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Bending of Linear Nitric Oxide Ligands in Four-Coordinate Transition Metal Complexes. Crystal and Molecular Structure of Dinitrosyldithioacetylacetonatocobalt(–I), Co(NO)₂(SacSac)

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The crystal and molecular structure of dinitrosyldithioacetylacetonato cobalt, Co(NO)₂(SacSac), has been determined at 294 K from three-dimensional data measured by counter methods. The compound crystallizes in the centrosymmetric monoclinic space group $C2/m$ (C_{2h}^3, No. 12) with $a = 16.565$ (2) Å, $b = 7.604$ (2) Å, $c = 8.709$ (1) Å, $\beta = 114.90$ (1)°, $V = 995.05$ Å³, $\rho_{calcd} = 1.67$ g cm⁻³ for $Z = 4$. The structure was solved by conventional Patterson and Fourier techniques and refined by full-matrix least squares to final residuals $R = 0.040$ and $R_w = 0.040$ for 580 independent reflections with $I/\sigma(I) \geq 3.0$. The molecule has exact m symmetry with the mirror plane containing the Co(SacSac) unit. The coordination geometry around the cobalt is a slightly distorted tetrahedron. Bond distances of interest are Co–S = 2.217 (2), 2.224 (2) Å, Co–N = 1.650 (6) Å, and N–O = 1.120 (5) Å. The Co–N–O angle is 168.9 (5)° and the N–Co–N angle is 115.5 (3)°. From a comparison of the details of this structure with those of other tetracoordinate dinitrosyls containing the {M(NO)₂}¹⁰ functional group, it is evident that "linear" M–N–O systems are invariably partially bent with M–N–O angles ranging from 158.9 to 178.7°. The angles N–M–N and O–M–O are found to be linearly correlated with O–M–O ≤ N–M–N ≤ 130° for M = first-row transition metal (attracto conformer) and 130° ≤ N–M–N ≤ O–M–O for M = second- and third-row transition metals (repulso conformer). The conditions and requirements leading to partial bending of "linear" nitrosyl ligands in tetracoordinate complexes are discussed.

Introduction

The nitric oxide ligand is amphoteric and can act either as a one-electron donor (NO⁻; bent MNO) or as a three-electron donor (NO⁺; linear MNO).[1] In order to characterize this unusual ligand property, a large number of metal–nitrosyl complexes have been studied by x-ray crystallography.[2,3] Recent interest has centered on the four-coordinate dinitrosyl complexes of the group 8 metals, especially since several have been found to promote the catalytic reduction of nitric oxide by carbon monoxide to form nitrous oxide and carbon dioxide.[4–8] To date, all such complexes have been shown to have a distorted tetrahedral coordination about the metal with M–N–O groups which are approximately linear rather than fully bent (i.e., M–N–O = 120°). This structural evidence is consistent with the nitrosyl ligands acting essentially as three-electron donors (NO⁺) with the metal atom having, at least formally, both a closed-shell d¹⁰ configuration and an unusually low oxidation state (e.g., Fe(–II), Co(–I)).

Attempts to correlate structure and bonding with chemical reactivity require, as a prerequisite, both the synthesis of new four-coordinate dinitrosyls and a knowledge of the fine details of their geometrical structures. At present, relevant crystallographic data are limited to the phosphine (PPh₃) series M(NO)₂P₂, in which M is Fe, Ru, Os, Co⁺, Rh⁺, and Ir⁺,

some polynuclear bridged species containing the functional Fe(NO)₂ or Co(NO)₂ group, and the monomeric compounds Fe(NO)₂(f₆fos)[9] and Fe(NO)₂(CO)₂. Although the supporting ligands are commonly phosphines and so, to some degree, in competition with nitric oxide for π-electron density from the central metal atom, in several instances π-donating ligands such as halogens complete the coordination sphere. The binuclear complex [Fe(NO)₂SEt)]₂ provides the only example so far structurally characterized of a sulfur donor ligand completing the coordination environment.

All of the complexes possess pseudotetrahedral geometry (see Table V), but, interestingly, pronounced differences in the magnitude of the N–M–N angle are observed. It has been suggested[10] that "opening up" of the N–M–N angle can be rationalized in terms of increased repulsion between the nitrosyl ligands concomitant with increasing extent of back-bonding from the metal. The alternative molecular orbital description[3] of pseudotetrahedral dinitrosyls correlates the observed distortions from an idealized T_d geometry in these d¹⁰ complexes in terms of changes in metal/ligand parentage of the HOMO. Either approach leads to the expectation that larger N–M–N angles are matched with NO⁻ character, and smaller N–M–N angles with NO⁺ character. The more strongly reducing second- and third-row transition metals favor the former; the

less strongly reducing first-row transition metals favor the latter. The contribution of the supporting ligands should be determined by their σ,π-accepting (or donating) and steric properties in the customary way. In the case of $Os(NO)_2$-$(PPh_3)_2$ there is evidence from the ESCA spectrum that the electron density on the osmium center is actually more consistent with a real oxidation state of between 0 and II rather than the formal oxidation state of −II, confirming that near-linear nitrosyl ligands are especially effective in delocalizing π density from the electron-rich Os(−II) atom.[10,11]

As the finer details of molecular structure appear to reflect the electronic requirements of the metal center, we decided to determine the crystal structure of the new cobalt dinitrosyl in which coordination is completed by the sulfur chelate, dithioacetylacetone.[12] The reaction of nitric oxide with square-planar bis(dithioacetylacetonato)cobalt(II) yields two nitrosyls, dark brown $Co(NO)(SacSac)_2$ and dark red-brown $Co(NO)_2(SacSac)$. Interestingly, the mononitrosyl is unstable in solution and disproportionates into $Co(SacSac)_3$ and the monomeric diamagnetic dinitrosyl. On the basis of the infrared $\nu(N-O)$ stretching frequencies of 1750 and 1820 cm^{-1}, it was inferred that the nitrosyl groups were bound linearly (i.e., NO^+) and that the diamagnetic formally Co(−I) species was pseudotetrahedrally coordinated.[12] The molecular structure described below substantiates this geometry and additionally reveals small but significant distortions from ideal N−Co−N and Co−N−O angles which have led us to examine further the exact nature of the correlation between these angles.

