Volume 22
Number 3
February 2, 1983

Inorganic Chemistry

Contribution from the Departments of Chemistry, Howard University, Washington, D.C. 20059,
and University of Virginia, Charlottesville, Virginia 22901

Spectral Analysis of Bis(*N*,*N*-diisopropyldithiocarbamato)nitrosyliron, $Fe(NO)[S_2CN(CH(CH_3)_2)_2]_2$, and Preparation and Crystal Structure of Its Cobalt Analogue

GREG A. BREWER,[1b] RAY J. BUTCHER,[1a] BAHRAM LETAFAT,[1a] and EKK SINN*[1b]

Received January 29, 1982

The title {FeNO} complex was previously shown to have a linear Fe–N–O linkage, perpendicular to the S_4 plane of the dithiocarbamate ligands. Its infrared and ESR spectra are now reported, including those of the complex doped in its {CoNO} analogue. The cobalt complex is "d^8" or $\{Co–N–O\}^8$ and diamagnetic while the iron complex is "d^7" or $\{Fe–N–O\}^7$ and the magnetic susceptibility shows that it has one unpaired electron per molecule as expected. Although the iron and cobalt complexes are isomorphous, they exhibit an important structural difference, which demonstrates the importance of crystal structures in making detailed comparisons between isomorphous compounds. Crystal data for $[Co(NO)(i\text{-Prdtc})_2]$: space group $P2_1/n$, $Z = 4$, $a = 9.252$ (3) Å, $b = 17.189$ (2) Å, $c = 14.018$ (7) Å, $\beta = 106.81$ (7)°, $V = 2134$ Å^3, $R = 6.5\%$, $R_w = 7.0\%$, 1819 reflections. The crystal structure of the cobalt complex reveals this to possess a bent Co–N–O linkage (~129°). This means that the doped-sample spectra may pertain to a modified form of the iron complex, one having a bent Fe–N–O linkage. The solid-state ESR of the pure, known linear, Fe–N–O complex at 295 K gives $g = 2.045$. In solution, where Fe–N–O could be linear or bent, $g = 2.047$ and A for the ^{14}N hyperfine is 14.4 G, while for the compound doped in the diamagnetic cobalt complex $\langle g \rangle = 2.047$ ($g_x = 2.054$, $g_y = 2.050$, $g_z = 2.037$) and $\langle A \rangle = 13.92$ G ($A_x = 12.5$, $A_y = 13.0$, $A_z = 16.25$ G).

Introduction

The coordination chemistry of nitric oxide is one of the most active areas and has been extensively and frequently reviewed.[2-6] This is partly due to the relevance of the nitrosyl group as a potential electron sink in the catalytic cycles[7,8] and the interest in oxidation of nitrogen oxides by homogeneous systems.[5]

As part of our studies of the properties of cobalt and iron dithiocarbamates (dtc),[9-13] we have been interested in their nitroso derivatives,[14] $[M(NO)(dtc)_2]$, M = Co, Fe. The ferric tris analogues, $[Fe(dtc)_3]$, in which the NO group is replaced by a third dtc ligand, generally exhibit spin-state equilibria ($S = {}^1/_2 \rightleftarrows S = {}^5/_2$).[9-13] Although the $\{Fe–N–O\}^7$ complexes with tetramethylcyclam[15] and salen[16-18] exhibit $S = {}^1/_2 \rightleftarrows S = {}^3/_2$ spin equilibria, the isoelectronic $[Fe(NO)(i\text{-Prdtc})_2]$ exhibits a stronger crystal field and is pure low spin, $S = {}^1/_2$. Although a considerable body of literature already exists on the $[M(NO)(dtc)_2]$ complexes,[19-27] there had been no good direct evidence on the nature of the Fe–N–O bond in $[Fe(NO)(dtc)_2]$ complexes. Prior to our recent observation of a linear (179°) Fe–N–O linkage,[14] without positional disorder in $[Fe(NO)(i\text{-Prdtc})_2]$, crystal structures determined for $[Fe(NO)(dtc)_2]$ complexes suffered from positional disorder

