	7	1*
-11	6	4*
-10	21	22
-9	6	7*
-8	4	5*
-7	27	27
-6	33	33
-5	33	35
-4	70	70
-3	67	62
-2	21	24
-1	37	37
0	51	50
1	37	37
2	27	24
3	66	62
4	70	70
5	33	35
6	32	33
7	26	27
8	6	5*
9	8	7
10	21	22
11	6	4*
12	0	1*
13	17	17
14	15	14
H,K=	0,	-2
-15	6	5*
-14	9	5
-13	8	1*
-12	15	15
-11	4	1*
-10	30	30
-9	6	2*
-8	12	11
-7	17	17
-6	7	8*
-5	0	4*
-4	10	10
-3	8	7
-2	37	33
-1	43	36
0	83	98
1	42	36
2	38	33
3	9	7
4	10	10
5	3	4*
6	7	8*
7	17	17
8	12	11
9	6	2*
10	29	30
11	5	1*
12	13	15
13	5	1*
14	6	5*
15	7	5*
H,K=	0,	0
-14	4	9*
-12	30	30
-10	87	86
-8	58	60
-6	51	51
-4	114	105
4	114	105
6	50	51
8	56	60
10	84	86
12	31	30
14	8	9*
H,K=	1,	-11
-7	15	13
-6	9	5*
-5	25	23
-4	7	3*
-3	12	11
-2	12	8
-1	6	8*
0	6	6*
1	8	3*
2	6	4*
3	23	21
4	8	2*
5	25	25
6	8	1*
H,K=	1,	-9
-11	2	6*
-10	3	8*
-9	6	6*
-8	11	12
-7	20	19
-6	33	34
-5	16	13
-4	28	28
-3	4	4*
-2	4	2*
-1	20	19
0	16	14
1	9	8
2	16	17
3	17	14
4	29	29
5	18	18
6	18	18
7	11	11
8	9	1
9	0	3*
10	4	1*
H,K=	1,	-7
-13	9	7*
-12	5	1*
-11	13	11
-10	26	27
-9	3	5*
-8	39	39
-7	7	5*
-6	14	15
-5	4	3*
-4	18	17
-3	4	5*
-2	12	12
-1	24	23
0	54	56
1	13	14
2	60	59
3	6	7*
4	7	6*
5	1	5*
6	6	5*
7	7	5*
8	8	7*
9	9	9*
10	21	21
11	10	10*
12	13	14
H,K=	1,	-5
-14	7	6*
-13	16	15
-12	5	0*
-11	17	18
-10	4	4*
-9	10	8
-8	24	24
-7	9	8
-6	34	35
-5	62	62
-4	3	2*
-3	35	35
-2	10	11
-1	18	21
0	5	3*
1	7	3*
2	30	30
3	8	6
4	52	51
5	26	25
6	16	16
7	31	32
8	21	20
9	29	31
10	0	2*
11	6	8*
12	21	21
13	8	2*
H,K=	1,	-3
-15	20	19
-14	8	7*
-13	16	17
-12	11	10
-11	10	10
-10	3	4*
-9	14	12
-8	12	11
-7	30	28
-6	22	18
-5	101	101
-4	42	45
-3	38	40
-2	72	67
-1	37	37
0	31	31
1	58	59
2	8	7
3	54	51
4	19	17
5	90	92
6	16	17
7	20	20
8	7	7*
9	7	9*
10	4	3*
11	8	8*
12	3	3*
13	12	11
14	8	3*
H,K=	1,	-1
-16	3	5*
-15	3	2*
-14	5	6*
-13	7	9*
-12	39	41
-11	8	2*
-10	42	43
-9	16	15
-8	24	25
-7	5	1*
-6	1	0*
-5	3	3*
-4	60	52
-3	4	1*
-2	95	99
1	26	24
2	62	59
3	22	21
4	26	24
5	4	5*
6	15	15
7	15	17
8	54	57
9	17	20
10	44	46
11	6	2*
12	15	14
13	8	7*
14	5	6*
15	4	3*
H,K=	2,	-12
-3	8	6*
-2	0	1*
-1	13	13
0	10	7
1	17	15
H,K=	2,	-10
-9	8	4*
-8	11	9
-7	18	16
-6	15	14
-5	25	25
-4	7	3*
-3	12	13
-2	8	4*
-1	6	1*
0	8	4*
1	8	5*
2	15	12
3	19	20
4	16	17
5	27	27
6	3	5*
7	7	7*
8	0	2*
H,K=	2,	-8
-12	5	2*
-11	7	3*
-10	24	24
-9	3	5*
-8	24	26
-7	8	4
-6	13	11
-5	6	4*
-4	5	5*
-3	4	3*
-2	10	7
-1	12	9
0	35	37
1	9	7
2	33	31
3	8	4*
4	13	14
5	9	9
6	9	6
7	6	2*
8	9	7
9	11	7
10	15	18
H,K=	2,	-6
-14	7	6*
-13	10	7
-12	5	4*
-11	16	13
-10	38	40
-9	12	12
-8	41	42
-7	11	8
-6	2	3*
-5	16	17
-4	22	22
-3	40	39
-2	15	16
-1	42	42
0	74	74
1	36	35
2	64	59
3	5	1*
4	6	7*
5	5	9*
6	18	15
7	18	18
8	10	8
9	15	18
10	23	23
11	7	5*
12	20	24
H,K=	2,	-4
-15	21	20
-14	3	3*
-13	22	23
-12	7	7*
-11	6	7*
-10	5	10*
-9	21	21
-8	4	3*
-7	25	25
-6	7	5*
-5	62	61
-4	5	2*
-3	83	84
-2	29	27
-1	15	17
0	12	11
1	16	15
2	44	44
3	37	38
4	24	22
5	62	63
6	29	26
7	32	33
8	34	36
9	10	10