Experimental Section

Crystals of dinitrosyldithioacetylacetonatocobalt(−I) suitable for x-ray analysis were provided by Dr. A. R. Hendrickson of Australian National University. Preliminary Weissenberg and precession photographs of a number of crystals showed the crystal class to be monoclinic, the systematic absences $h + k = 2n + 1$ for (hkl) data being consistent with the space groups $C2$, Cm, and $C2/m$. The latter centrosymmetric space group was found to adequately describe the crystal structure (vide infra). The crystals were found to decompose rapidly in the x-ray beam. A freshly prepared single crystal, in the form of a prism with perpendicular distances of 0.084, 0.163, and 0.312 mm between the sets of crystal faces (100) and ($\bar{1}$00), (001) and (00$\bar{1}$), and (010) and (0$\bar{1}$0), respectively, was mounted on a quartz fiber and coated with a thin film of epoxy cement. This crystal was used for the entire data collection.

The crystal was transferred to a Picker FACS-I four-circle diffractometer with the crystallographic $\bar{b}$ axis approximately collinear with the diffractometer ϕ axis. The orientation matrix and unit cell dimensions were determined by least-squares refinement[13] of the 2θ, ω, χ, and ϕ setting angles of 12 carefully centered reflections in the range $70° < 2\theta < 91°$ using graphite crystal monochromated Cu Kα_1 radiation (λ 1.540 51 Å, takeoff angle 1.5°).

Crystal Data: $C_5H_7CoN_2O_2S_2$, mol wt 250.19, monoclinic, $a = 16.565$ (2) Å, $b = 7.604$ (2) Å, $c = 8.709$ (1) Å, $\beta = 114.90$ (1)°, $V = 995.05$ Å^3, $\rho_{calcd} = 1.67$ g cm^{-3} for $Z = 4$, $F(000) = 504$, space group $C2/m$ (C_{2h}^3, No. 12).[14]

Data Collection. The reflection intensities were measured by the θ–2θ scan technique at a 2θ scan rate of 2°/min employing monochromatic Cu Kα radiation at a takeoff angle of 3.0°. The scan range of a reflection extended from 0.95° below the Kα_1 peak to 0.95° above the Kα_2 peak accumulating p counts. Stationary-counter background measurements (b_1, b_2) were made at the scan range limits for a total time t_b (=20 s). The intensities of three standard reflections [indices (0,−4,0), (802), and (−6,0,5)] were measured after every 100 reflections and were found to decrease linearly with time to 68.3%, 71.4%, and 73.8% of their initial values over the period of data collection (~50 h). A total of 1822 reflections (including standards) of the forms $\pm h,-k,\pm l$ in the range $3° < 2\theta < 125°$ and $\pm h,+k,+l$ in the range $3° < 2\theta < 70°$ were measured.

The intensities were corrected for Lorentz–polarization factors and for anisotropic decay.[15] Reflections for which the individual background measurements were significantly different (viz., $|b_1 - b_2|/(b_1 + b_2)^{1/2} > 5.0$) were eliminated from the data set. Assuming a linear variation of the background intensity over the scan range,

the net integrated intensity I and its standard deviation $\sigma(I)$ for each reflection were calculated according to $I = p - (t_p/t_b)(b_1 + b_2)$ and $\sigma(I) = [p + (t_p/t_b)^2(b_1 + b_2)]^{1/2}$. The structure factor amplitudes and standard deviations were calculated from $F_o = (I/LP)^{1/2}$ and $\sigma(F_o) = \{[\sigma(I)/LP]^2 + [\rho F_o^2]^2\}^{1/2}/2F_o$ where ρ (=0.002$^{1/2}$) is an arbitrary constant to allow for instrumental instability.[16,17] The reflection data were then corrected for absorption effects by an analytical method[18] (μ = 173.9 cm^{-1}; transmission factor range 0.248–0.568). Unobserved reflections ($I/\sigma(I) < 3.0$) were deleted from the data set and the remainder were sorted and equivalent forms for the point group $2/m$ averaged to the forms $+h,+k,\pm l$. The statistical R factor for the 580 observed independent reflections was 0.019.

Structure Solution and Refinement. In view of the extreme solubility of the compound in most organic solvents, no attempt was made to determine its density experimentally; a reasonable calculated density of 1.67 g cm^{-3} required four molecules in the unit cell and hence only half of the molecule to be independent in the space group $C2/m$. A three-dimensional Patterson function was solved for the Co and two S atoms which were located on the crystallographic mirror plane in the $4i$ positions of the centrosymmetric space group. A difference Fourier synthesis phased by these atoms revealed the remaining nonhydrogen atoms.

Block-diagonal least-squares refinement (4 × 4, or 3 × 3, 6 × 6 matrices) of the positional and isotropic thermal parameters of the nonhydrogen atoms, using unit weights for individual reflections, converged at $R = 0.117$, $R_w = 0.112$. Anisotropic temperature factors of the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$ were introduced for all nonhydrogen atoms and the refinement was continued with individual reflection weights assigned as $[\sigma(F_o)]^{-2}$ to residual values of $R = 0.044$, $R_w = 0.045$.