---

(1) (a) Howard University. (b) University of Virginia.
(2) Enemark, J. H.; Feltham, R. D. *Coord. Chem. Rev.* **1974**, *13*, 339.
(3) Hoffmann, R.; Chen, M.; Elian, M.; Rossi, A. R.; Mingos, D. M. P. *Inorg. Chem.* **1974**, *13*, 2666.
(4) Caulton, K. G. *Coord. Chem. Rev.* **1975**, *14*, 317.
(5) Eisenberg, R.; Meyer, C. D. *Acc. Chem. Res.* **1975**, *8*, 26.
(6) Bottomley, F. *Coord. Chem. Rev.* **1978**, *26*, 7.
(7) Collman, J. P.; Hoffman, N. W.; Morris, D. E. *J. Am. Chem. Soc.* **1969**, *91*, 5659.
(8) Rakowski, M. C.; Hirsekorn, F. J.; Stahl, L. S.; Muetterties, E. L. *Inorg. Chem.* **1976**, *15*, 2379.
(9) Ewald, A. H.; Martin, R. L.; Sinn, E.; White, A. H. *Inorg. Chem.* **1969**, *8*, 101. Golding, R. M.; Lukeman, B. D.; Sinn, E. *J. Chem. Phys.* **1972**, *56*, 4147. Golding, R. M.; Sinn, E.; Tennant, W. C. *Ibid.* **1972**, *56*, 5296.
(10) Healy, P. C.; Sinn, E. *Inorg. Chem.* **1975**, *14*, 109. Golding, R. M.; Healy, P. C.; Newman, P. W. G.; Sinn, E.; White, A. H. *Ibid.* **1972**, *11*, 2435. Golding, R. M.; Healy, P.; Newman, P.; Sinn, E.; Tennant, W. C.; White, A. H. *J. Chem. Phys.* **1970**, *52*, 3105.
(11) Butcher, R. J.; Sinn, E. *J. Chem. Soc., Dalton Trans.* **1975**, 2517; *J. Am. Chem. Soc.* **1976**, *98*, 2440, 5159.
(12) Butcher, R. J.; Ferraro, J. R.; Sinn, E. *J. Chem. Soc., Chem. Commun.* **1976**, 910; *Inorg. Chem.* **1976**, *15*, 2077.
(13) Cukauskas, E. J.; Deaver, B. S., Jr.; Sinn, E. *J. Chem. Soc., Chem. Commun.* **1974**, 698; *J. Chem. Phys.* **1977**, *67*, 1257.
(14) Butcher, R. J.; Sinn, E. *Inorg. Chem.* **1980**, *19*, 3622.
(15) Hodges, K. D.; Wollmann, R. G.; Kessel, S. L.; Hendrickson, D. N.; Van Derveer, D. G.; Barefield, E. K. *J. Am. Chem. Soc.* **1979**, *101*, 906.
(16) Earnshaw, A.; King, E. A.; Larkworthy, L. F. *Chem. Commun.* **1965**, 180; *J. Chem. Soc. A* **1969**, 2459.
(17) Haller, K. J.; Johnson, P. L.; Feltham, R. D.; Enemark, J. H.; Ferraro, J. R.; Basile, L. J. *Inorg. Chim. Acta* **1979**, *33*, 119.
(18) Wills, F. W.; McCann, S. W.; Wickman, H. H.; Kessel, S. L.; Hendrickson, D. N.; Feltham, R. D. *Inorg. Chem.* **1982**, *21*, 2306.
(19) Colapietro, M.; Domenicano, A.; Scarmuzza, L.; Vacciago, A.; Zambonelli, L. *Chem. Commun.* **1967**, 583.
(20) Davies, G. R.; Mais, R. H. B.; Owston, P. G. *Chem. Commun.* **1968**, 81.
(21) Davies, G. R.; Jarvis, J. A. J.; Kilbourn, B. T.; Mais, R. H. B.; Owston, P. G. *J. Chem. Soc. A* **1970**, 1275.
(22) Enemark, J. J.; Feltham, R. D. *J. Chem. Soc., Dalton Trans.* **1972**, 718.
(23) Gibson, J. *Nature* (*London*) **1962**, *196*, 64.
(24) Gray, H. B.; Bernal, I.; Billig, E. *J. Am. Chem. Soc.* **1962**, *84*, 3404.
(25) Goodman, B. A.; Raynor, J. B.; Symons, M. C. R. *J. Chem. Soc. A* **1969**, 2572.
(26) Ileperuma, O. A.; Feltham, R. D. *J. Am. Chem. Soc.* **1976**, *98*, 6038.
(27) Wayland, B. B.; Olson, L. W. *J. Chem. Soc., Chem. Commun.* **1973**, 897.