10	7	6*
11	7	5*
12	16	16
13	10	8
H,K=	2,	-2
-16	8	8*
-15	15	12
-14	23	25
-13	18	16
-12	22	22
-11	13	13
-10	4	7*
-9	16	14
-8	16	15
-7	27	27
-6	20	20
-5	21	23
-4	24	24
-3	80	82
-2	106	99
-1	67	65
0	105	98
1	33	32
2	42	37
3	0	1*
4	15	14
5	29	30
6	34	37
7	50	53
8	24	24
9	25	26
10	10	9
11	7	6*
12	6	5*
13	2	1*
14	11	6
H,K=	2,	0
-16	6	3*
-14	7	7*
-12	19	19
-10	59	59
-8	6	2*
-6	47	45
-4	13	19
-2	92	97
2	46	33
4	16	20
6	21	20
8	41	41
10	32	32
12	5	4*
14	11	9
H,K=	3,	-11
-7	10	8*
-6	8	1*
-5	19	20
-4	6	4*
-3	13	15
-2	6	9*
-1	10	8
0	9	8*
1	6	11*
2	5	1*
3	19	18
4	10	7*
5	12	13
H,K=	3,	-9
-11	8	5*
-10	7	4*
-9	10	12*
-8	18	18
-7	12	9
-6	14	15
-5	11	10
-4	6	6*
-3	10	7
-2	4	2*
-1	4	2*
0	16	15
1	6	1*
2	24	25
3	9	6*
5	10	10
6	0	1*
7	11	11
8	5	1*
9	10	7
H,K=	3,	-7
-14	13	14
-13	5	1*
-12	9	9*
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7	14	14
8	9	5*
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7	21	22
8	11	11
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1	8	4*
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-9	18	18
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1	7	3*
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3	0	1*
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4	22	23
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2	0	3*
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-11	17	16
-10	8	7*
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-8	12	11
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-6	32	31
-5	14	14
-4	36	37
-3	12	12
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-1	18	20
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2	5	2*
3	11	10
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-10	13	10
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-8	14	12
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1	11	6
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-9	11	10
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-6	8	7*
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-14	8	7*
-13	8	3*
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-11	12	13
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-8	18	18
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H,K=	17,	-1
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-12	9	9*
-11	19	20
-10	8	7*
-9	0	2*
-8	20	19
-7	9	5*
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-2	13	9
-1	13	14
0	12	11
H,K=	18,	-4
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-7	16	16
-6	5	0*
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-10	6	1*
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-7	8	4*
-6	25	26
-5	5	1*
-4	4	0*
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-2	14	13
H,K=	18,	0
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-12	7	1*
-10	8	4*
-8	8	8*
-6	21	22
-4	17	16
-2	0	1*