A difference Fourier at this stage failed to locate the hydrogen atoms. Their positions were calculated with a C–H distance of 0.95 Å,[19] and they were assigned an isotropic temperature parameter of $1.1B_c$ where B_c is the equivalent isotropic thermal parameter of the carbon to which the hydrogen atom is bonded. The methyl groups were assumed to be freely rotating and were simulated by placing one-eighth of an hydrogen atom at intervals of 15° of arc such that the m molecular symmetry was retained. The hydrogen atom parameters were recalculated after every cycle. Full-matrix least-squares refinement using this model converged at $R = 0.040$, $R_w = 0.040$, the maximum atomic parameter shift in the final cycle being less than 0.1 of its estimated standard deviation.

A final difference Fourier showed all residual peaks to be in the range −0.50 to +0.40 e/Å^3. Analysis of the weighting scheme showed the function $\sum w(|F_o| - |F_c|)^2$ to be virtually independent of $|F_o|$ or $(\sin\theta)/\lambda$, and there was no evidence of extinction effects. The standard deviation of an observation of unit weight, defined as $\{\sum w(|F_o| - |F_c|)^2/(m - n)\}^{1/2}$ where m is the number of observations (580) and n the number of parameters (67), was 1.94 (cf. a value of 1.00 for ideal weighting).

Atomic scattering factors for nonhydrogen atoms were taken from ref 20 and were corrected for the real and imaginary parts of anomalous dispersion.[21] The hydrogen scattering curve was taken from ref 22. The final observed and calculated structure factors are available[23] and the final atomic parameters are presented in Table I.

All computing was carried out on the Univac 1108 computer of the Australian National University Computer Center. The computer programs used have been described elsewhere[24] with the exception of HYDGEN (hydrogen position calculation, H. Hope, U. C. Davis) which was modified for local use and for methyl hydrogen positions (D. Taylor, P. O. Whimp).

Description of the Structure

The principal interatomic distances and angles, together with nonbonded intra- and intermolecular contacts, are listed in Table II. Stereoviews of an individual molecule and the unit cell contents are presented in Figures 1 and 2, respectively. Root-mean-square amplitudes of vibration are given in Table III.

The crystal structure consists of discrete pseudotetrahedral $Co(NO)_2(SacSac)$ molecules (Figure 1) of crystallographic m symmetry with the mirror plane containing the SacSac ligand and bisecting the N−Co−N angle thereby requiring the
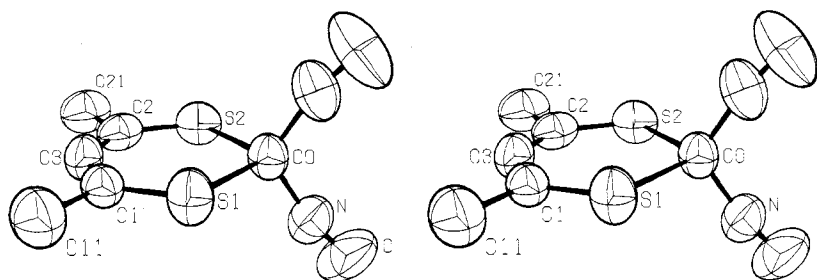
Figure 1. Stereoview of the $Co(NO)_2(SacSac)$ molecule. Vibrational ellipsoids are drawn at 50% probability level.

Table I. Final Atomic Parameters[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	0.063 19 (7)	0.0	0.272 38 (12)	0.005 72 (6)	0.029 95 (32)	0.016 52 (20)	0.0	0.003 83 (9)	0.0
S(1)	0.118 9 (1)	0.0	0.552 7 (2)	0.006 0 (1)	0.040 0 (6)	0.017 7 (3)	0.0	0.005 2 (1)	0.0
S(2)	0.188 5 (1)	0.0	0.236 6 (2)	0.008 0 (1)	0.032 2 (5)	0.022 5 (3)	0.0	0.008 3 (2)	0.0
C(1)	0.229 9 (4)	0.0	0.651 7 (8)	0.005 9 (4)	0.020 6 (16)	0.016 6 (11)	0.0	0.003 4 (6)	0.0
C(2)	0.281 5 (4)	0.0	0.419 8 (10)	0.006 1 (4)	0.020 6 (16)	0.031 9 (19)	0.0	0.008 0 (8)	0.0
C(3)	0.289 8 (4)	0.0	0.582 8 (9)	0.004 3 (3)	0.026 7 (18)	0.024 0 (15)	0.0	0.002 7 (6)	0.0
C(11)	0.264 1 (5)	0.0	0.838 9 (10)	0.009 3 (5)	0.036 5 (22)	0.024 8 (16)	0.0	0.004 3 (7)	0.0
C(21)	0.363 0 (6)	0.0	0.389 5 (12)	0.009 0 (5)	0.031 1 (21)	0.043 2 (23)	0.0	0.010 1 (10)	0.0
N	0.006 7 (3)	0.1834 (7)	0.200 1 (5)	0.007 6 (3)	0.042 8 (15)	0.020 3 (8)	0.0044 (6)	0.004 5 (4)	−0.0002 (9)
O	−0.042 9 (3)	0.2906 (8)	0.139 2 (6)	0.013 7 (4)	0.056 2 (17)	0.034 3 (10)	0.0157 (6)	0.006 0 (5)	0.0056 (10)

Atom[b]	x	y	z	B, Å²	Atom[b]	x	y	z	B, Å²
H(3)	0.350	0.0	0.665	6.2	H(21A)	0.347	0.0	0.271	9.2
H(11A)	0.215	0.0	0.870	8.8	H(21B)	0.397	0.102	0.439	9.2
H(11B)	0.299	−0.102	0.883	8.8	H(21C)	0.397	−0.102	0.439	9.2
H(11C)	0.299	0.102	0.883	8.8					

[a] Estimated standard deviations in the last significant digit(s) are given in parentheses in this and subsequent tables. [b] Atom H(nn) is bonded to C(nn). Representative coordinates of the methyl hydrogen atoms are given. The method of simulating the rotating methyl groups is described in the text.

