Stereochemical Control of Valence. 5. Comparison of the Molecular and Electronic Structures of Five- and Six-Coordinate *o*-Phenylenebis(dimethylarsine) Complexes of the $\{FeNO\}^7$ Group[1]

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Abstract: The structures of $[Fe(NO)(das)_2][ClO_4)]_2$ (**1**) and $[Fe(NO)(das)_2(NCS)][B(C_6H_5)_4]\cdot(CH_3)_2CO$ (**2**) (where das is *o*-phenylenebis(dimethylarsine)) have been determined from single-crystal x-ray diffraction data. Compound **1** crystallizes in space group $D_{2h}{}^{15}$-*Pbca* with eight molecules in a cell of dimensions $a = 16.561$ (10), $b = 20.248$ (10), and $c = 18.289$ (12) Å. The calculated and observed densities are 1.857 and 1.86 (1) g cm^{-3}, respectively. Compound **2** crystallizes in space group $C_i{}^1$-$P\bar{1}$ with two molecules in a cell of dimensions $a = 13.509$ (11) Å, $b = 14.988$ (16) Å, $c = 13.160$ (14) Å, $\alpha = 75.14$ (7)°, $\beta = 76.78$ (6)°, and $\gamma = 95.54$ (8)°. The observed and calculated densities are 1.473 and 1.461 (2) g cm^{-3}, respectively. Full-matrix least-squares refinements of both structures using the data having $F_o{}^2 \geqslant 3\sigma(F_o{}^2)$ gave $R = 0.0638$ for 2310 data for **1** and $R = 0.0580$ for 4675 data for **2**. Structure **1** consists of $[Fe(NO)(das)_2]^{2+}$ cations and two kinds of $ClO_4{}^-$ anions. One $ClO_4{}^-$ is well separated from the Fe atom and one interacts weakly with Fe···O = 2.66 Å. The five-coordinate cation has tetragonal pyramidal coordination geometry with the NO group occupying the axial position. The Fe–N–O angle is 173 (1)° and the Fe–N distance is 1.65 (2) Å. Structure **2** contains $[Fe(NO)(das)_2(NCS)]^+$ cations, $[B(C_6H_5)_4]^-$ anions, and one acetone of crystallization per formula unit. The six-coordinate cation has trans geometry with Fe–NO = 1.717 (8) Å and Fe–NCS = 1.996 (8) Å. The Fe–N–O angle is 158.6 (9)°. The EPR spectra of **1** and analogues of **2** are distinctly different. The properties of **1** and **2** are compared to $\{CoNO\}^8$ complexes of the same ligands and to other five- and six-coordinate complexes of the $\{FeNO\}^7$ group.

We have recently shown[2-5] that transition metal mononitrosyl compounds can be conveniently described as derivatives of covalent triatomic $\{MNO\}^n$ fragments.[6] This description of the bonding implies that the geometry, electronic structure, and chemical reactivity of each $\{MNO\}^n$ group can be controlled by the other ligands coordinated to the metal. The relationship between stereochemical change at the metal center and changes in the properties of the $\{FeNO\}^n$ group are of particular interest. We have previously demonstrated that the structure, bonding, and reactivity of the diamagnetic $\{CoNO\}^8$ group can be modified by stereochemical changes at the metal.[1,2,7]

Complexes of the $\{FeNO\}^7$ group offer very sensitive probes of stereochemical control of the valence electron distribution because many have ground states with $S = \frac{1}{2}$ and give electron paramagnetic resonance (EPR) spectra.[2] Of particular interest are ligand systems which stabilize multiple stereochemistries of the $\{FeNO\}^7$ group with different EPR spectra. Such complexes provide an ideal opportunity to relate molecular structure to the electronic structure of the $\{FeNO\}^7$ group and may ultimately be useful for interpreting the properties of biologically more important species such as nitrosyl hemoglobins.[8]

To our knowledge, in all complexes formed by the $\{FeNO\}^7$ group the iron atom has nearly tetragonal geometry with coordination numbers of either five or six. However, *both* five- and six-coordinate complexes of the $\{FeNO\}^7$ group have been isolated and characterized for just three ligand systems: CN^-,[9] das,[10] and TPP.[11-13] The structures of several of these complexes have previously been determined by x-ray crystallography,[9,11,12,14] but only $[Fe(NO)(CN)_4]^{2-}$, which has a nearly linear FeNO group, was free of disorder.[9] The structures of Fe(NO)(TPP) and Fe(NO)(TPP)(1-MeIm) reported recently by Scheidt and co-workers[11,12] have nonlinear disordered FeNO groups. An early structure determination[14] of $[Fe(NO)(das)_2Br][ClO_4]$ showed it to have trans geometry and a nonlinear FeNO group whose detailed geometry was obscured by disorder between the Br atom and the NO group. We have shown[1] that crystallographic disorder between X and NO in $[M(NO)(das)_2X]^+$ ions is eliminated when $X^- = NCS^-$. Consequently, $[Fe(NO)(das)_2][ClO_4]_2$ (**1**) and $[Fe(NO)(das)_2(NCS)][BPh_4]\cdot(CH_3)_2CO$ (**2**) were selected for the comparative structural and EPR studies reported below. The preparation, electronic spectra, infrared spectra, and solution conductivity of these compounds have been presented and discussed previously.[10,15,16]

Experimental Section

The compounds, $[Fe(NO)(das)_2][ClO_4]_2$ (**1**) and *trans*-$[Fe(NO)(das)_2(NCS)][BPh_4]\cdot(CH_3)_2CO$ (**2**) were prepared using methods which have been described previously.[10,15] The IR spectra were obtained using a Beckman IR-12 spectrophotometer. The EPR spectra of pure solids and of dilute solutions of the complexes in several solvents were obtained at room temperature and 77 K using a Varian E-3 spectrometer.

Crystal Structure Determination. Single crystals of **1** and **2** were prepared by Dr. T. E. Nappier. The crystal data are summarized in Table I. Data were collected on a Picker FACS-1 diffractometer equipped with an incident beam monochromator. Details concerning data collection, data processing, scattering factor tables, and computer programs used can be found in a previous publication.[1] The structure of **1** was solved by direct methods which revealed the positions of the Fe and As atoms. The remaining atoms were located by subsequent structure factor calculations and difference electron density maps. Refinement was based on F_o with $\Sigma w(|F_o| - |F_c|)^2$ being minimized. The weights were taken with $w = 4F_o{}^2/\sigma^2(F_o{}^2)$. Only data having $F_o{}^2 \geqslant 3\sigma(F_o{}^2)$ were used in refinement. The phenyl rings of the das ligands were refined as rigid groups[17] (D_{6h}-$6/mmm$ symmetry, C–C = 1.383 Å) with individual isotropic thermal parameters assigned to each C atom. The O atoms of the perchlorate anions were also refined as rigid groups (T_d-$\bar{4}3m$ symmetry, Cl–O = 1.42 Å) with individual isotropic thermal parameters. Hydrogen atoms were included as fixed contributors in the final refinement, and the final R factors are shown in Table I. A structure factor calculation for all 4025 data gave R = 0.122 and R_w = 0.0849.