0020-1669/83/1322-0371$01.50/0

Table I. Positional Parameters for $[Co(NO)(i\text{-}Prdtc)_2]$

atom[a]	x	y	z
Co	0.1467 (1)	−0.12696 (9)	0.2972 (1)
S(1A)	0.2941 (3)	−0.0330 (2)	0.3869 (3)
S(2A)	−0.0115 (3)	−0.0253 (2)	0.2841 (3)
S(1B)	0.2760 (3)	−0.2294 (2)	0.3793 (2)
S(2B)	−0.0308 (3)	−0.2220 (2)	0.2746 (2)
O[a]	0.307 (2)	−0.125 (1)	0.176 (1)
O′ [b]	0.221 (4)	−0.095 (2)	0.131 (2)
O″ [c]	0.177 (4)	−0.151 (2)	0.115 (3)
N(A)	0.1283 (9)	0.0987 (5)	0.3915 (7)
N(B)	0.0892 (9)	−0.3518 (5)	0.3724 (6)
N	0.193 (1)	−0.1269 (7)	0.1880 (7)
C(1A)	0.136 (1)	0.0262 (6)	0.3607 (8)
C(2A)	−0.017 (1)	0.1413 (7)	0.3599 (11)
C(3A)	−0.020 (2)	0.2081 (11)	0.2990 (12)
C(4A)	−0.099 (1)	0.1402 (11)	0.4360 (9)
C(5A)	0.256 (2)	0.1394 (8)	0.4590 (8)
C(6A)	0.372 (2)	0.1626 (10)	0.4143 (11)
C(7A)	0.297 (1)	0.1135 (10)	0.5620 (10)
C(1B)	0.109 (1)	−0.2804 (6)	0.3466 (8)
C(2B)	0.210 (1)	−0.3997 (6)	0.4430 (8)
C(3B)	0.337 (1)	−0.4180 (8)	0.4010 (11)
C(4B)	0.258 (2)	−0.3669 (9)	0.5476 (9)
C(5B)	−0.063 (1)	−0.3908 (6)	0.3388 (8)
C(6B)	−0.060 (1)	−0.4658 (7)	0.2867 (11)
C(7B)	−0.142 (1)	−0.3945 (9)	0.4204 (11)
H(2A)	−0.092 (11)	0.106 (7)	0.316 (8)
H(5A)	0.206 (14)	0.189 (8)	0.463 (10)
H(2B)	0.165 (10)	−0.449 (6)	0.446 (7)
H(5B)	−0.114 (10)	−0.358 (6)	0.288 (7)
H(3A1)	−0.113 (9)	0.238 (5)	0.277 (6)
H(3A2)	0.030 (14)	0.214 (8)	0.262 (9)
H(3A3)	0.025 (17)	0.247 (10)	0.357 (12)
H(4A1)	−0.205 (17)	0.169 (10)	0.422 (12)
H(4A2)	−0.027 (16)	0.179 (10)	0.480 (12)
H(4A3)	−0.110 (12)	0.095 (7)	0.463 (8)
H(6A1)	0.336 (14)	0.194 (8)	0.359 (10)
H(6A2)	0.414 (15)	0.113 (9)	0.404 (11)
H(6A3)	0.446 (14)	0.201 (8)	0.452 (10)
H(7A1)	0.356 (11)	0.159 (6)	0.602 (7)
H(7A2)	0.229 (11)	0.086 (7)	0.587 (8)
H(7A3)	0.354 (11)	0.085 (7)	0.562 (8)
H(3B1)	0.388 (10)	−0.377 (6)	0.392 (7)
H(3B2)	0.323 (16)	−0.456 (9)	0.339 (11)
H(3B3)	0.412 (14)	−0.462 (8)	0.441 (10)
H(4B1)	0.334 (11)	−0.413 (7)	0.583 (8)
H(4B2)	0.305 (11)	−0.325 (6)	0.547 (8)
H(4B3)	0.188 (10)	−0.357 (6)	0.573 (7)
H(6B1)	−0.011 (14)	−0.517 (8)	0.318 (9)
H(6B2)	−0.009 (13)	−0.472 (8)	0.237 (9)
H(6B3)	−0.170 (15)	−0.486 (8)	0.251 (10)
H(7B1)	−0.233 (11)	−0.416 (7)	0.393 (8)
H(7B2)	−0.085 (5)	−0.431 (3)	0.461 (3)
H(7B3)	−0.128 (7)	−0.346 (4)	0.439 (5)

[a] Multiplicity = 0.44. [b] Multiplicity = 0.28. [c] Multiplicity = 0.

Table II. Bond Lengths (Å)

Co–S(1A)	2.249 (2)	N–O	1.11 (1)
Co–S(2A)	2.253 (2)	N–O′	1.06 (3)
Co–S(1B)	2.249 (2)	N–O″	1.07 (2)
Co–S(2B)	2.273 (2)	N(A)–C(1A)	1.329 (9)
Co–N	1.707 (7)	N(A)–C(2A)	1.485 (9)
S(1A)–C(1A)	1.729 (7)	N(A)–C(5A)	1.461 (9)
S(2A)–C(1A)	1.720 (6)	N(B)–C(1B)	1.307 (7)
S(1B)–C(1B)	1.722 (7)	N(B)–C(2B)	1.505 (8)
S(2B)–C(1B)	1.715 (6)	N(B)–C(5B)	1.506 (7)

Table III. Bond Angles (deg)

S(1A)–Co–S(2A)	76.29 (7)	Co–S(2B)–C(1B)	87.0 (2)
S(1A)–Co–S(1B)	97.48 (7)	Co–N–O	129.2 (9)
S(1A)–Co–S(2B)	153.03 (9)	Co–N–O′	149 (2)
S(1A)–Co–N	103.4 (3)	Co–N–O″	149 (2)
S(2A)–Co–S(1B)	152.39 (9)	C(1A)–N(A)–C(2A)	119.8 (6)
S(2A)–Co–S(2B)	96.88 (6)	C(1A)–N(A)–C(5A)	123.3 (6)
S(2A)–Co–N	104.7 (3)	C(2A)–N(A)–C(5A)	116.9 (7)
S(1B)–Co–S(2B)	76.38 (7)	C(1B)–N(B)–C(2B)	124.1 (5)
S(1B)–Co–N	102.9 (3)	C(1B)–N(B)–C(5B)	121.5 (5)
S(2B)–Co–N	103.6 (3)	C(2B)–N(B)–C(5B)	114.3 (5)
Co–S(1A)–C(1A)	88.0 (2)	S(1A)–C(1A)–S(2A)	107.5 (4)
Co–S(2A)–C(1A)	88.1 (2)	S(1A)–C(1A)–N(A)	127.3 (5)
Co–S(1B)–C(1B)	87.6 (2)	S(2A)–C(1A)–N(A)	125.2 (5)