Table II. Selected Interatomic Distances and Angles[a]

(a) Bond Distances, Å

Co–N	1.650 (6)	C(1)–C(11)	1.484 (9)
Co–S(1)	2.217 (2)	C(1)–C(3)	1.358 (9)
Co–S(2)	2.224 (2)	C(3)–C(2)	1.368 (9)
S(1)–C(1)	1.670 (7)	C(2)–C(21)	1.481 (10)
S(2)–C(2)	1.688 (7)	N–O	1.120 (5)

(b) Bond Angles, Deg

Co–N–O	168.9 (5)	S(1)–C(1)–C(3)	128.5 (5)
N–Co–N^I	115.5 (3)	S(2)–C(2)–C(3)	129.3 (6)
O–Co–O^I	106.6 (2)	C(1)–C(3)–C(2)	133.3 (6)
N–Co–S(1)	109.1 (2)	S(1)–C(1)–C(11)	113.2 (5)
N–Co–S(2)	111.1 (2)	C(11)–C(1)–C(3)	118.3 (6)
S(1)–Co–S(2)	100.0 (1)	C(3)–C(2)–C(21)	119.0 (7)
Co–S(1)–C(1)	115.2 (3)	S(2)–C(2)–C(21)	111.7 (6)
Co–S(2)–C(2)	113.7 (3)		

(c) Nonbonded Contacts <3.5 Å

Intramolecular

N···N^I	2.790 (11)	N···S(2)	3.210 (5)
N···S(1)	3.166 (5)	S(1)···S(2)	3.402 (2)

Intermolecular

O···O^{II}	3.184 (12)	O···N^{III}	3.354 (5)
O···O^{III}	3.288 (9)		

[a] Transformations of the coordinates (x, y, z) denoted by Roman numeral superscripts: I $(x, \bar{y}, z)$; II $(x, 1 - y, z)$; III $(\bar{x}, y, \bar{z})$.

Table III. Principal Root-Mean-Square Amplitudes of Vibration (Å)

Atom	Min	Intermed	Max
Co	0.228 (1)	0.259 (2)	0.296 (1)
S(1)	0.224 (2)	0.262 (2)	0.342 (2)
S(2)	0.225 (2)	0.307 (3)	0.309 (2)
C(1)	0.229 (7)	0.246 (9)	0.270 (9)
C(2)	0.239 (10)	0.246 (10)	0.319 (9)
C(3)	0.219 (9)	0.280 (9)	0.294 (9)
C(11)	0.277 (9)	0.327 (10)	0.349 (10)
C(21)	0.302 (10)	0.303 (11)	0.370 (10)
N	0.253 (5)	0.275 (6)	0.376 (6)
O	0.262 (6)	0.344 (5)	0.514 (6)

Table IV. Weighted Least-Squares Plane[a]

(a) Plane of $Co(NO)_2$ Entity

$$0.6404X + 0.0Y - 0.7681Z = -1.6216$$

(b) Distances (Å) of Atoms from Plane

Co	0.000 (1)	N^I	0.009 (5)
N	0.009 (5)	O^I	−0.006 (5)
O	−0.006 (5)		

[a] The plane is defined as $LX + MY + PZ = d$ where X, Y, and Z are orthogonal (Å) coordinates derived from the fractional cell coordinates x, y, and z by $X = 16.5652x - 3.6671z$, $Y = 7.6042y$, and $Z = 7.8994z$. The in-plane atoms are weighted according to $w = 3/[\sigma^2(X) + \sigma^2(Y) + \sigma^2(Z)]$. Transformations of the asymmetric unit are denoted by Roman numeral superscripts which are defined in Table II.

two nitrosyl moieties to be equivalent. The virtual point symmetry of the molecule, however, is C_{2v} with the C_2 axis passing through the Co and C(3) atoms. A prominent feature of the crystal packing (Figure 2) is the arrangement of the planar Co(SacSac) units in parallel planes at intervals of $b/2$ (=3.802 Å). The pentaatomic $\{Co(NO)_2\}$ entity is planar within experimental error (Table IV) and is orthogonal to the Co(SacSac) plane. The shortest Co–Co distance is 4.304 (2) Å and the shortest intermolecular contact, between neighboring nitrosyl oxygen atoms, is 3.18 Å.

The geometry of the $\{Co(NO)_2\}$ 10-electron functional group is typical of that found in a number of 18-electron cobalt dinitrosyl complexes which have been structurally characterized (Table V). The Co–N bond length of 1.650 (6) Å is within the range 1.61–1.73 Å for a cobalt atom coordinated by NO and is in excellent agreement with the corresponding Fe–N bond lengths of 1.65 Å and 1.67 Å found in the iso-
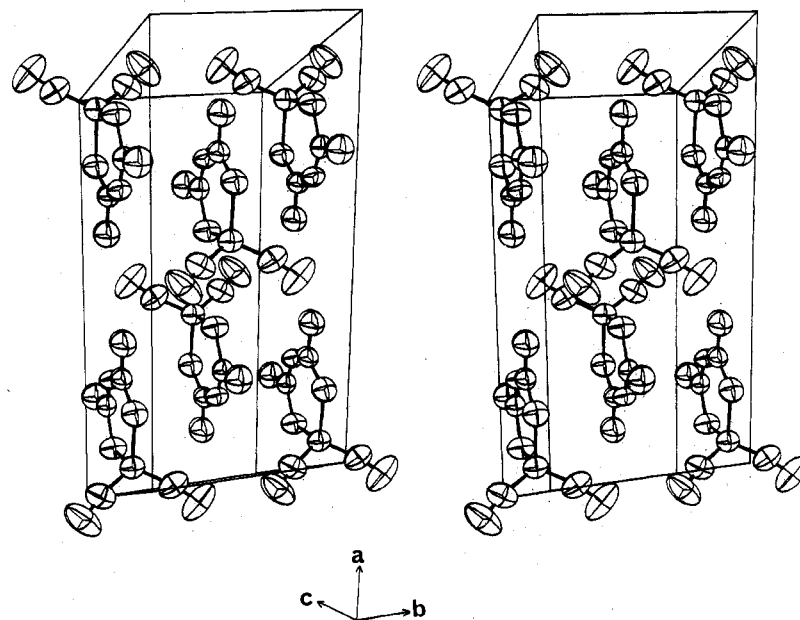
Figure 2. Stereoview of the unit cell contents.