The coordinates of the Fe and As atoms of **2** were determined from a Patterson function and the remaining atoms located by structure factor calculations and difference electron density maps. The phenyl rings of the tetraphenylborate anion were refined as rigid groups (C–C = 1.392 Å) with individual isotropic thermal parameters. All other

Table I. Crystal Data

	$[Fe(NO)(das)_2][ClO_4]_2$	$[Fe(NO)(das)_2(NCS)]$- $[B(C_6H_5)_4]\cdot[(CH_3)_2CO]$
Color	Violet	Brown
Habit	Rectangular parallelpiped	Rectangular parallelpiped
Dimensions	0.20 × 0.31 × 0.28 mm	0.22 × 0.22 × 0.57 mm
Space group	*Pbca*	$P\bar{1}$
Cell parameters[a]	a = 16.561 (10)	a = 13.509 (11) (13.16)[b]
	b = 20.248 (10)	b = 14.988 (16) (13.51)
	c = 18.289 (12)	c = 13.160 (14) (14.99)
	α = 90.00	α = 75.14 (7) (95.54)
	β = 90.00	β = 76.78 (6) (104.86)
	γ = 90.00	γ = 95.54 (8) (103.72)
Calcd density	1.857 g cm^{-3}	1.473 g cm^{-3} (including acetone)
Obsd density	1.86 (1) g cm^{-3} [c]	1.461 (2) g cm^{-3}
Z	8	2
λ (Å)	0.71069 (Mo Kα)	0.71069
Scan technique	θ-2θ	θ-2θ
Scan width	1.6°	1.8°
Takeoff angle	1.7°	1.8°
Scan rate	1°/min	0.5°/min and 1.0°/min[d]
Background time	10 s	10 s
$2\theta_{max}$	45°	45°
No. of unique data	4025	6037
No. of data >3σ	2310	4675
μ	53.1 cm^{-1}	32.04 cm^{-1}
Transmission factors	0.209-0.414[e]	0.402-0.567[f]
Faces of crystal	{100}, {001}, (11$\bar{2}$), (0$\bar{2}\bar{1}$), (041)	{101}, {100}, {1$\bar{1}$1}, {$\bar{1}$,1,1}
Final R	0.0638	0.0580
Final R_w	0.0775	0.0788
σ for reflection of unit weight	2.33	2.75

[a] At ambient temperature. [b] Values in parentheses are for the standard setting of the right-handed reduced cell.[33] This cell is related to the one used in the structure determination by $a_r = c$, $b_r = -a$, and $c_r = -b$. [c] Densities were determined by the gradient column method. The solvents for $[Fe(NO)(das)_2(NCS)][B(C_6H_5)_4]\cdot[(CH_3)_2CO]$ were bromobenzene and chlorobenzene; those for $[Fe(NO)(das)_2][ClO_4]_2$ were carbon tetrachloride and ethyl iodide. [d] Two separate scale factors were used for this data set. [e] A Gaussian absorbtion correction was performed. [f] An analytical absorbtion correction was performed.

Table II. Final Atomic Parameters for $[Fe(NO)(das)_2][ClO_4]_2$

Atom[a]	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	.09557(14)	.26498(10)	.38629(13)	36.2(11)	19.1(6)	23.8(10)	3.8(7)	-3.8(9)	-1.6(6)
As(1)	.00373(11)	.35518(7)	.40415(9)	35.0(8)	17.7(4)	27.0(6)	.4(5)	1.7(6)	-2.4(4)
As(2)	.16567(12)	.34062(8)	.30777(11)	28.3(8)	22.5(5)	43.4(9)	-2.4(5)	3.1(7)	-2.7(5)
As(3)	.16345(11)	.16792(8)	.34021(10)	33.7(8)	21.0(5)	39.5(8)	5.0(6)	-2.1(7)	-1.4(5)
As(4)	.00452(15)	.18621(9)	.43676(12)	92.6(15)	21.5(5)	42.1(9)	4.4(7)	34.8(10)	6.5(6)
Cl(1)	.4611(3)	.24600(21)	.28497(29)	59.0(26)	23.6(13)	45.0(23)	.9(16)	4.0(21)	1.8(13)
Cl(2)	.2368(3)	.01009(26)	.0536(3)	57(3)	40.8(19)	71(3)	-15.7(20)	-7.3(26)	.4(19)
N	.1541(11)	.2767(8)	.4585(10)	71(10)	42(6)	33(7)	19(6)	-21(7)	-6(5)
O(1)	.1900(12)	.2795(10)	.5116(11)	120(14)	81(8)	77(11)	6(8)	-66(10)	-8(8)
C(13)	-.0021(11)	.3862(8)	.5068(9)	56(10)	31(5)	24(7)	-2(6)	5(7)	-6(5)
C(14)	.2726(11)	.3624(9)	.3443(13)	35(9)	36(7)	97(14)	-5(6)	-26(9)	-11(8)
C(15)	.2569(11)	.1439(9)	.3973(11)	40(9)	39(7)	56(10)	12(6)	-3(8)	10(7)
C(16)	.0406(25)	.1690(12)	.5417(12)	342(42)	50(10)	19(9)	-24(16)	42(16)	11(7)
C(17)	-.1127(10)	.3531(8)	.3749(10)	26(8)	29(5)	50(9)	2(5)	1(7)	1(6)
C(18)	.1862(12)	.3261(9)	.2024(10)	68(13)	43(7)	39(9)	-1(7)	20(8)	-8(7)
C(19)	.1997(11)	.1578(9)	.2427(11)	45(9)	36(6)	50(9)	12(7)	11(7)	-8(6)
C(20)	-.1083(15)	.1950(11)	.4443(22)	67(14)	43(9)	259(33)	0(9)	110(19)	8(13)

[a] x, y, and z are in fractional coordinates. Anisotropic thermal parameters are in the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. The standard deviations of the least significant figure are given in parentheses.

atoms were refined anisotropically. The weighting scheme was the same as that used for **1**. Final R factors are shown in Table I. A structure factor calculation on all 6037 data gave R = 0.074 and R_w = 0.082. The final atomic parameters for **1** and **2** appear in Tables II and III, respectively. Final group parameters are in Table IV and derived group parameters appear in Tables V and VI. Tables of $10|F_o|$ and $10|F_c|$ are available (see note at end of paper).

Description of the Structures. The structure of **1** consists of discrete five-coordinate $[Fe(NO)(das)_2]^{2+}$ ions surrounded by two types of perchlorate anions. One type of perchlorate has no specific interaction with the cation. The second type has a weak electrostatic interaction with the cation and an Fe···O distance of 2.66 Å. A similar weak interaction occurs[18] in $[Co(CNC_6H_5)_5][ClO_4]_2$ between the five-coordinate tetragonal pyramidal $[Co(CNC_6H_5)_5]^{2+}$ ion and a perchlorate ion. A stereoview of the packing of **1** is shown in Figure 1 and the distance and angles are given in Table VII.

Two projections of the five-coordinate cation of **1** are shown in Figures 2 and 3. Selected distances and angles also appear in these figures which illustrate the tetragonal pyramidal coordination geometry of the cation. The four As atoms comprise the basal plane of the pyramid and the average Fe-As distance is 2.399 Å. The Fe atom is 0.32 Å above the plane of the four As atoms (Table VIII). The phenyl rings of both das ligands are below the plane of the four As atoms so that the overall geometry of the $Fe(das)_2$ portion of the molecule is "domed".

The NO group occupies the axial position of the pyramid with Fe-N = 1.66 (2) Å and Fe-N-O = 172.8 (17)°. Similar parameters for the $\{FeNO\}^7$ group have been reported[9] for the tetragonal pyramidal

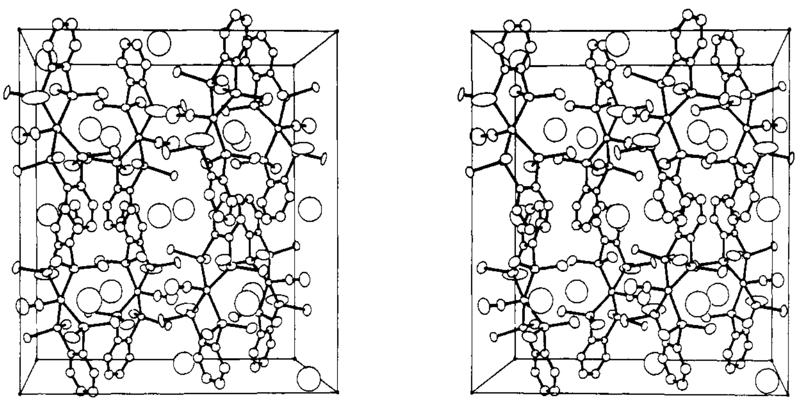

Figure 1. Stereoview of the packing in **1**. The ClO_4^- ions are represented by a single open circle for clarity. The positive direction of the *a* axis is into the page. The positive direction of the *c* axis is to the right.