of the nitrosyl oxygen. Although it had been generally assumed that all the Fe–N–O linkages were bent, neither *linear* nor *bent* Fe–N–O had been ruled out, and the prior spectral data were shown to be compatible with either.[14] The value of the ν_{N-O} frequency has been used as a structural criterion for the Fe–N–O moiety; the linear Fe–N–O linkage in $[Fe(NO)(i\text{-}Prdtc)_2]$ fails to fit into the correlation. Comparisons of structural and ESR measurements have also been used as structural criteria for the Fe–N–O linkage, and we report the ESR data for $[Fe(NO)(i\text{-}Prdtc)_2]$ in pure form, in frozen solution, and in the solid state doped into its cobalt analogue. The cobalt complex has the same space group as its iron analogue and very similar unit cell parameters, indicating that the two are closely isomorphous. The cobalt complex should therefore be a good diamagnetic medium in which to disperse the iron compound for ESR measurements, since the two compounds should have much the same structure. It also seems reasonable to hope that the isomorphous cobalt complex would have the same linear M–N–O linkage. A crystal structure of the cobalt complex was performed to check this, and the result was quite unexpected.

Experimental Section

Preparation of Compounds. Sodium *N,N*-diisopropyldithiocarbamate was prepared by the procedure of Gleu and Schwab[28] (diisopropylamine (126 mL) was dissolved in ethanol (200 mL), treated with CS_2 (65 mL) and then aqueous NaOH (150 mL), and recrystallized from ethanol–ether).

$$(i\text{-}Pr)_2NH + CS_2 + NaOH \rightarrow Na[S_2CN(i\text{-}Pr)_2] + H_2O \quad (1)$$

$[Fe(NO)(i\text{-}Prdtc)_2]$ was prepared by literature methods.[14,29] $\nu_{NO} = 1700\ cm^{-1}$.

$[Co(NO)(en)_2](ClO_4)_2$ was prepared as a red precipitate by bubbling NO into a deoxygenated solution of $Co(ClO_4)_2 \cdot 6H_2O$ (10.0 g) in methanol (150 mL), which had been treated with ethylenediamine (5 mL). $\nu_{NO} = 1663\ cm^{-1}$.

$[Co(NO)(i\text{-}Prdtc)_2]$. $Na(i\text{-}Prdtc)$ (1.87 g) in methanol solution (100 mL) was added dropwise, under nitrogen, to solid $[Co(NO)(en)_2](ClO_4)_2$ over a 10-min period. The mixture was stirred for 2 h, the solvent removed, and the crude product treated with 50 mL of oxygen-free water. The mixture was again stirred for 2 h. The dark brown precipitate was dried in the open air and recrystallized from a minimum of dichloromethane at −10 °C. The product was identified by its infrared spectrum.

Nitric oxide was prepared in high purity by the dropwise addition of acidified iron(II) sulfate solution (278 g of $FeSO_4 \cdot 7H_2O$/L of 2 N H_2SO_4) to $NaNO_2$ (69 g/L).

ESR spectra were recorded on a Varian E-109 spectrophotometer at 9.1 GHz and 100 mW of power. The cavity temperature was maintained with the Varian variable-temperature controller using nitrogen as the carrier gas. The doped samples were prepared by dissolving the desired amounts of the iron and cobalt complexes in chloroform and evaporating the solution to dryness under vacuum. Solution spectra of the iron complex were measured in chloroform.

Magnetic susceptibilities were measured on a SQUID magnetometer in the range 4–80 K. The calibration of the instrument and measurement techniques are as described previously.[30,31]

---

(28) Gleu, K.; Schwab, R. *Angew. Chem.* **1950**, *62*, 324.

(29) Adams, D. M.; Raynor, J. B. "Advanced Practical Inorganic Chemistry"; Wiley: New York, 1965.

(30) O'Connor, C. J.; Sinn, E.; Cukauskas, E. J.; Deaver, B. S., Jr. *Inorg. Chim. Acta* **1979**, *32*, 29.

(31) O'Connor, C. J.; Deaver, B. S., Jr.; Sinn, E. *J. Chem. Phys.* **1979**, *70*, 5161.

(32) Freyberg, D. P.; Mockler, G. M.; Sinn, E. *J. Chem. Soc., Dalton Trans.* **1975**, 447.

(33) Corfield, P. W. R.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 197.