Table V. Bond Lengths (Å) and Angles (deg) in Some Four-Coordinate Tetrahedral Metal Dinitrosyl Complexes

| Compd[a]	M–N	N–O	M–N–O	N–M–N	O–M–O	M–X	X–M–X	Ref
[Co(NO)₂(SacSac)]	1.650 (6)	1.120 (5)	168.9 (5)	115.5 (3)	106.6 (2)	2.217 (2),[c] 2.224 (2)	100.0 (1)	This work
[Co(NO)₂Cl]₂	1.73 (3)	1.12	166 (3)	110 (2)	99	2.13 (3),[d] 2.33 (2)	88 (1)	35
[Co(NO)₂I]ₓ	1.61[b]	1.17	171	118	110 (1)	2.593[d]	96.2	34
[Co(NO)₂(NO₂)]ₓ	1.67[b]	1.12		112	102			36
[Co(NO)₂(PPh₃)₂]⁺	1.664 (5), 1.663 (5)	1.156 (5), 1.157 (5)	171.2, 170.9	132.4	134.6	2.273 (5), 2.282 (5)	106.7	27
[Rh(NO)₂(PPh₃)₂]⁺	1.818 (4)	1.158 (6)	158.9 (4)	157.5 (3)	173.7	2.354 (1)	115.88 (5)	28
[Ir(NO)₂(PPh₃)₂]⁺	1.771 (12)	1.213 (13)	163.5 (10)	154.2 (7)	167.5 (5)	2.339 (3)	116.3 (2)	33
[Fe(NO)₂(PPh₃)₂]	1.650 (7)	1.190 (10)	178.1 (7)	123.8 (4)	122.4	2.267 (2)	111.9 (1)	25
[Ru(NO)₂(PPh₃)₂]	1.762 (6), 1.776 (6)	1.190 (7), 1.194 (7)	177.7 (6), 170.6 (5)	139.2 (3)	142.7 (2)	2.337 (2), 2.353 (2)	103.85 (6)	31
[Ru(NO)₂(PPh₃)₂]	1.748 (20), 1.688 (20)	1.215 (18), 1.229 (18)	174.7 (17), 168.0 (16)	139.9 (8)	146.8	2.332 (9), 2.346 (9)	105.5 (2)	32
[Os(NO)₂(PPh₃)₂]	1.771 (6), 1.776 (7)	1.195 (8), 1.211 (7)	178.7 (7), 174.0 (6)	139.1 (3)	140.6	2.324 (2), 2.340 (2)	103.51 (6)	10
[Fe(NO)₂I]₂[e]	1.67[b]	1.15	161	116	98 (3)	2.58[d]	107.4	34
[Fe(NO)₂(f₆fos)]	1.645 (7), 1.661 (7)	1.177 (10), 1.184 (10)	176.9 (7), 177.8 (7)	125.4 (4)	123.8	2.248 (2), 2.240 (2)	86.8 (1)	9
[Fe(NO)₂(SEt)₂][e]	1.67[b]	1.17	167.5	117.4	106.6	2.27[d]	106.0	26

[a] Abbreviations used: X, nonnitrosyl ligand; SacSac, dithioacetylacetone; Ph, C_6H_5; Et, ethyl; f₆fos, $Ph_2PC=C(PPh_2)CF_2CF_2CF_2$. [b] Average values for bond lengths and angles. [c] Bidentate X ligand. [d] Bridging X ligand. [e] Complex contains metal-metal bond.

electronic complexes of Fe(NO)₂(PPh₃)₂[25] and [Fe(NO)₂-(SEt)]₂.[26] The Co–N bond length of 1.66 Å reported[27] for the cation [Co(NO)₂(PPh₃)₂]⁺ is also very similar. Inspection of the schematic MO diagram (Figure 3) reveals that there are three MO's of the {Co(NO)₂}[10] moiety which are essentially π bonding with respect to Co and N in C_{2v}, consistent with the observed shortening of this bond length.

The N–Co–N angle of 115.5 (3)°, although slightly greater than the ideal tetrahedral angle, is notably smaller than the corresponding angle (132.4°) reported[27] for the [Co(NO)₂-(PPh₃)₂]⁺ cation. While other pseudotetrahedral dinitrosyls of the first-row transition metals have N–M–N angles in the range 110–124°, much larger values (139–158°) are found for the heavier transition metals Rh, Ir, Ru, and Os (Table V). This variation in the N–M–N angles appears to be largely independent of the steric requirements of the supporting ligands. In the series [M(NO)₂(PPh₃)₂] with M = Co⁺, Rh⁺, Ir⁺, Fe, Ru, and Os, the bulky triphenylphosphine ligands remain in a tetrahedral disposition with the P–M–P angle

relatively constant in the range 104–116°. Despite this almost uniform steric environment, the N–M–N angle varies widely between 124 and 158°, the variation presumably being electronic in origin. Interestingly, in the cation [Rh(NO)₂-(PPh₃)₂]⁺,[28] the N–Rh–N angle of 157.5° combined with the P–Rh–P angle of 115.9° is so far distorted from an ideal tetrahedral geometry that it might better be described in terms of a notional trigonal-bipyramidal arrangement with two equatorial phosphines and two displaced axial nitrosyls, with the remaining equatorial coordination site vacant.