Table III. Final Atomic Parameters for $[Fe(NO)(das)_2(NCS)][B(C_6H_5)_4]\cdot[(CH_3)_2CO]$

Atom	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	-.25995(10)	.30812(9)	.05629(10)	41.7(9)	29.8(7)	48.4(9)	10.0(6)	-10.2(7)	-9.7(6)
As(1)	-.18859(8)	.45995(7)	-.06583(8)	56.8(8)	35.0(6)	56.4(8)	8.9(5)	-14.5(6)	-4.2(5)
As(2)	-.32039(8)	.38873(7)	.18617(8)	62.9(8)	34.2(6)	61.0(8)	7.1(5)	- 2.7(6)	-14.0(5)
As(3)	-.34695(7)	.15967(6)	.17221(7)	47.2(7)	32.1(6)	49.9(7)	7.2(5)	-6.3(6)	-10.5(5)
As(4)	-.21682(8)	.23069(7)	-.08103(8)	56.1(8)	44.5(6)	50.0(8)	11.6(5)	-9.8(6)	-15.8(5)
S	-.56835(28)	.33158(26)	-.0592(4)	85.9(28)	86.7(26)	190(5)	26.6(22)	-85(3)	-27.6(27)
O(1)	-.1007(8)	.2787(10)	.1534(9)	77(8)	241(14)	167(12)	-21(8)	-62(8)	58(10)
O(2)	-.1257(11)	.2008(11)	-.4421(15)	145(14)	221(17)	327(24)	53(12)	-1(15)	-134(17)
N(1)	-.1494(6)	.2967(6)	.0979(6)	53(6)	51(5)	63(7)	9(5)	-26(5)	-5(5)
N(2)	-.3889(6)	.3189(5)	.0084(6)	46(6)	51(5)	70(7)	13(5)	-24(5)	-12(5)
B	-.2773(9)	-.2087(7)	.4383(9)	63(9)	31(6)	59(9)	7(6)	-7(7)	-16(6)
C(1)	-.1912(7)	-.4523(6)	.0182(8)	55(7)	36(6)	66(8)	12(5)	-22(6)	-15(5)
C(2)	-.1429(7)	-.3578(7)	-.0302(9)	47(7)	39(6)	91(9)	11(5)	-23(7)	-14(6)
C(3)	-.1470(9)	-.2989(7)	.0347(11)	68(9)	43(7)	120(12)	9(6)	-35(9)	-8(7)
C(4)	-.1993(9)	-.3310(8)	.1490(11)	76(9)	54(7)	136(13)	25(7)	-48(9)	-44(8)
C(5)	-.2481(8)	-.4232(7)	.1996(9)	59(8)	44(7)	111(11)	15(6)	-19(8)	-27(7)
C(6)	-.2438(7)	-.4843(6)	.1283(9)	55(7)	29(5)	96(10)	13(5)	-28(7)	-21(6)
C(7)	-.3519(7)	.0754(6)	.0840(8)	56(7)	37(6)	64(8)	18(5)	-26(6)	-22(5)
C(8)	-.4113(8)	-.0159(7)	.1309(8)	52(8)	42(6)	89(9)	7(6)	-18(7)	-13(6)
C(9)	-.4156(9)	-.0741(8)	.0641(10)	72(9)	52(7)	120(12)	12(6)	-30(9)	-45(8)
C(10)	-.3612(10)	-.0434(8)	-.0454(11)	88(10)	63(8)	123(13)	11(8)	-32(10)	-53(8)
C(11)	-.3017(9)	.0474(8)	-.0948(9)	85(10)	71(8)	97(10)	29(7)	-33(8)	-60(8)
C(12)	-.2994(7)	.1061(7)	-.0255(8)	54(7)	47(6)	73(9)	4(5)	-16(7)	-24(6)
C(13)	-.2570(10)	.5183(8)	-.1762(9)	134(13)	56(7)	96(11)	38(8)	-73(10)	0(7)
C(14)	-.4648(8)	.4104(8)	.2088(11)	51(8)	63(8)	174(15)	13(6)	9(9)	-54(9)
C(15)	-.4924(7)	.1496(7)	.2488(8)	36(7)	49(6)	91(9)	7(5)	17(6)	-11(6)
C(16)	-.2423(11)	.2841(9)	-.2239(8)	169(15)	92(9)	53(9)	49(10)	-64(9)	-23(7)
C(17)	-.0416(8)	.4793(7)	-.1461(9)	58(8)	50(7)	97(10)	2(6)	16(7)	9(7)
C(18)	-.3059(11)	.3429(8)	.3367(8)	182(16)	75(9)	39(8)	23(9)	-32(9)	-12(7)
C(19)	-.2849(8)	.0933(7)	.2848(7)	82(9)	50(6)	55(8)	20(6)	-33(7)	-7(6)
C(20)	-.0751(8)	.2048(9)	-.1217(10)	51(8)	84(9)	135(13)	26(7)	3(8)	-43(9)
C(21)	-.4628(9)	.3251(7)	-.0204(8)	70(9)	35(6)	75(9)	6(6)	-24(7)	-10(6)
C(22)	-.0662(13)	.2192(16)	.4618(18)	76(13)	162(20)	208(24)	37(14)	-24(14)	-43(18)
C(23)	-.0391(12)	.1406(11)	.4136(14)	114(14)	98(12)	213(20)	25(10)	-18(13)	-86(13)
C(24)	-.0191(15)	.3099(12)	.4070(21)	120(17)	79(12)	403(38)	15(12)	-83(20)	3(18)

Table IV. Parameters for Rigid Groups[a]

Group	x_c	y_c	z_c	ϕ	θ	ρ
			$[Fe(NO)(das)_2(NCS)][B(C_6H_5)_4]\cdot(CH_3)_2CO$			
R1	−0.2513 (3)	−0.1565 (3)	−0.3555 (3)	−0.154 (5)	2.632 (3)	−1.633)5)
R2	−0.1188 (3)	−0.07245 (28)	0.2372 (3)	−1.241 (6)	−2.280 (3)	1.403 (6)
R3	−0.2366 (4)	−0.4131 (4)	0.4760 (4)	−1.444 (5)	2.928 (5)	−2.881 (5)
R4	−0.4932 (4)	−0.1879 (3)	0.4044 (3)	−3.072 (4)	2.644 (4)	2.643 (5)
			$[Fe(NO)(das)_2][ClO_4]_2$			
R1	0.0728 (4)	0.4857 (3)	0.3151 (4)	−3.075 (6)	−2.882 (7)	−2.526 (7)
R2	0.0419 (5)	0.0401 (4)	0.3680 (4)	2.892 (7)	3.000 (7)	0.584 (7)
ClO_4-1	0.4632 (5)	0.2462 (4)	0.2841 (5)	−1.694 (8)	2.743 (8)	−0.039 (8)
ClO_4-2	0.2369 (7)	0.0061 (6)	0.0562 (7)	2.132 (24)	2.020 (10)	2.040 (26)

[a] x_c, y_c, and z_c are the fractional coordinates of the center of the group. The angles ϕ, θ, and ρ (in radians) bring about alignment except for translation of an internal coordinate system within the group with a fixed external coordinate system.

complex $[Fe(NO)(CN)_4]^{2-}$ (Fe-N = 1.565 Å, Fe-N-O = 177.1°).

Both perchlorate anions are ordered and were refined as rigid groups. However, each group has one O atom with an isotropic thermal parameter significantly smaller than the other three, suggesting that the anions may be undergoing torsional libration about a threefold axis.