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[a] The asterisks indicate data not used in the refinement.

Considering the current interest in trigonal-prismatic coordination, it is worthwhile to consider how closely the present structure resembles the limiting octahedral and trigonal-prismatic forms. Sulfur atoms S(1), S(2), and S(3)′ (triangle S_3, closest to the viewer in Figures 1 and 2) define one triangular face common to idealized octahedral and trigonal-prismatic forms. Atoms S(1)′, S(2)′, and S(3) define the corresponding opposite face (triangle S_3'). In the idealized polyhedra these faces are parallel. They are closely so in the present structure, making an angle of only 4.9° with one another. The vertex angles of both S_3 and S_3'

TABLE II

FRACTIONAL ATOMIC COORDINATES AND ANISOTROPIC TEMPERATURE FACTORS[a,b]

Atoms	x	y	z	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Fe	0[c]	0.0645 (2)	1/4[c]	27 (1)	58 (2)	48 (1)	0[d]	21 (1)	0[d]
S(1)	0.0152 (2)	0.2175 (2)	0.3562 (2)	44 (1)	78 (2)	50 (1)	6 (1)	29 (1)	−6 (1)
S(2)	0.1522 (1)	0.0116 (2)	0.3473 (2)	27 (1)	87 (2)	52 (1)	2 (1)	19 (1)	15 (1)
S(3)	0.0269 (1)	−0.0797 (2)	0.1533 (2)	32 (1)	94 (3)	57 (2)	1 (1)	18 (1)	23 (2)
C(1)	0.0085 (6)	0.3607 (8)	0.2981 (6)	36 (4)	57 (9)	70 (6)	5 (5)	28 (5)	1 (2)
C(2)	0.0242 (10)	0.4801 (13)	0.3621 (13)	75 (8)	131 (16)	142 (14)	−16 (9)	70 (9)	−41 (11)
C(3)	0.1372 (5)	−0.0901 (7)	0.2509 (6)	30 (4)	46 (8)	54 (5)	1 (4)	20 (4)	4 (5)
C(4)	0.2058 (6)	−0.3344 (10)	0.1540 (8)	32 (5)	121 (13)	86 (8)	−21 (6)	19 (5)	−6 (8)
C(5)	0.3060 (10)	−0.2848 (14)	0.4060 (10)	99 (10)	168 (19)	116 (12)	−32 (11)	45 (9)	−75 (12)
C(6)	0.1850 (7)	−0.2352 (9)	0.1632 (8)	57 (6)	79 (10)	80 (7)	2 (6)	42 (6)	21 (7)
C(7)	0.2239 (8)	−0.1665 (12)	0.1073 (8)	79 (7)	153 (15)	78 (8)	10 (8)	59 (7)	1 (9)
N	0.2022 (5)	−0.1588 (6)	0.2536 (6)	35 (4)	71 (7)	73 (5)	4 (4)	33 (4)	20 (5)
F(1)	0.0579 (10)	0.4541 (9)	0.4563 (8)	287 (14)	150 (11)	125 (8)	−16 (10)	105 (9)	−73 (8)
F(2)	0.0786 (7)	0.5642 (9)	0.3559 (9)	170 (9)	185 (11)	305 (15)	−115 (9)	169 (10)	−161 (11)
F(3)	−0.0496 (7)	0.5447 (9)	0.3352 (9)	130 (7)	170 (12)	286 (14)	24 (8)	112 (9)	104 (11)

[a] The numbers in the parentheses in all tables are the estimated standard deviations in the least significant figures. [b] The form of the anisotropic thermal ellipsoid is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. [c] Special position parameters fixed by symmetry. [d] The symmetry of the special position of Fe restrains its thermal parameters to $\beta_{12} = \beta_{23} = 0$.