Although it is generally believed that the π-accepting capacity of coordinated nitric oxide (NO⁺) is only fully developed when M–N–O is linear, it has been suggested that the linear-to-bent NO⁺-to-NO⁻ transition requires relatively little energy.[10] Examples of the fully bent nitrosyl (NO⁻) conformation are well documented[3,29] for five-coordinate complexes but a corresponding example in a four-coordinate complex has yet to be reported. Accordingly, it is of some interest that, although the {Co(NO)₂} moiety in Co(NO)₂-
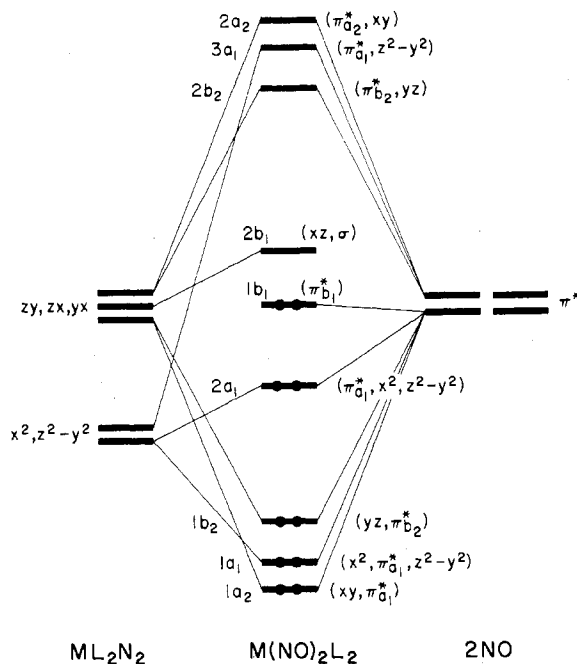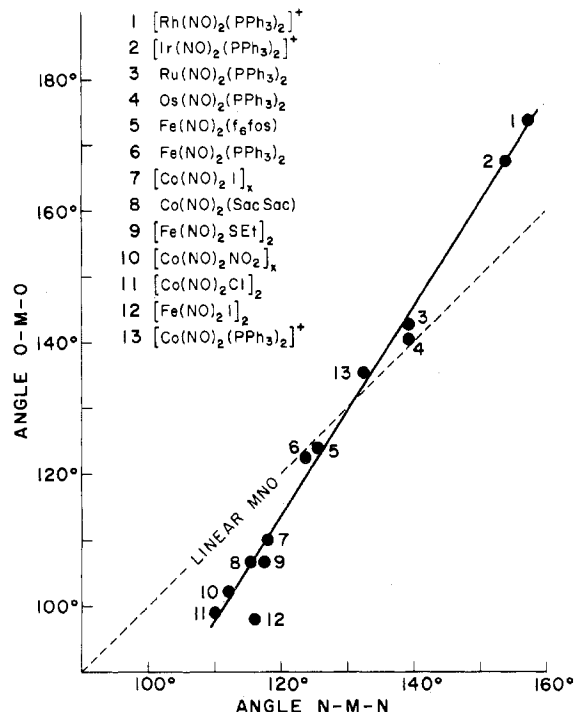
Figure 3. Schematic correlation diagram for pseudotetrahedral (C_{2v}) Co(NO)$_2$(SacSac): left, 3d energy levels of a tetrahedral complex CoN$_2$S$_2$; center, molecular orbitals of complex assuming energy of π^* (NO) is juxtaposed with the 3d manifold; right, π^* orbitals of two nitric oxide ligands.

Figure 4. Correlation of O–M–O angle with the N–M–N angle for $\{M(NO)_2\}^{10}$ complexes.

(SacSac) is planar, the two nitrosyl ligands are definitely bent toward each other, the O–Co–O angle of 106.6 (2)° being approximately 9° less than the N–Co–N angle. This departure from linearity of the Co–N–O grouping (168.9°) is similar to that found (171.1°) in the cation [Co(NO)$_2$(PPh$_3$)$_2$]$^+$. Indeed, examination of the data in Table V reveals that "linear" nitrosyls are invariably geniculated, i.e., partially bent, and that, in the case of [Rh(NO)$_2$(PPh$_3$)$_2$]$^+$, the Rh–N–O angle is as much as 21.1° less than the ideal angle of 180°. For the second- and third-row transition metals, the nature of the distortion changes the M–N–O angles so that the nitrosyl groups bend away from each other.

In order to illustrate the "bending-toward" and "bending-apart" distortions of the M(NO)$_2$ group, we have plotted the O–M–O angles of the complexes listed in Table V as a function of the N–M–N angle (Figure 4). Perhaps unexpectedly, there is a very good linear correlation between the two angles with O–M–O > N–M–N for the second- and third-row transition metals and vice versa for the first-row transition metals. The only exception is the complex [Co-(NO)$_2$(PPh$_3$)$_2$]$^+$ where the O–M–O angle (134.6°) is marginally larger than the N–M–N angle (132.4°). [It should be noted here that the O–M–O angle is directly proportional to the M–N–O angle only when the M(NO)$_2$ moiety has nearly exact C_{2v} symmetry.] Since the complexes are likely to involve widely disparate steric and crystal packing forces, it is highly probable that electronic influences are the cause of the partial bending of the "linear" nitrosyls.

The N–O bond length, 1.120 (5) Å, is shorter than in other recent accurate determinations (1.156–1.229 Å), but this may result from considerable librational shortening (maximum rms amplitude for the oxygen atom is 0.514 Å approximately normal to N–O bond). Some measure of this correction can be gauged in that if the oxygen atom is assumed to ride on the nitrogen atom, the resulting corrected N–O bond length is 1.208 Å.