The structure of the $[Fe(NO)(das)_2(NCS)]^+$ cation of **2** is shown in Figure 4 and the inner coordination sphere is depicted in Figure 5. Selected distances and angles are shown in the figures and in Tables

Table V. Derived Parameters for Group Atoms in $[Fe(NO)(das)_2][ClO_4]_2$

Group[a]	Atom	x	y	z	B
R1	C(1)	0.0430 (6)	0.4318 (4)	0.3530 (5)	3.0 (3)
	C(2)	0.0039 (5)	0.4921 (5)	0.3573 (6)	4.3 (4)
	C(3)	0.0337 (7)	0.5459 (4)	0.3194 (7)	5.0 (4)
	C(4)	0.1026 (7)	0.5395 (4)	0.2772 (6)	5.3 (4)
	C(5)	0.1417 (5)	0.4793 (5)	0.2729 (6)	4.5 (4)
	C(6)	0.1119 (6)	0.4255 (4)	0.3108 (6)	3.8 (4)
R2	C(7)	0.0941 (6)	0.0924 (5)	0.3566 (6)	4.2 (4)
	C(8)	0.1110 (6)	0.0312 (6)	0.3267 (6)	6.0 (5)
	C(9)	0.0588 (8)	−0.0211 (4)	0.3381 (7)	6.2 (5)
	C(10)	0.0104 (7)	−0.0122 (5)	0.3794 (7)	5.7 (5)
	C(11)	0.0273 (6)	0.0490 (6)	0.4093 (6)	5.4 (4)
	C(12)	0.0250 (7)	0.1013 (4)	0.3979 (6)	3.3 (3)
ClO_4-1	O(2)	0.4750 (7)	0.3156 (4)	0.2869 (7)	7.5 (4)
	O(3)	0.4900 (9)	0.2173 (6)	0.3506 (6)	12.8 (6)
	O(4)	0.5079 (8)	0.2194 (6)	0.2249 (7)	10.3 (5)
	O(5)	0.3798 (6)	0.2324 (7)	0.2741 (9)	12.7 (6)
ClO_4-2	O(6)	0.2746 (10)	0.0629 (7)	0.0261 (11)	16.7 (8)
	O(7)	0.2906 (9)	−0.0485 (8)	0.0518 (11)	16.6 (8)
	O(8)	0.1654 (8)	−0.0083 (7)	0.0163 (8)	9.9 (5)
	O(9)	0.2169 (12)	0.0182 (10)	0.1305 (7)	19.8 (10)

[a] The estimated standard deviations are derived from those of the group atoms and are meant to be used in error analysis on intergroup distances. The intra-ring C-C is 1.383 Å. The Cl-O distance is 1.42 Å. *B* is the individual isotropic thermal parameter (in $Å^2$) for each atom in the group.

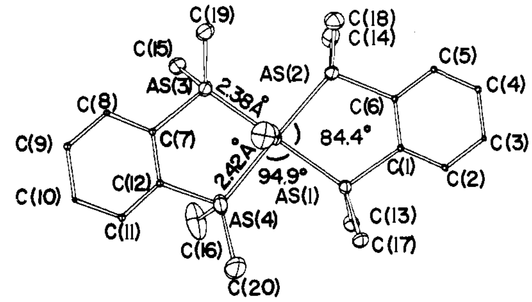

Figure 2. Perspective view of **1** normal to the plane of the As atoms. H atoms have been omitted and phenyl C atoms have been made arbitrarily small for clarity.

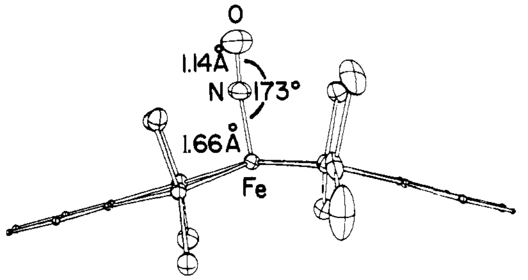

Figure 3. Perspective view of **1** parallel to the plane of the four As atoms. The cation shown in this figure is enantiomeric to that in Figure 2.

IX and X. The geometry about the six-coordinate Fe atom is nearly tetragonal, with Fe atom displaced 0.13 Å from the plane of the four As atoms toward the NO group. The average Fe-As distance is 2.373 Å, and the phenyl rings of the das ligands adopt the "stepped" conformation found in several trans six-coordinate[1,19] complexes.

The $\{FeNO\}^7$ group of **2** is distinctly nonlinear with Fe-N-O = 158.6 (9)° and Fe-N = 1.717 (8) Å. To our knowledge the only other well-characterized six-coordinate complex containing the $\{FeNO\}^7$ group is Fe(NO)(TPP)(1-MeIm)[11] with Fe-N = 1.743 (4) Å and Fe-N-O = 140°. The Fe-N(2) distance in **2** of 1.996 (8) Å is a normal Fe-N distance. This contrasts with Fe(NO)(TPP)(1-MeIm)[11] where the Fe-N distance trans to the nonlinear nitrosyl group is lengthened to 2.180 (4) Å.

EPR Spectra. Table XI summarizes the *g* values for **1**, **2**, and other *trans*-$[Fe(NO)(das)_2X]^+$ complexes as polycrystalline samples at 77 K. The large line widths preclude resolution of the ligand hyperfine splitting. Spectra of the complexes in CH_2Cl_2 solution at room tem-

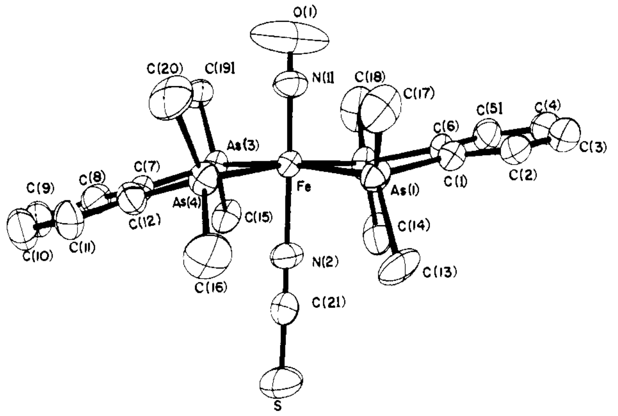

Figure 4. Perspective view and numbering scheme for **2**. H atoms have been omitted for clarity.

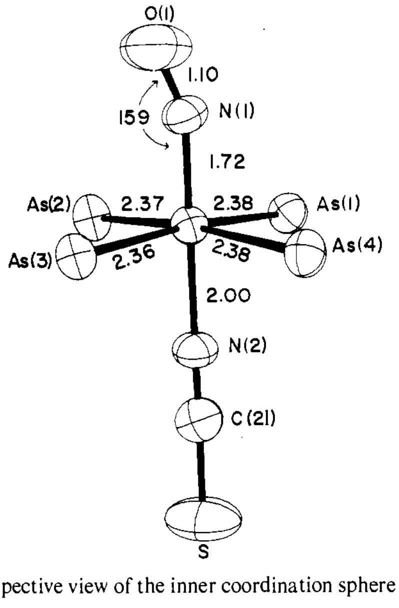

Figure 5. Perspective view of the inner coordination sphere of **2**.

Table VI. Derived Parameters for Group Atoms in $[Fe(NO)(das)_2(NCS)][B(C_6H_5)_4]\cdot[(CH_3)_2CO]$