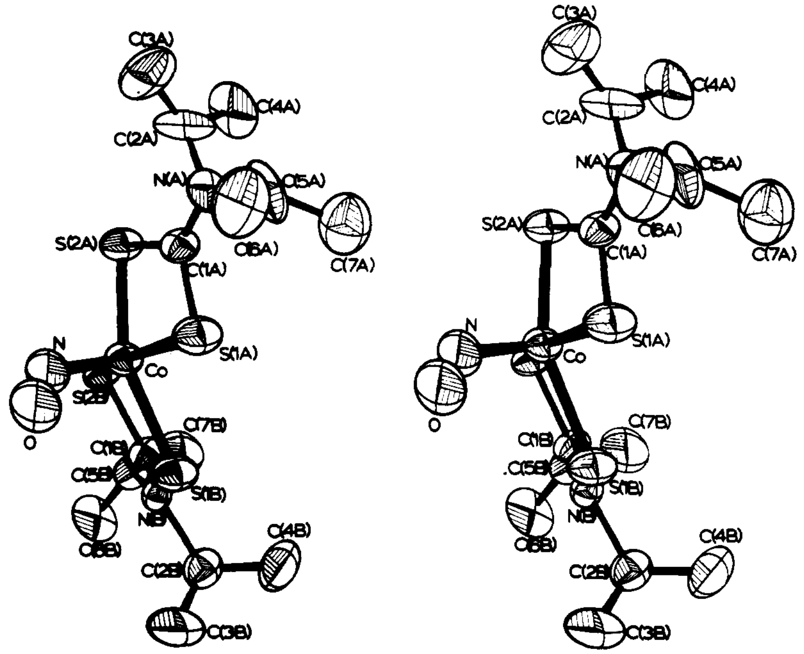

Figure 1. Stereopair view of the [Co(NO)(*i*-Prdtc)$_2$] molecule, showing the principal orientation of the Co–N–O linkage.

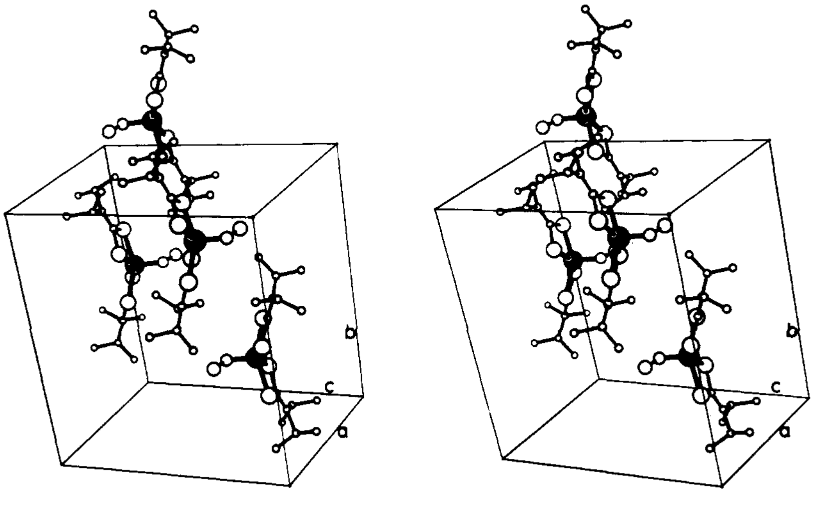

Figure 2. Molecular packing in the unit cell of [Co(NO)(*i*-Prdtc)$_2$].

Table IV. Magnetic Moments

T, K	4.28	4.50	5.21	5.67	6.14	7.16	8.32	9.89	11.64	14.8
μ_{eff}, μ_B	1.741	1.738	1.741	1.740	1.748	1.747	1.747	1.751	1.751	1.772
T, K	16.7	19.8	22.4	24.5	26.3	34.5	49.1	72.7		
μ_{eff}, μ_B	1.751	1.754	1.750	1.756	1.754	1.771	1.763	1.760		

Results and Discussion

Final positional and thermal parameters for [Co(NO)(*i*-Prdtc)$_2$] are given in Table I. Tables II and III contain the bond lengths and angles. The digits in parentheses in the tables are the estimated standard deviations in the least significant figures quoted and were derived from the inverse matrix in the course of least-squares-refinement calculations. Figure 1 is a stereopair view of the molecule, showing the principal orientation of the Co–N–O linkage, while Figure 2 shows the molecular packing in the unit cell.

For our purposes, the most remarkable feature of the structure is the bent Co–N–O linkage. This observation is unambiguous despite the positional disorder of the nitrosyl oxygen. The oxygen atom has multiple occupancy positions, of which only the main three were included in the calculation: the principal oxygen position gives a Co–N–O angle of 129.2 (9)°, and the lower occupancy (and therefore less precisely determined) oxygen positions give 149 (2)° for Co–N–O. This stands in stark contrast to the linear (179°) Fe–N–O linkage observed in the iron analogue of this complex and complicates

---

(34) Supplementary material.

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

(36) Karlin, K. B.; Rabinowitz, H. D.; Lewis, D. L.; Lippard, S. J. *Inorg. Chem.* **1977**, *16*, 3262.

(37) Rae, A. I. M. *Chem. Commun.* **1967**, 1245.

(38) D. G. Van Der Veer, reported in: Eisenberg, R.; Meyer, C. D. *Acc. Chem. Res.* **1975**, *8*, 26.

(39) Enemark, J. H.; Feltham, R. D.; Huie, B. T.; Johnson, P. L.; Swedo, K. B. *J. Am. Chem. Soc.* **1977**, *99*, 3285.

(40) Kopf, J.; Schmidt, J. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1977**, *32B*, 275.

(41) Alderman, P. R. H.; Owston, P. G.; Rowe, J. M. *J. Chem. Soc.* **1962**, 668.

(42) Snyder, D. A.; Weaver, D. L. *Inorg. Chem.* **1970**, *9*, 2761.