The tetrahedral coordination sphere of the central cobalt atom is completed by the essentially symmetric coordination of a SacSac$^-$ ligand. Not unexpectedly the Co–S distances,

2.217 (2) and 2.224 (2) Å, are significantly longer than found in the d^7 square-planar cobalt(II) complex Co(SacSac)$_2$, 2.166 (3) Å.[30] There are no previously reported examples of a cobalt(–I)–sulfur bond with which the present values may be directly compared. However, if the difference in the covalent radii for phosphorus (1.10 Å) and sulfur (1.03 Å) is taken into account, an average Co–P bond length of 2.278 Å in the complex [Co(NO)$_2$(PPh$_3$)$_2$]$^+$ would indicate an analogous Co^{-I}–S bond length of ca. 2.22 Å, in agreement with the current value. The longer M–S distance (2.27 Å) in [Fe-(NO)$_2$(SEt)]$_2$ may result from the thiol functioning as a μ_1-bridging ligand.

The geometry of the coordinated SacSac$^-$ ligand is similar to that observed in other metal complexes of dithioacetyl-acetone. The average C–S and C–C ("backbone") bond lengths 1.679 (7) and 1.363 (9) Å, respectively, are indicative of extensive π-electron delocalization within the ligand. These bond lengths are marginally shorter than the most precise values for the SacSac ligand available[30] [C–S = 1.685 (3) Å and C–C = 1.381 (4) Å in Ni(SacSac)$_2$] and this, coupled with the planarity of the Co(SacSac) unit, may indicate that some of the excess electron density on the metal is possibly delocalized into the ligand π-electron system. The average C–CH$_3$ bond length, 1.482 (10) Å, is also a little shorter than expected [C(sp^2)–C(sp^3), 1.51 Å]. In all other structures of metal–dithioacetylacetone complexes, the hydrogen atoms have not been included in the scattering model and so the C–CH$_3$ bond lengths could be expected to be longer [e.g., 1.509 (5) Å in Ni(SacSac)$_2$] than in the present structure. Indeed, before the rotating methyl group was included in the model for Co(NO)$_2$(SacSac), the C–CH$_3$ bond lengths averaged 1.528 Å.

Discussion

The distortions which are found in pseudotetrahedral four-coordinate dinitrosyl complexes have been discussed by several groups of workers.[3,10,29] Of particular interest have been the large variations in the N–M–N angle coupled with partial bending of the expected linear M–N–O groups. It has been suggested that increased metal–nitrosyl back-bonding,

which would open up the N–M–N angle as a consequence of increased repulsion between the M–N bonds, would result in distortion from linearity of the M–N–O group. From the available structural data, it is evident that departure from M–N–O linearity can be in either of two senses (again assuming C_{2v} symmetry for the $M(NO)_2$ moiety) which for convenience we will term the "attracto" (O–M–O < N–M–N) or the "repulso" (O–M–O > N–M–N) conformers, A and B.

A

"attracto" conformer
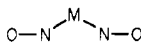
B

"repulso" conformer

The attracto conformation is characteristic of the first-row and the repulso conformation occurs with the second- and third-row transition metal dinitrosyls; i.e., geniculation of the coordinated nitrosyl appears to be determined primarily by the nature of the metal center and the charge on the complex rather than by the σ- or π-donating capabilities of the supporting ligands.

In order to understand the factors which may determine the extent and sense of the deviation from linearity in these dinitrosyls, we draw on recent theoretical interpretations of the electronic structure of nitric oxide complexes, especially that of Enemark and Feltham.[3] They treat the $\{M(NO)_2\}$ moiety as a covalently bound functional group perturbed by the coordination of two additional ligands. For the pseudotetrahedral (C_{2v}) complexes with the N–M–N fixed at 90°, their derived electronic configuration is $(1a_2)^2(1a_1)^2(2a_1)^2$-$(1b_2)^2(1b_1)^2$. There is a low-lying orbital LUMO also of b_1 symmetry which is orthogonal to $1b_1$ only for N–M–N = 90°. Since the observed values of this angle lie in the range 110–158°, these two levels in practice interact strongly and so give rise to a parentage for the $1b_1$ HOMO which can vary from being predominantly d(metal) to mainly π^*(nitric oxide). Enemark and Feltham's MO scheme leads to the following conclusions.

(a) If d_{xz} is much lower than $\pi^*_{b_1}(NO)$, then nearly tetrahedral geometry will be expected with perhaps some slight bending of the M–N–O groups so as to move the two O atoms closer together (i.e., the attracto conformer) because of the respective contributions of $\pi^*_{a_1}(NO)$ and $\pi^*_{b_2}(NO)$ to the $1a_1$ and $1b_2$ molecular orbitals (see Figure 5). Geniculation of the two NO groups to yield the attracto conformer should be favored by 3d metals and good π-accepting ligands.

(b) If $\pi^*_{b_1}(NO)$ is much lower than d_{xz}, the repulso conformer is favored, since $\pi^*_{b_1}(NO)$ is antibonding with respect to the two N atoms and antibonding with respect to the two O atoms (see Figure 5). Thus the population of this orbital in the ground state should favor increases in the N–M–N angle and geniculation of the nitrosyl group in the sense that the angle O–M–O becomes greater than N–M–N. This conformer should be favored by 4d and 5d transition metals and ligands which are poor π acceptors.

The excellent correlation (Figure 4) between N–M–N and O–M–O angles is in harmony with these expectations although the near linearity is possibly fortuitous since the available structural data on dinitrosyl complexes are not extensive.