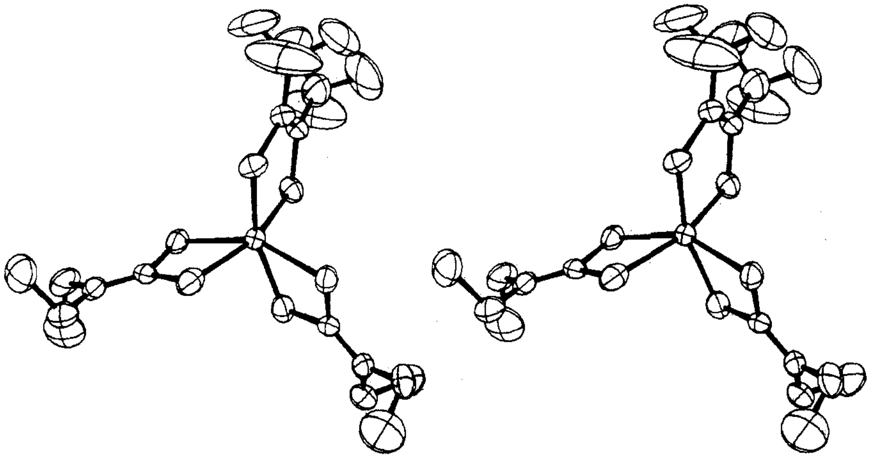

Figure 2.—A stereoscopic view of the $Fe[S_2CN(C_2H_5)_2]_2[S_2C_2(CF_3)_2]$ molecule. The ellipsoids are drawn to include 50% of the probability distribution. Hydrogen atoms are not shown. The view is down the axis through Fe which is perpendicular to the plane defined by S(1), S(2), S(3)′.

TABLE III

SELECTED INTERATOMIC DISTANCES (Å) AND BOND ANGLES (DEG)[a]

Distances

Fe–S(1)	2.195 (3)	S(1)–C(1)	1.702 (9)
Fe–S(2)	2.302 (2)	S(2)–C(3)	1.730 (8)
Fe–S(3)	2.318 (3)	S(3)–C(3)	1.706 (8)
S(1)–S(1)′	3.049 (4)	C(1)–C(1)′	1.360 (17)
S(2)–S(3)	2.799 (3)	C(1)–C(2)	1.515 (17)
S(1)–S(2)	3.221 (3)	C(2)–F(1)	1.289 (19)
S(1)–S(3)′	3.136 (3)	C(2)–F(2)	1.312 (17)
S(2)–S(3)′	3.204 (3)	C(2)–F(3)	1.294 (17)
S(1)–S(2)′	3.648 (3)	C(3)–N	1.302 (10)
S(1)–S(3)	4.466 (3)	C(4)–N	1.484 (12)
S(2)–S(2)′	4.472 (4)	C(6)–N	1.496 (12)
S(3)–S(3)′	3.557 (4)	C(4)–C(5)	1.491 (18)
		C(6)–C(7)	1.515 (15)

Angles

S(1)–Fe–S(1)′	88.0 (1)	C(1)′–C(1)–C(2)	125.4 (7)
S(2)–Fe–S(3)	74.6 (1)	S(2)–C(3)–S(3)	109.1 (4)
S(1)–Fe–S(2)	91.5 (1)	S(2)–C(3)–N	124.0 (6)
S(1)–Fe–S(3)	163.4 (1)	S(3)–C(3)–N	126.9 (6)
S(1)′–Fe–S(2)	108.4 (1)	C(3)–N–C(4)	121.4 (8)
S(1)′–Fe–S(3)	88.0 (1)	C(3)–N–C(6)	120.3 (7)
Fe–S(1)–C(1)	106.3 (3)	C(4)–N–C(6)	118.3 (7)
Fe–S(2)–C(3)	88.2 (3)	N–C(4)–C(5)	111.9 (9)
Fe–S(3)–C(3)	88.2 (3)	N–C(6)–C(7)	110.8 (8)
S(1)–C(1)–C(1)′	119.7 (3)	C(1)–C(2)–F(1)	113.2 (11)
S(1)–C(1)–C(2)	114.9 (8)	C(1)–C(2)–F(2)	112.6 (12)
		C(1)–C(2)–F(3)	113.3 (12)