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

Table V. Comparison of Isoelectronic Pentacoordinate Nitrosyl Complexes

compd^g	ν_{N-O}, cm^{-1}	ordered/ disordered NO	geometry	M-N, Å	N-O, Å	M-N-O, deg	ref
Fe(TPP)(NO)	1700	d	SBP, apical NO	1.717 (7)	1.122 (12)	149.2 (6)	35
Fe(N_2S_2)(NO)	1650	o	SBP, apical NO	1.693 (5)	1.170 (6)	155.2 (5)	36
			SBP, apical NO	1.702 (5)	1.130 (6)	158.4 (5)	36
Fe(Me_2dtc)$_2$(NO)	1690	d	SBP, apical NO	1.705 (16)	1.016 (19)	173.3 (15)	20, 21
Fe(Me_2dtc)$_2$(NO)^a	1690	o	SBP, apical NO	1.720 (5)	1.102 (7)	170.4 (6)	21
[Fe(S_2C_2(CN)$_2$)$_2$(NO)]$^{2-}$	1645	d	SBP, apical NO	1.56 (2)	1.06 (4)	165 (2)	37, 38
Fe(Et_2dtc)$_2$(NO)	1673	d	SBP, apical NO	1.69 (4)	1.16 (5)	174 (4)	19
[Fe(das)$_2$(NO)]$^{2-}$	1760	o	SBP, apical NO	1.655 (18)	1.141 (27)	172.8 (17)	39
[Fe(CN)$_4$(NO)]$^{2-}$	1755	o	SBP, apical NO	1.565^b	1.161^b	177.1^b	40
[Fe(TMC)(NO)]$^{2-}$	1840	o	int,^{d} apical NO	1.737 (6)	1.137 (6)	177.5 (5)	15
Fe(salen)(NO)^c	1710	d	SBP, apical NO	1.783 (16)	1.11 (4), 1.09 (2)	144 (5), 150 (4)	17
Fe(salen)(NO)^{c,e}	1630	d	SBP, apical NO	1.81 (15), 1.81 (11)	1.15^f	132 (5), 122 (7)	17
Fe(*i*-Pr$_2$dtc)$_2$(NO)	1695	o	SBP, apical NO	1.676 (3)	1.161 (3)	179.0 (3)	14
Co(*i*-Pr$_2$dtc)$_2$(NO)	1610	d	SBP, apical NO	1.707 (7)	1.11 (1)	129.2 (9)	this work
Co(S_2CNMe$_2$)$_2$(NO)^h		d	SBP	1.7	1.1	127	41
[Co($C_2H_8N_2$)$_2$Cl(NO)]$^+$	1611	o	OCT	1.820 (11)	1.043 (17)	124.4 (1)	42
[Co(das)$_2$(NO)]$^{2+\,i}$	1852	o	TBP	1.68	1.17	179	43
[Co(das)(NO)(SCN)]$^{+\,i}$	1587	o	OCT	1.85	1.01	135	43

[a] Data collected at −80 °C. [b] No esd's reported; $R_f = 10.2\%$. [c] $S = {}^3/_2 \rightleftarrows S = {}^1/_2$ temperature-dependent spin equilibrium reported. [d] Geometry reported to be intermediate between trigonal bipyramidal and square-based pyramidal but biased toward the latter. [e] Data collected at −175 °C. [f] N-O bond distance fixed at 1.15 Å. [g] Abbreviations: SBP = square-based pyramid; TPP = 5,10,15,20-tetraphenylporphinato; N_2S_2 = $C_8H_{18}N_2S_2$; Me$_2$dtc = dimethyldithiocarbamato; Et$_2$dtc = diethyldithiocarbamato; das = *o*-phenylenebis(dimethylarsine); TMC = tetramethylcyclam ($C_{14}H_{32}N_4$); salen = *N*,*N*′-ethylenebis(salicylaldiminato); *i*-Pr$_2$dtc = diisopropyldithiocarbamato; OCT = octahedral; TBP = trigonal bipyramidal. [h] No esd's given; R = 12.2%. [i] No esd's given.

the spectral analysis of the latter. The observation of the linear Fe–N–O group contrasts with previous conclusions about related compounds. ESR data for [Fe(NO)(Etdtc)$_2$] in EPA glass[25] were interpreted in terms of a single nonlinear FeNO species on the EPR time scale or possibly a linear FeNO group which cannot then be normal to the plane of the four S atoms. In [Fe(NO)(*i*-Prdtc)$_2$], not only is Fe–N–O linear but it is also normal to the S_4 plane.

The linear Fe–N–O and bent Co–N–O groups constitute the only noteworthy differences between the two structures where otherwise similarities abound. This dramatic difference between the two complexes demonstrates the importance of crystal structures in making detailed comparisons between isomorphous compounds. In addition to the similar cell parameters, analogous metal–ligand bond lengths are just as close (Å): ⟨Fe–S⟩ = 2.288; ⟨Co–S⟩ = 2.256; Fe–N = 1.676; Co–N = 1.707. The Co–N bond is essentially normal to the S_4 plane. This is indicated by the structural details. The four S–Co–N angles have quite similar values ranging from 102.9 (3) to 104.7 (3)° averaging 103.7°; this is analogous to the iron complex for which related angles average 106.6°. The two apical planes made up of a diagonal of the pyramid base and the N atom are essentially perpendicular (89.1, 89.6°) to the base. These two apical planes are inclined at 79.0° to each other rather than 90° because the S_4 pyramid base closely approximates a rectangle rather than a square (long sides 3.381 (5), 3.386 (5) Å; short sides 2.781 (5), 2.797 (5) Å). Again, these structural features are analogous to those of the iron complex. The Co atom is displaced 0.53 Å above the S_4 plane, a little less than the analogous displacement of 0.65 Å in the iron complex.