Group[a]	Atom	x	y	z	B
R1	C(1)	−0.2660 (5)	−0.1811 (4)	−0.4466 (4)	3.50 (19)
	C(2)	−0.2711 (5)	−0.2505 (3)	−0.3512 (5)	3.81 (20)
	C(3)	−0.2564 (6)	−0.2259 (4)	−0.2601 (4)	4.55 (22)
	C(4)	−0.2366 (6)	−0.1320 (5)	−0.2644 (4)	5.02 (24)
	C(5)	−0.2315 (5)	−0.0626 (3)	−0.3597 (5)	4.80 (23)
	C(6)	−0.2462 (5)	−0.0871 (4)	−0.4509 (4)	4.04 (21)
R2	C(1)	−0.1892 (4)	−0.1361 (4)	0.3278 (4)	3.20 (18)
	C(2)	−0.2114 (4)	−0.1138 (4)	0.2271 (5)	3.41 (19)
	C(3)	−0.1411 (5)	−0.0501 (4)	0.1366 (4)	4.37 (22)
	C(4)	−0.0485 (5)	−0.0088 (4)	0.1467 (4)	4.78 (23)
	C(5)	−0.0263 (4)	−0.0311 (5)	0.2474 (6)	5.60 (26)
	C(6)	−0.0966 (5)	−0.0948 (5)	0.3379 (4)	4.79 (23)
R3	C(1)	−0.2556 (6)	−0.3214 (4)	0.4539 (6)	4.33 (22)
	C(2)	−0.3364 (4)	−0.3954 (6)	0.5111 (6)	5.47 (26)
	C(3)	−0.3175 (6)	−0.4871 (5)	0.5332 (6)	7.3 (3)
	C(4)	−0.2177 (7)	−0.5048 (4)	0.4981 (7)	6.7 (3)
	C(5)	−0.1369 (5)	−0.4308 (6)	0.4410 (7)	7.3 (3)
	C(6)	−0.1558 (5)	−0.3391 (5)	0.4189 (6)	5.49 (26)
R4	C(1)	−0.3973 (4)	−0.1992 (4)	0.4228 (5)	3.69 (20)
	C(2)	−0.4509 (5)	−0.1341 (4)	0.4605 (5)	3.94 (20)
	C(3)	−0.5469 (5)	−0.1229 (4)	0.4421 (6)	4.78 (23)
	C(4)	−0.5892 (4)	−0.1767 (5)	0.3860 (6)	5.45 (25)
	C(5)	−0.5355 (5)	−0.2417 (5)	0.3483 (6)	6.08 (28)
	C(6)	−0.4395 (5)	−0.2530 (4)	0.3667 (5)	4.72 (23)

[a] The estimated standard deviations are derived from those of the group atoms and are meant to be used in error analysis on inter-ring distances. The intra-ring C-C is 1.392 Å. B is the individual isotropic thermal parameter (in Å) for each group.

Table VII. Selected Interatomic Distance (Å) and Angles (deg) in $[Fe(NO)(das)_2][ClO_4]_2$

		Distances	
N-O(1)	1.141 (27)[a]	As(2)-C(6)	1.936 (9)
Fe-N	1.655 (18)[a]	As(2)-C(14)	1.943 (19)
Fe-As(1)	2.399 (3)	As(2)-C(18)	1.979 (19)
Fe-As(2)	2.399 (3)	As(3)-C(7)	1.936 (10)
Fe-As(3)	2.416 (3)	As(3)-C(15)	1.929 (19)
Fe-As(4)	2.381 (3)	As(3)-C(19)	1.892 (20)
As(1)-C(1)	1.926 (9)	As(4)-C(12)	1.891 (9)
As(1)-C(13)	1.983 (16)	As(4)-C(16)	2.039 (26)
As(1)-C(17)	2.001 (16)	As(4)-C(20)	1.882 (25)
		Angles	
Fe-N-O(1)	172.8 (17)	C(14)-As(2)-C(18)	102.2 (9)
As(1)-Fe-As(2)	84.39 (9)	Fe-As(3)-C(7)	108.2 (3)
As(3)-Fe-As(4)	83.39 (10)	Fe-As(3)-C(15)	112.9 (6)
As(1)-Fe-As(4)	93.19 (11)	Fe-As(3)-C(19)	124.4 (5)
As(2)-Fe-As(3)	94.90 (11)	C(18)-As(3)-C(19)	103.2 (8)
As(1)-Fe-As(3)	164.11 (12)		
As(2)-Fe-As(4)	165.04 (14)	Fe-As(4)-C(12)	110.5 (3)
		Fe-As(4)-C(16)	107.1 (10)
N-Fe-As(1)	98.8 (6)	Fe-As(4)-C(20)	126.4 (8)
N-Fe-As(2)	95.9 (6)	C(16)-As(4)-C(20)	103.7 (16)
N-Fe-As(3)	97.1 (6)		
N-Fe-As(4)	99.1 (6)		
		As(1)-C(1)-C(2)	121.7 (7)
Fe-As(1)-C(1)	109.5 (3)	As(1)-C(1)-C(6)	118.3 (6)
Fe-As(1)-C(13)	113.6 (5)	As(2)-C(6)-C(1)	118.6 (6)
Fe-As(1)-C(17)	123.9 (5)	As(2)-C(6)-C(5)	121.4 (8)
		As(3)-C(7)-C(8)	121.8 (8)
C(13)-As(1)-C(17)	102.3 (8)	As(3)-C(7)-C(12)	118.2 (7)
		As(4)-C(12)-C(7)	118.2 (7)
Fe-As(2)-C(6)	109.1 (3)		
Fe-As(2)-C(14)	112.4 (7)	As(4)-C(12)-C(11)	121.8 (8)
Fe-As(2)-C(18)	124.9 (6)		

[a] When the second atom is assumed to ride on the first, the interatomic distances are 1.235 (23) Å for N-O(1) and 1.687 (17) Å for Fe-N.

perature and in frozen acetone solutions at 77 K are also unresolved, but the g values are similar to those in Table XI. The line widths for the room temperature solution spectra of the six-coordinate complexes are extremely broad (FWHM > 100 G). Additional information

Table VIII. Distances of Atoms from Least-Squares Planes in Ångstroms

Plane	Atom	$[Fe(NO)(das)_2(NCS)]$-$[B(C_6H_5)_4]\cdot(CH_3)_2CO$	$[Fe(NO)(das)_2]$-$[ClO_4]_2$
As(1),As(2), As(3), As(4)	Fe	0.131[a]	0.324[b]
	As(1)	0.007 (1)	−0.006
	As(2)	−0.008 (1)	0.009
	As(3)	0.007 (1)	−0.009
	As(4)	−0.007 (1)	0.016

[a] Equation of plane: $12.999x - 1.949y + 6.184z - 3.761 = 0$.
[b] Equation of plane: $9.251x + 2.795y + 14.958z - 7.079 = 0$.

Table IX. Selected Interatomic Distances (Å) $[Fe(NO)(das)_2(NCS)][B(C_6H_5)_4]\cdot(CH_3)_2CO$

N(1)-O(1)	1.096 (10)[a]	As(4)-C(20)	1.967 (10)
Fe-N(1)	1.717 (8)[a]	C(1)-C(6)	1.386 (13)
Fe-N(2)	1.996 (8)	C(1)-C(2)	1.415 (13)
N(2)-C(21)	1.153 (11)	C(2)-C(3)	1.374 (15)
C(21)-S	1.628 (11)	C(3)-C(4)	1.433 (15)
Fe-As(1)	2.379 (2)	C(4)-C(5)	1.415 (15)
Fe-As(2)	2.374 (2)	C(5)-C(6)	1.442 (14)
Fe-As(3)	2.359 (2)	C(7)-C(12)	1.380 (13)
Fe-As(4)	2.379 (2)	C(7)-C(8)	1.421 (13)
As(1)-C(1)	1.921 (9)	C(8)-C(9)	1.396 (14)
As(1)-C(13)	1.967 (10)	C(9)-C(10)	1.385 (15)
As(1)-C(17)	1.970 (10)	C(10)-C(11)	1.418 (16)
As(2)-C(6)	1.944 (9)	C(11)-C(12)	1.424 (13)
As(2)-C(14)	1.975 (11)	O(2)-C(22)	1.272 (20)
As(2)-C(18)	1.986 (10)	C(22)-C(23)	1.510 (23)
As(3)-C(7)	1.929 (9)	C(22)-C(24)	1.373 (23)
As(3)-C(15)	1.956 (9)	B-R1 C(1)	1.705 (14)
As(3)-C(19)	1.970 (9)	B-R2 C(1)	1.684 (10)
As(4)-C(12)	1.944 (10)	B-R3 C(1)	1.711
As(4)-C(16)	1.970 (10)	B-R4 C(1)	1.695

[a] When the second atom is assumed to ride on the first the interatomic distances are 1.246 (13) for N(1)-O(1) and 1.729 (9) for Fe-N(1).