are all 60 ± 1.5°. For true octahedral coordination these triangles would be staggered (60° mutual rotation) while for trigonal-prismatic geometry they would be eclipsed (0° mutual rotation). As seen from Figure 2 the actual structure is intermediate, with a mutual rotation of about 38.3° as defined by the angle made by the plane including S(1), Fe, and the midpoint of S(2)–S(3)′ with the plane passing through S(1)′, Fe, and the midpoint of S(2)′–S(3). For the complexes $Fe[S_2CN(C_4H_9)_2]_3$[13] and $Fe[S_2COC_2H_5]_3$[14] which contain the $Fe–S_6$ core, this angle has been reported as 32 and 41°, respectively. The interligand sulfur–sulfur distances in these triangles are all near 3.2 Å [S(1)–S(2) = 3.221 (3) Å, S(1)–S(3)′ = 3.136 (3) Å, S(2)–S(3)′ = 3.204 (3) Å]. These interligand sulfur distances are shorter than those found for $Co[S_2CN(C_2H_5)_2]_3$ (average 3.32 (1) Å)[15] but longer than in seven-coordinate $Mo[S_2CN(C_4H_9)_2]_3NO$ (average 3.03 (5) Å)[16] and trigonal-prismatic $V[S_2C_2(C_6H_5)_2]_3$ (average 3.06 (9) Å).[17] The present coordination geometry is best described as an

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(13) B. F. Hoskins and B. P. Kelly, *Chem. Commun.*, 1517 (1968).

(14) B. F. Hoskins and B. P. Kelly, *ibid.*, 45 (1970).

(15) S. Merlino, *Acta Crystallogr.*, *Sect. B*, **24**, 1441 (1968).

(16) T. F. Brennan and I. Bernal, *Chem. Commun.*, 138 (1970).

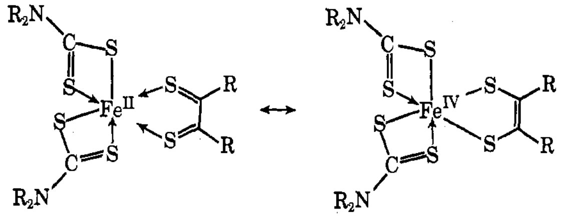
(17) R. Eisenberg, E. I. Steifel, R. C. Rosenberg, and H. B. Gray, *J. Amer. Chem. Soc.*, **88**, 2874 (1966).

octahedron distorted toward a trigonal prism; this type of distortion is appropriate for the trigonal twist mechanism of $\Delta \rightleftarrows \Lambda$ interconversion found for complexes of this type.[4] This mechanism requires an achiral trigonal-prismatic transition state.

1,1-Dithiolate Moieties, dtc.—No unusual features are found for the dithiocarbamate ligands which are expected to behave classically as ligands of charge 1−. The dtc sulfur–iron distances (2.302 (2) and 2.318 (3) Å) compare favorably with those found in low-spin (μ_{eff} = 2.72 BM at 296°) $\mathrm{Fe[S_2COC_2H_5]_3}$ (2.308 (3) and 2.326 (3) Å)[14] but are somewhat shorter than found for high-spin (μ_{eff} = 5.32 BM at room temperature) $\mathrm{Fe[S_2CN(C_4H_9)_2]_3}$ (average 2.418 (6) Å).[13] As does the present structure, the complex $\mathrm{Fe(CH_3C_6H_4CS_3)(CH_3C_6H_4CS_2)_2}$[18] contains one five-membered and two four-membered chelate rings; the Fe–S distances involved in the latter moieties (average 2.31 (2) Å) agree with those found here. In all of these complexes the iron is in a formal 3+ oxidation state. The Fe–S(3) bond is the longer of the two Fe–S(dtc) distances by 0.016 Å and is the one trans to the tfd ligand; however this difference is small and no significant trans effect is apparent. The bite size of the dtc ligand (*i.e.*, the S(2)–S(3) distance) is 2.799 (3) Å which agrees well with those found previously (2.78 (1), 2.80 (1)[15] and 2.81 (1), 2.82 (1) Å[16]). The S(2)–Fe–S(3) angle of 74.6 (1)° is close to those of $\mathrm{Fe[S_2CN(C_4H_9)_2]_3}$ (73°)[13] and $\mathrm{Co[S_2CN(C_2H_5)_2]_3}$ (76°).[15]