The magnetic moments of [Fe(NO)(*i*-Prdtc)$_2$] in Table IV indicate one unpaired electron for the {Fe–N–O}^{7} system. There is a very small lowering of the values at the lowest temperatures, possibly due to intermolecular interactions, but otherwise the magnetic moment is essentially constant, with a spatially averaged g value of 2.03. In agreement with this, the room-temperature ESR spectrum of the pure solid [Fe(NO)(*i*-Prdtc)$_2$] complex, with a known linear Fe–N–O linkage, consists of a single broad resonance centered at g =

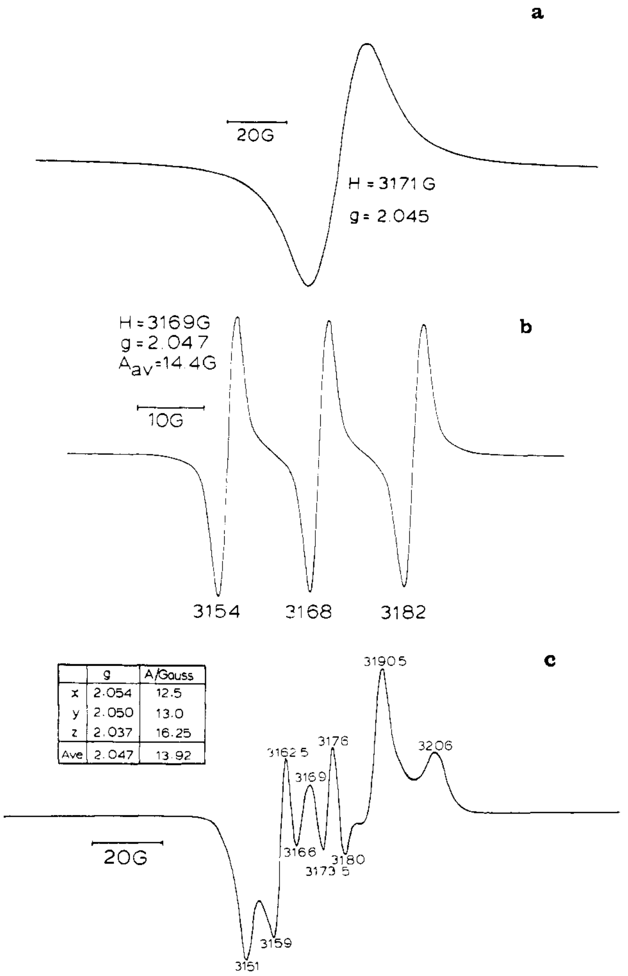

Figure 3. (a) Room-temperature ESR spectrum of the pure [Fe(NO)(*i*-Prdtc)$_2$] complex, with the linear Fe–N–O linkage. (b) Solution spectrum of [Fe(NO)(*i*-Prdtc)$_2$] in chloroform at 213 K. (c) ESR spectrum at 103 K of [Fe(NO)(*i*-Prdtc)$_2$] diluted 1:300 in [Co(NO)(*i*-Prdtc)$_2$], which has a bent Co–N–O linkage.

2.045. The solution ESR spectrum in chloroform at 213 K reveals a three-line pattern characteristic of the ^{14}N ligand hyperfine interaction with the unpaired electron and corresponds to $\langle A \rangle = 14.4$ G and $\langle g \rangle = 2.047$. The iron complex need not retain its linear Fe–N–O group, but there is also no known reason for this group to bend in solution. Although the solution g value agrees well with that in the solid, this does not establish a linear Fe–N–O group in both cases. The three components of **g**, and **A**, were determined from the spectrum of the iron compound in the diamagnetic [Co(NO)(i-Prdtc)$_2$] host at 100 K. The method used was illustrated by Goodman et al.[25] The results are tabulated with the spectra in Figure 3c. The average g and A values calculated from these results are similar to those obtained in the other media (Figure 3a,b). This indicates either that the Fe–N–O group remains linear despite the nonlinearity of the cobalt host or, more likely, that the Fe–N–O group is bent but without great influence on the ESR parameters, especially the g value. The g values are similar to, but larger than, those for [Fe(NO){S$_2$CN(C$_2$H$_5$)$_2$}$_2$],[25] which has 2.042, 2.038, 2.027 for g_x, g_y, g_z compared with 2.054, 2.050, 2.037 in the present complex. The A values are also generally slightly larger at 12.5, 13.0, 16.25 G for A_x, A_y, A_z in the present complex, compared with 12.8, 11.1, 14.5 G. Although the slightly larger values could be a manifestation of greater electron coupling in the linear Fe–N–O linkage, the difference is small enough to be explicable in terms of other causes.