Table X. Selected Interatomic Angles (deg) in $[Fe(NO)(das)_2(NCS)][B(C_6H_5)_4]\cdot[(CH_3)_2CO]$

Fe-N(1)-O(1)	158.6 (9)	Fe-As(4)-C(16)	118.8 (4)
Fe-N(2)-C(21)	179.2 (8)	Fe-As(4)-C(20)	118.3 (4)
		C(16)-As(4)-C(20)	102.8 (6)
N(2)-C(21)-S	178.7 (9)		
N(1)-Fe-N(2)	179.0 (4)	As(1)-C(1)-C(2)	121.5 (7)
		As(1)-C(1)-C(6)	117.8 (7)
As(1)-Fe-As(2)	85.07 (5)	As(2)-C(6)-C(1)	118.5 (7)
As(3)-Fe-As(4)	85.64 (5)	As(2)-C(6)-C(5)	119.0 (8)
As(1)-Fe-As(4)	94.13 (5)	As(3)-C(7)-C(8)	120.2 (7)
As(2)-Fe-As(3)	94.45 (5)	As(3)-C(7)-C(12)	119.0 (7)
As(1)-Fe-As(3)	173.99 (7)	As(4)-C(12)-C(7)	117.6 (7)
As(2)-Fe-As(4)	173.30 (7)	As(4)-C(12)-C(11)	120.8 (8)
N(1)-Fe-As(1)	92.74 (27)		
N(1)-Fe-As(2)	91.19 (28)	C(1)-C(2)-C(3)	118.5 (10)
N(1)-Fe-As(3)	93.26 (26)	C(2)-C(3)-C(4)	121.6 (10)
N(1)-Fe-As(4)	95.50 (28)	C(3)-C(4)-C(5)	121.0 (10)
N(2)-Fe-As(1)	88.12 (23)	C(4)-C(5)-C(6)	115.7 (10)
N(2)-Fe-As(2)	89.41 (23)	C(5)-C(6)-C(1)	122.4 (9)
N(2)-Fe-As(3)	85.88 (23)	C(6)-C(1)-C(2)	120.7 (9)
N(2)-Fe-As(4)	83.91 (23)	C(7)-C(8)-C(9)	118.7 (10)
		C(8)-C(9)-C(10)	120.2 (10)
Fe-As(1)-C(1)	108.32 (29)	C(9)-C(10)-C(11)	122.5 (10)
Fe-As(1)-C(13)	120.4 (4)	C(10)-C(11)-C(12)	116.4 (10)
Fe-As(1)-C(17)	116.3 (3)		
C(13)-As(1)-C(17)	104.8 (5)	C(11)-C(12)-C(7)	121.5 (9)
		C(12)-C(7)-C(8)	120.8 (9)
Fe-As(2)-C(6)	107.0 (3)	O(2)-C(22)-C(23)	120.0 (20)
Fe-As(2)-C(14)	117.1 (4)	O(2)-C(22)-C(24)	119.3 (23)
Fe-As(2)-C(18)	119.6 (4)	C(23)-C(22)-C(24)	120.4 (20)
C(14)-As(2)-C(18)	103.9 (6)		
Fe-As(3)-C(7)	108.30 (29)	R1C(1)-B-R2C(1)	110.2 (7)
Fe-As(3)-C(15)	117.32 (29)	R1C(1)-B-R3C(1)	107.0
Fe-As(3)-C(19)	118.4 (3)	R1C(1)-B-R4C(1)	110.1
C(15)-As(3)-C(19)	104.8 (4)	R2C(1)-B-R3C(1)	109.8
		R2C(1)-B-R4C(1)	109.0
Fe-As(4)-C(12)	107.69 (29)	R3C(1)-B-R4C(1)	110.7

Table XI. EPR Data for Diarsine Complexes of the $\{FeNO\}^7$ Group[a]

Compound	$g_\perp$	$g_\parallel$	FWHM[b]
$[Fe(NO)(das)_2][ClO_4]_2$	2.019[c]		16.5
$[Fe(NO)(das)_2Cl]BPh_4$	1.997	1.979	45
$[Fe(NO)(das)_2Br]ClO_4$	1.988	2.015	60
$[Fe(NO)(das)_2(NCS)]ClO_4$	1.990	1.973	55
$[Fe(NO)(das)_2NO_2]ClO_4$	1.991	1.964	68
$[Fe(NO)(das)_2N_3]ClO_4$	1.998	1.966	54

[a] Polycrystalline solids at 77 K. [b] Full width at half-maximum. [c] Peak not resolved.

about the g tensors in six-coordinate $\{FeNO\}^7$ complexes is provided elsewhere[20] by the single-crystal spectrum of $[Fe(NO)(das)_2Cl][ClO_4]$ diluted in the diamagnetic host *trans*-$[CoCl_2(das)_2][ClO_4]$.

Discussion

The properties of five-coordinate derivatives of the $\{FeNO\}^7$ group with $S = 1/2$ ground states which have been structurally characterized are summarized in Table XII. Even a cursory examination of the data in Table XII shows that $[Fe(NO)(das)_2]^{2+}$ (**1**) has structural and spectral properties which are very similar to both the dithiocarbamate and the tetracyanide complexes. Gray et al.[21] first proposed that the g factors of $Fe(NO)(dtc)_2$ complexes are consistent with a molecular orbital scheme which places the unpaired electron in an a_1 orbital comprised primariy of d_{z^2} and $\sigma^*(NO)$. This scheme was later revised by Symons et al.,[22] but they retained the key feature of a $(\sigma^*,d_{z^2})^1$ electron configuration for these complexes. A much more recent SCCC-MO calculation carried out by Dorn and Schmidt[23] for the structurally analogous $[Fe(NO)(CN)_4]^{2-}$ complex also indicates that σ^*,d_{z^2} is the HOMO.

We have proposed a general molecular orbital framework for tetragonal $\{MNO\}^n$ complexes[2-5] which incorporates the features set forth by others[21-23] and which also places the unpaired electron of an $\{MNO\}^7$ group in an a_1 molecular orbital containing a large contribution from d_{z^2} ($4a_1$, Figure 6b). A key feature of this scheme is the close proximity of the HOMO ($4a_1$) and the LUMO (3e) which enables their relative energies to be controlled by the nature and stereochemistry of the other ligands coordinated to the metal. The scheme in Figure 6b has been previously used to discuss the structures and magnetic properties of $Fe(NO)(dtc)_2$ complexes in detail.[2] The properties of **1** are also consistent with the molecular orbital scheme shown in Figure 6b.

The formation of the six-coordinate complex **2** from the five-coordinate complex **1** by addition of NCS^- results in a decrease in the Fe-N-O angle from 173 to 159° and in substantial decreases in g (2.018-1.986) and ν_{NO} (1760-1620 cm^{-1}). All of these changes are adequately explained by the molecular orbital schemes of Figure 6. The addition of the sixth ligand to **1** makes the $4a_1(d_{z^2})$ orbital (Figure 6b) more antibonding, thereby raising its energy. For **1**, $4a_1$ and 3e are suf-

Table XII. Properties of Five- and Six-Coordinate $\{FeNO\}^7$ Complexes

	Coord no.	g values	ν_{NO} (cm^{-1})^e	Fe-N-O (deg)	Ref
$Fe(NO)(S_2CN(CH_3)_2)_2$	5	$g_z = 2.028, g_x = 2.048, g_y = 2.039$	1690	170.4 (6)	*a*, *b*
$Fe(NO)(S_2CN(C_2H_5)_2)_2$	5	$g_z = 2.025, g_x = 2.039, g_y = 2.035$	1691	174 (4)	*c*, 22
$[Fe(NO)(CN)_4]^{2-}$	5	$g_\parallel = 2.0072, g_\perp = 2.0347$	1755	177.1	9
$[Fe(NO)(das)_2]^{2+}$	5	$g = 2.019$	1760	172.8 (17)	This work
$[Fe(NO)(S_2C_2(CN)_2)_2]^{2-}$	5	$g = 2.028$	1650	~160	29, 30
Fe(NO)(TPP)	5	$g_1 = 2.102, g_2 = 2.064, g_3 = 2.010$	1670	149.2 (6)	11, 26
$[Fe(NO)(das)_2(NCS)]^+$	6	$g_\parallel = 1.973, g_\perp = 1.990$	1620	158.6 (9)	This work
Fe(NO)(TPP)(1-MeIm)	6	*d*	1625	140	12