The carbon–sulfur dtc distances of 1.730 (8) and 1.706 (8) Å compare well with averages of 1.71 (2) and 1.70 (1) Å found for $\mathrm{Fe[S_2CN(C_4H_9)_2]_3}$[13] $\mathrm{Co[S_2CN(C_2H_5)_2]_3}$,[15] respectively. The nitrogen atom is coplanar with C(3), C(4), and C(6) to within 0.006 Å of the least-squares plane passing through these four atoms. The C(3)–N bond length of 1.30 (1) Å is shorter than the 1.41 (3) Å distance for the corresponding bond in $\mathrm{Fe[S_2CN(C_4H_9)_2]_3}$[13] but quite close to those found in $\mathrm{Co[S_2CN(C_2H_5)_2]_3}$ (average 1.32 (1) Å)[15] and $\mathrm{Mo[S_2CN(C_2H_5)_2]_3NO}$ (1.30 (2) Å);[16] the latter two distances have been taken as evidence for a high degree of double-bond character. Indeed, applying the semiempirical equation of Nishimoto and Forster[19] for the correlation of C–N bond orders and bond lengths, the present C–N bond length corresponds to a bond order of 1.8. Of the two dynamical processes detectable by nmr, the one corresponding to C–N bond rotation requires the greater energy of activation (E_a = 17 kcal/mol),[5] consistent with a fairly high C–N bond order. The other C–N lengths of 1.48 (1) and 1.50 (1) Å are reasonable for C–N single bonds. The dtc ethyl groups are unremarkable with the terminal methyl carbon atoms exhibiting considerable amplitude of thermal motion.

1,2-Dithiolene Moiety, tfc.—The description of the electronic structures and the determination of the effective oxidation levels of the metal and ligand moieties in dithiolene complexes are subjects of some interest.[4] Two limiting, nonequivalent, valence-bond (VB) structures, **2** and **3**, can be drawn for this complex (ignoring the trivial resonance possible for the dtc ligands). In principle, an estimate of the relative importance of the two structures should be possible from a consideration of C–C and C–S bond lengths of the tfd ligand. In practice, however, it is found that these parameters are not as sensitive or as reliable in this regard as might be hoped. The present tfd C–C bond length of 1.36 (2) Å and C–S bond length of 1.702 (9) Å are perhaps significantly longer and shorter, respectively, than the corresponding average distances 1.31 (4) and 1.76 (3) Å, respectively, in $\mathrm{[(C_6H_5)_3PCl][Au(tfd)_2]}$,[20] where it is reasonable that the tfd ligands have been reduced to the dithiolato(2−) level. This implies that structure **2** contributes considerably to the structure and, considering that 2+ is a more reasonable oxidation level for iron than 4+, perhaps is more heavily weighted than structure **3** in the VB description of the electronic structure. The present C–C and C–S distances compare reasonably well with those in $\mathrm{[Ni(tfd)_2](perylene)}$ (1.38 (2) and 1.72 (1) Å, respectively),[21] and are virtually identical with those in $\mathrm{(C_6H_5)_3AsFe(tfd)_2}$ (average 1.37 (1) and 1.70 (1) Å, respectively).[22] The generally accepted[4c,d] electronic description of these and other neutral dithiolene complexes involves the effective 1− oxidation state for the ligands, in the present case corresponding to an equal weighting of structures **2** and **3**. Moreover, implicit in structure **2** is the possibility that "π-back-bonding" may modify the structure in such a way as to decrease the C–S and increase the C–C bond orders. Thus, a reasonable description of the electronic structure might involve limiting resonance structures **2** and **3**, with the former somewhat more heavily weighted and implying some metal to ligand π charge transfer. Both structures **2** and **3** are consistent with either singlet or triplet spin states, depending on the details of the iron and ligand orbital energy levels. The above VB description implies an effective 3+ oxidation level for the iron but not in the classical sense where an odd number of unpaired electrons would be expected on the iron atom.