The lower value of the ν_{N-O} energy in the bent Co–N–O linkage (1610 cm^{-1}) than in its linear Fe–N–O analogue (1695 cm^{-1}) is in keeping with the general trend that is apparent for linear and bent M–N–O groups (Table V). However, it should be noted that this is only a trend, with a number of exceptions, the most noteworthy of which is that the ν_{N-O} for the linear Fe–N–O in [Fe(NO)(i-Prdtc)$_2$] falls well within the range of the bent linkages! Thus, while comparisons of very similar complexes can give some structural information, the individual values of ν_{N-O} bear no general relationship to structures. All other features in the region 4000–800 cm^{-1} are identical for the two compounds. In the far-infrared region, a strong absorption is observed for both compounds at 375 cm^{-1}, which is assigned as the M–S stretch. In the M–NO stretching region, the iron complex exhibits a single sharp peak at 280 cm^{-1} for the ordered linear Fe–NO group. By contrast, the bent Co–NO group manifests itself as three peaks in the region 275–305 cm^{-1}, possibly reflecting the threefold Co–N–O disorder.

On the basis of the very low bending frequency for the {Fe–N–O}^{7} group, we had previously suggested that minor changes in the molecular packing can have a substantial effect on the Fe–N–O angle. The dramatic difference in the structure of the M–N–O group in the otherwise extremely similar and crystallographically isomorphous [Fe(NO)(i-Prdtc)$_2$] and [Co(NO)(i-Prdtc)$_2$] complexes further supports this. The activation of the nitrosyl group in the catalytic reduction of CO is believed to require interconversion between linear and bent M–N–O configurations.[44] However, this interconversion has only been observed in two cases where an extra ligand is added to the coordination sphere.[39,45] The present results provide an example in which the geometry is determined by very minor molecular changes, indicative of a very facile interconversion between the geometries.

Acknowledgment. Support received under NSF Grant No. CHE0770B72 and MBS Grant No. 5S06RR08016-11 NIH/DDR is gratefully acknowledged.

Registry No. Fe(NO)(i-Prdtc)$_2$, 72251-12-8; [Co(NO)(en)$_2$](ClO$_4$)$_2$, 15334-82-4; Co(NO)(i-Prdtc)$_2$, 83897-62-5.

Supplementary Material Available: Listings of thermal parameters, bond lengths and angles, least-squares planes, and structure factor amplitudes (16 pages). Ordering information is given on any current masthead page.

---

(44) Hendrickson, D. E.; Meyer, C. D.; Eisenberg, R. *Inorg. Chem.* **1977**, *16*, 970.

(45) Enemark, J. H.; Feltham, R. D.; Riker-Napperi, J.; Bizot, K. F. *Inorg. Chem.* **1975**, *14*, 624.

Contribution from the Department of Chemistry,
Texas A&M University, College Station, Texas 77843

A Bis(diphosphine)hexachloroditantalum Complex with a Ta–Ta Double Bond: Hexachlorobis[bis(dimethylphosphino)ethane]ditantalum(III)

F. ALBERT COTTON,* LARRY R. FALVELLO, and ROBERT C. NAJJAR

Received April 21, 1982

The title compound has been prepared in good yield by reaction of bis(dimethylphosphino)ethane with Ta$_2$Cl$_6$(Me$_2$S)$_3$. It has an edge-sharing bioctahedral structure with the metal atoms, two bridging chlorine atoms, and the phosphorus atoms forming a central plane and four chlorine atoms occupying axial positions to complete octahedra about each metal atom. The Ta atoms are drawn together with Ta–Cl–Ta and Cl–Ta–Cl angles in the central bridging unit of 66.88 (4) and 113.12 (4)°, respectively, and a Ta═Ta distance of 2.710 (1) Å. The molecule differs structurally from the previously reported Ta$_2$Cl$_6$(PMe$_3$)$_4$ in the location of all phosphorus atoms in equatorial positions and chemically in its lack of reaction with H$_2$. The crystals belong to space group $P2_1/n$ with $a = 9.342$ (1) Å, $b = 13.353$ (1) Å, $c = 10.632$ (1) Å, $\beta = 95.70$ (1)°, and $Z = 2$. Each molecule lies on a crystallographic inversion center. Refinement of a model omitting hydrogen atoms converged with $R_1 = 0.024$ and $R_2 = 0.037$, with use of 1958 data and 109 variables. Low solubility has thwarted effects to study the compound in solution.

Introduction

In continuation of our studies[1] of the chemistry of niobium and tantalum in their III oxidation state, we have been examining compounds containing halide ions and phosphine molecules as ligands. Both Ta^{III} and Nb^{III} have a marked tendency to form binuclear complexes in which there are M═M double bonds, although there are mononuclear compounds as well. In the case of mixed halo–phosphine complexes both mono- and dinuclear complexes have been reported.[2-4] Two compounds of the type Ta$_2$Cl$_6$(PR$_3$)$_4$ have

---

(1) Cotton, F. A.; Falvello, L.; Najjar, R. C. *Inorg. Chim. Acta* **1982**, *63*, 107.

(2) Sattelberger, A. P.; Wilson R. B., Jr.; Huffman, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7111.

(3) Hubert-Pfalzgraf, L. G.; Tsunoda, M.; Riess, J. G. *Inorg. Chim. Acta* **1981**, *52*, 231.

0020-1669/83/1322-0375$01.50/0 © 1983 American Chemical Society