[a] H. Crain, Ph.D. Thesis, University of Arizona, 1975. [b] G. R. Davies, J. A. J. Jarvis, B. T. Kilbourn, R. H. B. Mais, and P. G. Owston, *J. Chem. Soc. A*, 1275 (1967). [c] M. Colapietro, A. Domenicano, L. Scaramuzza, A. Vaciago, and L. Zambonelli, *Chem. Commun.*, 583 (1967). [d] The EPR spectrum of this compound has not been reported. Fe(NO)(TPP)(pip) has $g_1 = 2.08$, $g_2 = 2.04$, and $g_3 = 2.003$. [e] Solid in KBr.

ficiently close together that the increase in coordination number leads to a crossing or near degeneracy of these two molecular orbitals as shown in 6b → 6c. As has been frequently pointed out,[24-27] bending of the FeNO group lowers the symmetry of the complex and allows $4a_1$ and 3e to mix thereby lifting all but Kramer's degeneracy from the HOMO. The end result is shown in Figure 6d: a bent FeNO moiety with one electron in the 2a′ molecular orbital. For the orientation shown, 2a′ will contain substantial contributions from d_{xz} of the metal as well as from the s and p_x orbitals of the N atom of the nitrosyl group. The 2a′ molecular orbital can also, of course, contain a contribution from d_{z^2} and other atomic orbitals of a′ symmetry. Molecular orbital scheme 6d is consistent with the fact that **2** and its analogues have *g* less than the free electron value of 2.002.

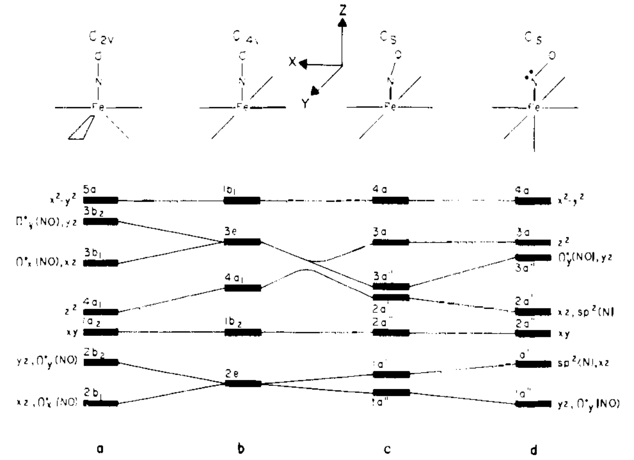

Figure 6. Molecular orbital diagram correlating the energy levels of the $\{FeNO\}^n$ group in ligand fields of various symmetries.

From the above discussion of the properties of **1** and **2** it is clear that the molecular and electronic structures of the $\{FeNO\}^7$ group can be controlled by the stereochemistry of the other ligands coordinated to the metal. **1** and **2** are also closely related to the five- and six-coordinate $\{CoNO\}^8$ complexes, $[Co(NO)(das)_2][ClO_4]_2$ and $[Co(NO)(das)_2(NCS)][NCS]$, whose structures we have described previously.[1,7] The latter pair of complexes differ from **1** and **2** in that the HOMO of the $\{MNO\}^n$ group is doubly rather than singly occupied. Thus, intercomparisons of these pairs of $\{FeNO\}^7$ and $\{CoNO\}^8$ complexes can provide insight into the relationship between electron-electron repulsion within the HOMO and the stereochemistry adopted by an $\{MNO\}^n$ complex.

The five-coordinate complexes $[Fe(NO)(das)_2]^{2+}$ (**1**) and $[Co(NO)(das)_2]^{2+}$ have similar M-N-O angles (173 and 178°, respectively) but completely different coordination geometries. The $\{FeNO\}^7$ complex has TP geometry with an axial nitrosyl group, whereas the $\{CoNO\}^8$ complex has TBP geometry with an equatorial nitrosyl group. These coordination differences are consistent with molecular orbital diagrams 6a and 6b which show that a change from TP to TBP geometry can lower the energy of the HOMO ($4a_1$). This change in stereochemistry also decreases the electron-electron repulsion for a $(4a_1)^2$ electron configuration because in TBP geometry the $4a_1$ orbital can be delocalized over the π orbitals of the other two ligands in the equatorial plane. Thus, $[Co(NO)(das)_2]^{2+}$ adopts TBP geometry. In **1** there is only a single electron in the $4a_1$ orbital and its only electron-electron repulsions are with electrons in other filled molecular orbitals. This comparison of **1** and $[Co(NO)(das)_2]^{2+}$ supports the conclusion that the HOMO is $4a_1$ (d_{z^2}) and shows that the addition of a second electron to this orbital results in a major change in the stereochemistry about the metal but little change in the geometry of the coordinated NO group.[28]

On the other hand, the six-coordinate complexes $[Fe(NO)(das)_2(NCS)]^+$ (**2**) and $[Co(NO)(das)_2(NCS)]^+$ have similar coordination geometries but very different M-N-O angles (159 and 132°, respectively). These results are consistent with the molecular orbital scheme of Figure 6d and emphasize that the addition of a second electron to 2a′, a component of $3e(\pi^*(NO);xz,yz)$, results in major changes in the geometry and electronic properties of the coordinated NO ligand but little change in the stereochemistry at the metal atom. The six-coordinate complex $[Fe(NO)(das)_2(NCS)]^{2+}$ has a linear $\{FeNO\}^6$ group[15] as expected for a $(2e)^4(1b_2)^2$ electron configuration (Figure 6b).

The above comparisons of das complexes of the $\{FeNO\}^7$ and $\{CoNO\}^8$ groups support the general molecular orbital schemes in Figure 6 and illustrate the importance of the electron distribution in the HOMO for determining the geometries and electronic properties of $\{MNO\}^n$ groups.[1-5,24-27] The differences in M-N-O angles between five- and six-coordinate complexes also quantitatively demonstrate the stereochemical control of valence electron distribution exerted by the coordination geometry about the metal.[1-5,7] For the $\{FeNO\}^7$ group the increase in coordination number leads to the transfer of *one* electron from $4a_1(d_{z^2})$, a predominantly metal orbital, to a component of $3e(\pi^*(NO);xz,yz)$, a predominantly ligand orbital, thereby decreasing the Fe-N-O angle from 173 to 159°. For the $\{CoNO\}^8$ group the corresponding change from five- to six-coordinate involves the transfer of *two* electrons between the HOMO and LUMO and hence a concomitantly larger decrease in the Co-N-O angle from 178 to 132°. The limiting description of the latter internal redistribution of electrons is an intramolecular redox reaction in which a five-coordinate $Co^I(NO^+)$ complex is converted to a six-coordinate $Co^{III}(NO^-)$ complex.[7,29,34]

Compounds **1** and **2** can also be compared with the five- and six-coordinate TPP complexes of the $\{FeNO\}^7$ group, Fe(NO)(TPP) and Fe(NO)(TPP)(1-MeIm).[12] The FeNO groups of the latter two compounds are both more strongly bent than **2** with angles of 149 and 140°, respectively. Wayland and Olson[26] have reported the EPR data for Fe(NO)(TPP) and Fe(NO)(TPP)(pip). The EPR spectra of the two complexes are distinctly different with Fe(NO)(TPP)(pip) exhibiting ^{14}N hyperfine splitting by both the piperidine ligand and the NO ligand, whereas the signal in Fe(NO)(TPP) is split by ^{14}N of the NO ligand only. However, both complexes have rhombic g tensors with all components greater than 2.002. The EPR results for these bent $\{FeNO\}^7$ groups contrast sharply with the spectra for **2** and its analogues which have $g < 2.002$.