2 **3**

The present Fe–S(1) distance of 2.195 (3) Å is virtually identical with that found (2.20 (1) Å)[23] for the Fe–S bond not involved in dimer formation in $\mathrm{[Fe(S_2C_2(CN)_2)_2]^{2-}}$, and is slightly longer than that determined for $\mathrm{As(C_6H_5)_3Fe(tfd)_2}$ (2.15 (1) Å).[22]

The $\mathrm{C{-}CF_3}$ groups are normal with the fluorine atoms exhibiting a large degree of anisotropic thermal motion indicative of significant torsional vibrational amplitude (see Figure 2).

Effect of Spin-State Equilibrium.—The present structural determination is unique in that, to our knowledge, it represents the first study of a crystal wherein roughly equal numbers of component molecules

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[18] D. Coucouvanis and S. J. Lippard, *J. Amer. Chem. Soc.*, **91**, 307 (1969).

[19] K. Nishimoto and L. S. Forster, *Theoret. Chim. Acta*, **4**, 155 (1966).

[20] J. H. Enemark and J. A. Ibers, *Inorg. Chem.*, **7**, 2636 (1968).

[21] R. D. Schmitt, R. M. Wing, and A. H. Maki, *J. Amer. Chem. Soc.*, **91**, 4394 (1969).

[22] E. F. Epstein, I. Bernal, and A. L. Balch, *Chem. Commun.*, 136 (1970); E. F. Epstein and I. Bernal, to be submitted for publication.

[23] W. C. Hamilton and I. Bernal, *Inorg. Chem.*, **6**, 2003 (1967).

exist in different electronic spin states. Hoskins and Kelly studied $Fe[S_2CN(C_4H_9)_2]_3$[13] and $Fe[S_2COC_2H_5]_3$[14] which, while exhibiting spin-state equilibria to a small extent, represent very nearly the high-spin ($S = {}^5/_2$) and low-spin ($S = {}^1/_2$) extremes, respectively. The Fe–S bond length in the former complex was found to be approximately 0.1 Å longer than that found in the latter, indicating significant Fe–S antibonding character for the $S = {}^5/_2$ electronic state. The fact that good single crystals of the present complex are obtained with 50% $S = 1$ spin state populated at the temperature of the X-ray measurements suggests that the $S = 1$ state has minimal antibonding character. Furthermore, the sulfur atom thermal ellipsoids are normal, except that the ellipsoid of the dtc sulfur atom, S(3), trans to the tfd ligand is elongated along the Fe–S bond axis (see Figure 2). This may or may not be indicative of some spin-state influence on this Fe–S bond length.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
NORTHWESTERN UNIVERSITY, EVANSTON, ILLINOIS 60201

The Crystal and Molecular Structure of Hydridonitrosyltris(triphenylphosphine)iridium(I) Perchlorate, $[IrH(NO)(P(C_6H_5)_3)_3][ClO_4]$