The similarity of the Fe-N-O angles of Fe(NO)(TPP) and Fe(NO)(TPP)(1-MeIm) and the similarity of the g values for Fe(NO)(TPP) and Fe(NO)(TPP)(pip) suggest that the electronic structure of the $\{FeNO\}^7$ group in these complexes is little affected by an increase in coordination number from five to six. Wayland and Olson[26] have proposed a molecular orbital scheme for Fe(NO)(TPP) that places the unpaired electron in an orbital which is primarily d_{z^2} and σ(NO). Their model accounts for the relatively large g values of Fe(NO)(TPP), but the addition of a sixth ligand should strongly perturb d_{z^2} and thereby alter the relative composition of the HOMO and the properties of the $\{FeNO\}^7$ group. Thus, it is surprising that the magnitudes of g and the Fe-N-O angle are little different for the five- and six-coordinate TPP complexes of the $\{FeNO\}^7$ group.

The similarity of the properties of the five- and six-coordinate TPP complexes of $\{FeNO\}^7$ are also not easily explicable by b and c of Figure 6. It should be pointed out, however, that Figure 6 as well as the other qualitative molecular orbital schemes proposed[24-27] for metal nitrosyl complexes assume that the HOMO is comprised primarily of metal d orbitals and orbitals of the NO ligand with little contribution from the orbitals of the other ligands coordinated to the metal. This simplifying assumption appears valid for many metal nitrosyl complexes[2,27] including the $\{FeNO\}^7$ species **1**, **2**, and[23] $[Fe(NO)(CN)_4]^{2-}$, but may not be applicable to porphyrin complexes of $\{MNO\}^n$ groups. Recent molecular orbital calculations[30] on $\{FeNO\}^7$ complexes of the porphyrin core suggest that the HOMO contains substantial contributions from porphyrin π-orbitals and little contribution from d_{z^2}. Such a delocalized electronic structure could account for the unique properties of the $\{FeNO\}^7$ group in Fe(NO)(TPP) and Fe(NO)(TPP)(1-MeIm). Substantial participation of ligand π-orbitals in the HOMO may also be important in $[Fe(NO)(S_2C_2(CN)_2)_2]^{2-}$ which contains the highly delocalized maleonitriledithiolate ligand.[31,32]

In summary, this work has shown that the $\{FeNO\}^7$ group is sensitive to stereochemical control of valence electron distribution and that **1** and **2** are conveniently and adequately described as derivatives of the covalent $\{FeNO\}^7$ triatomic fragment. However, comparison of Fe(NO)(TPP) and Fe(NO)(TPP)(L) with **1** and **2** suggests that current models[2,23-27,30] may be too simple to adequately describe the subtle differences between ground state structural and electronic properties of the porphyrin complexes.

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Supplementary Material Available: Listings of structure factor amplitudes (30 pages). Ordering information is given on any current masthead page.

References and Notes

(1) For part 4 see J. H. Enemark, R. D. Feltham, J. Riker-Nappier, and K. F. Bizot, *Inorg. Chem.*, **14**, 624 (1975).

(2) J. H. Enemark and R. D. Feltham, *Coord. Chem. Rev.*, **13**, 339 (1974).

(3) R. D. Feltham and J. H. Enemark, *Theor. Chim. Acta*, **34**, 165 (1974).

(4) J. H. Enemark and R. D. Feltham, *J. Am. Chem. Soc.*, **96**, 5002 (1974).

(5) J. H. Enemark and R. D. Feltham, *J. Am. Chem. Soc.*, **96**, 5004 (1974).

(6) n is the number of electrons primarily associated with metal d and/or π^*(NO) orbitals. See ref 2–5 for details.

(7) J. H. Enemark and R. D. Feltham, *Proc. Natl. Acad. Sci. U.S.A.*, **69**, 3534 (1972).

(8) J. C. W. Chien, *J. Chem. Phys.*, **51**, 4220 (1969).

(9) J. Schmidt, H. Kuhr, W. D. Dorn, and J. Kopf, *Inorg. Nucl. Chem. Lett.*, **10**, 55 (1974).

(10) W. Silverthorn and R. D. Feltham, *Inorg. Chem.*, **6**, 1662 (1967).

(11) W. R. Scheidt and M. E. Frisse, *J. Am. Chem. Soc.*, **97**, 17 (1975).

(12) W. R. Scheidt and P. L. Piciulo, *J. Am. Chem. Soc.*, **98**, 1913 (1976).

(13) Ligand abbreviations used in this paper are: TPP = tetraphenylporphine dianion; das = *o*-phenylenebis(dimethylarsine); 1-MeIm = 1-methylimidazole; pip = piperdine; dtc = dithiocarbamate.

(14) R. W. Perry, Ph.D. Thesis, University of Wisconsin, 1968.

(15) T. E. Nappier, R. D. Feltham, J. H. Enemark, A. Kruse, and M. Cooke, *Inorg. Chem.*, **14**, 806 (1975).

(16) R. D. Feltham, W. Silverthorn, H. Wickman, and W. Wesolowski, *Inorg. Chem.*, **11**, 676 (1972).

(17) (a) S. J. LaPlaca and J. A. Ibers, *Acta Crystallogr.*, **18**, 511 (1965); (b) R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 773 (1965).

(18) F. A. Jurnak, D. R. Greig, and K. N. Raymond, *Inorg. Chem.*, **14**, 2585 (1975).

(19) (a) N. C. Stephenson, *J. Inorg. Nucl. Chem.*, **24**, 791 (1962); (b) *ibid.*, **24**, 797 (1962); (c) *Acta Crystallogr.*, **17**, 592 (1964); (d) *ibid.*, **17**, 1517 (1964); (e) F. W. B. Einstein and G. A. Rodley, *J. Inorg. Nucl. Chem.*, **29**, 347 (1967); (f) V. F. Duckworth, C. M. Harris, and N. C. Stephenson, *Inorg. Nucl. Chem. Lett.*, **4**, 419 (1968); (g) P. J. Pauling, D. W. Porter, and G. B. Robertson, *J. Chem. Soc. A*, 272 (1970); (h) P. K. Berstein, G. A. Rodley, R. Marsh, and H. B. Gray, *Inorg. Chem.*, **11**, 3040 (1972).

(20) H. Crain, Ph.D. Thesis, University of Arizona, 1975.

(21) H. B. Gray, I. Bernal, and E. Billig, *J. Am. Chem. Soc.*, **84**, 3404 (1962).

(22) B. A. Goodman, J. B. Raynor, and M. C. R. Symons, *J. Chem. Soc. A*, 2572 (1969).

(23) W. L. Dorn and J. Schmidt, *Inorg. Chim. Acta*, **16**, 223 (1976).

(24) C. G. Pierpont and R. Eisenberg, *J. Am. Chem. Soc.*, **93**, 4905 (1971).

(25) D. M. P. Mingos, *Inorg. Chem.*, **12**, 1209 (1973).

(26) B. B. Wayland and L. W. Olson, *J. Am. Chem. Soc.*, **96**, 6037 (1974).

(27) R. Hoffmann, M. M. L. Chen, M. Elian, A. R. Rossi, and D. M. P. Mingos, *Inorg. Chem.*, **13**, 2666 (1974).

(28) The TP geometry of **1** may also be stabilized somewhat by the weak electrostatic interaction between the Fe atom and a perchlorate O atom 2.66 Å away.

(29) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", 2nd ed, Wiley, New York, N.Y., 1967, p 573.

(30) M. P. Halton, *Inorg. Chim. Acta*, **8**, 137 (1974).

(31) D. G. Van Derveer, A. P. Gaughan, Jr., S. L. Soled, and R. Eisenberg, *Abstr. Am. Cryst. Assoc.*, 1, 190 (1973).

(32) J. A. McCleverty, N. M. Atherton, J. Locke, E. J. Wharton, and C. J. Winscom, *J. Am. Chem. Soc.*, **89**, 6082 (1967).

(33) M. J. Buerger, "X-Ray Crystallography", Wiley, New York, N.Y., 1942, p 364.

(34) B. A. Frenz and J. A. Ibers, *MTP Int. Rev. Sci.: Phys. Chem., Ser. One*, **11**, 33 (1972).