BY D. M. P. MINGOS AND JAMES A. IBERS*

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The structure of hydridonitrosyltris(triphenylphosphine)iridium(I) perchlorate, $[IrH(NO)(P(C_6H_5)_3)_3][ClO_4]$, has been determined from three-dimensional X-ray data collected by counter methods. The compound crystallizes in the space group $Pbc2_1$ of the orthorhombic system with four molecules in a unit cell of dimensions $a = 11.335$ (9), $b = 21.992$ (17), and $c = 19.170$ (15) Å. The observed and calculated densities are 1.53 (±0.02) and 1.54 g cm^{-3}, respectively. Least-squares refinement has led to a final value of the conventional R factor (on F) of 0.047 for the 1342 reflections having $F^2 > 3\sigma(F^2)$. The structure consists of well-separated monomeric ions and the geometry around the metal is described as distorted trigonal bipyramidal with the hydrido and nitrosyl ligands occupying the axial positions and the triphenylphosphine ligands the equatorial positions. The iridium atom lies 0.51 Å above the plane of the three phosphorus atoms. The hydrogen atom was not located in the structural determination. However its position has been inferred because the geometry of the other ligands around the metal is very similar to that found for the complexes $RhH(CO)(P(C_6H_5)_3)_3$ and $CoH(N_2)(P(C_6H_5)_3)_3$ for which the hydrogen atoms have been located. The iridium–nitrogen–oxygen bond angle of 175 (3)° suggests that this complex is best formulated as an NO^+ complex of iridium(I). Other important bond lengths in the molecule are as follows (Å): Ir–P, 2.346 (9), 2.341 (8), 2.334 (8); Ir–N, 1.68 (3); N–O, 1.21 (3). The bonding of the nitrosyl group in this complex is compared with that found in other iridium complexes, which have the nitrosyl ligand coordinated as NO^-. Also the geometries of the five-coordinate complexes $MH(X)(P(C_6H_5)_3)_3$ ($M = Co, X = N_2$; $M = Rh, X = CO$; $M = Ir, X = NO^+$) seem to be influenced by the degree of double bonding of the M–X bond, and it is proposed that electron-pair repulsions are responsible for the distortions from the ideal trigonal-bipyramidal geometry.

Introduction

Interest has been shown recently in the ability of nitric oxide to bond to transition metals in two quite distinct ways. The complexes which have the nitrosyl ligand coordinated in a linear fashion have been formulated as complexes of NO^+ because of their close similarity to carbonyl complexes. In contrast the complexes which have a metal–nitrogen–oxygen bond angle of approximately 120° have been formulated as complexes of NO^-, which is isoelectronic with O_2. A possible reason that NO^- and O_2 coordinate in a different fashion in certain iridium and rhodium complexes has been discussed previously.[1] It also appears that coordination of nitric oxide as NO is possible in certain paramagnetic complexes. However no structural evidence for this mode of coordination exists at present. We have shown that the iridium complexes $[IrX(NO)(CO)(P(C_6H_5)_3)_2][BF_4]$ (X = Cl, I)[2–4] and $IrXY(NO)(P(C_6H_5)_3)_2$ (X = Y = Cl;[1] X = I, Y = CH_3[5]) have the nitrosyl ligand coordinated as NO^-. The complex $[IrH(NO)(P(C_6H_5)_3)_3][ClO_4]$, which was prepared by Reed and Roper[6] from perchloric acid and $Ir(NO)(P(C_6H_5)_3)_3$, is closely related to the iridium complexes mentioned above and it was of interest to examine the mode of coordination of the nitrosyl ligand in this complex. The low electronegativity and minimal steric requirements of the hydrido ligand could have an unusual effect on the metal–nitrosyl geometry.

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[1] D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, **10**, 1035 (1971).

[2] D. J. Hodgson and J. A. Ibers, *ibid.*, **7**, 2345 (1968).

[3] D. J. Hodgson, N. C. Payne, J. A. McGinnety, R. G. Pearson, and J. A. Ibers, *J. Amer. Chem. Soc.*, **90**, 4486 (1968).

[4] D. J. Hodgson and J. A. Ibers, *Inorg. Chem.*, **8**, 1282 (1969).

[5] D. M. P. Mingos, W. T. Robinson, and J. A. Ibers, *ibid.*, **10**, 1043 (1971).

[6] C. A. Reed and W. R. Roper, *Chem. Commun.*, 155 (1969).