While this qualitative explanation for the sense in which the *cis*-dinitrosyls are geniculated is satisfying in terms of the relative energy and parentage of the $1b_1$ HOMO level, more quantitative arguments are difficult to formulate. This arises because under the pseudotetrahedral symmetry, not only can all five metal d orbitals interact with both the σ and π orbitals of the ligands but also the x^2, xy, and $z^2 - y^2$ and the nitrosyl π^* levels are likely to be juxtaposed in energy. A variety of level-ordering schemes becomes possible, and whether the $\{M(NO)_2\}$[10] functional group is geniculated or not, and in which sense, becomes especially sensitive to the nature of the
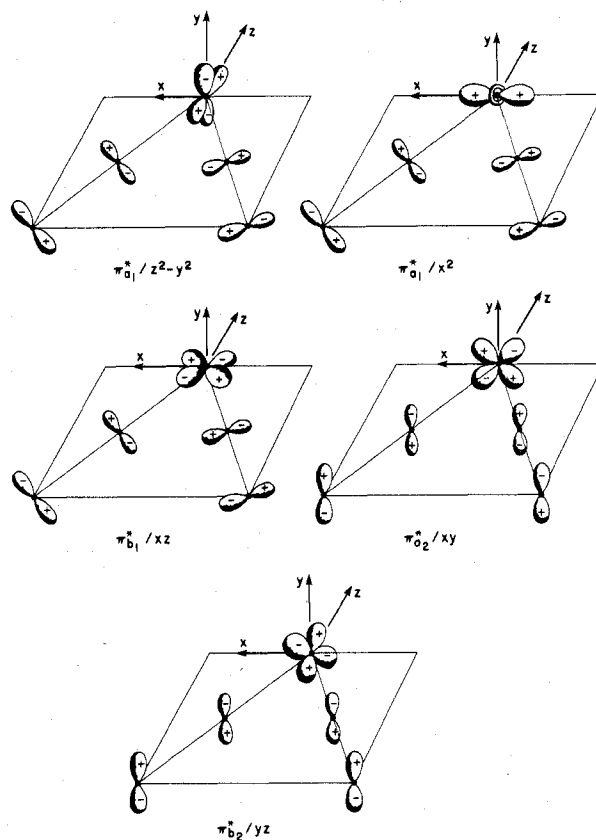

Figure 5. The ligand localized molecular orbitals in C_{2v} symmetry derived from the $\pi^*(NO)$ orbitals of two nitrosyl ligands. The interacting metal d orbitals are obtained from the conventional d orbitals by the transformation $x \to z, y \to z, z \to x$.

metal center M and probably less so to the electronic and steric character of the other supporting ligands. These expectations are reflected in Figure 4.

This explanation ascribes the origin of the geniculation wholly to the interaction of the d orbitals of the metal with the π^* orbitals of coordinated nitric oxide. At the same time, distortions of the ML_2N_2 core from tetrahedral symmetry must also reflect changing parentage of σ orbitals at the metal center. In particular, the d_{xz} orbital (Figure 5) is oriented appropriately for favorable overlap with σ orbitals of nitric oxide. If d_{xz} is much lower than $\pi^*_{b_1}(NO)$, a geometry closer to tetrahedral is anticipated; if $\pi^*_{b_1}(NO)$ is much lower than d_{xz}, the N–M–N angle expands toward 180° so that the geometry may be related to a distorted trigonal bipyramid with one sterically active lone pair of electrons lying in the yz plane. Although the magnitude and sense of geniculation of the coordinated nitric oxide cannot be rationalized quantitatively with such a scheme, the increase of N–M–N angle is consistent with the NO^+–NO^- dichotomy and increasing repulsions between bonding electrons in M–π^* bonds along the series (Co, Fe), Co^+, (Ru, Os).

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Stereochemistry of Bis(1,4-difluorobenzene)vanadium(0)[1]

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Bis(1,4-difluorobenzene)vanadium(0) crystallizes with four molecules in a unit cell having $I2/c$ symmetry and lattice constants of a = 13.850 (6), b = 7.104 (3), c = 11.192 (4) Å, and β = 109.11 (2)°. The structure was determined from 1378 observed diffractometer data in the range $(\sin\theta)/\lambda \leq 0.707$ Å^{-1}. The molecular structure consists of a vanadium atom "sandwiched" between two 1,4-difluorobenzene ligands in a dissymmetric arrangement approximating D_2 molecular symmetry. Planes of the two ligands are parallel and the carbon atoms from the two ligands are approximately eclipsed while the dihedral angle between fluorine atoms in opposite rings is 53°. A small "boat" deformation is observed for the 1,4-difluorobenzene ligand, the fluorine-substituted carbon atoms being displaced 0.06 Å from the mean plane of the ligand. The vanadium atom is 1.67 Å from this plane and V–C bond distances are 2.187 (3) and 2.204 (2) Å.

Since the discovery of ferrocene[2] in 1951, the study of transition metal "sandwich" compounds has been an active area of chemical research. Although the synthesis of the first arene "sandwich" compound, bis(benzene)chromium, was reported[3] in 1955, the structural characterization of this compound led to a controversy concerning the equivalence of the carbon–carbon bond lengths which lasted several years.[4] With the exception of bis(benzene)chromium, however, accurate structural parameters for bis(arene) complexes of the first-row transition metals are nonexistent and little is known about the structural effects of substitutent groups in these compounds. The bulk of available structural parameters deal with the arene tricarbonyl compounds which were originally studied by Bailey and Dahl[5] because they provide the advantage of localizing the hexacoordinate arrangement of metal orbitals, compared to the disordered possibility in the bis(arenes), and thus simplify the interpretation of the bonding. While similarities certainly exist between these two types of compounds, there are also substantial differences between them. Bailey and Dahl observed that the attachment of three strongly bonding CO groups significantly weakens the chromium to arene bonds as evidenced by an increase in the chromium–ring distances of ~0.1 Å[4] over the value in (C₆H₆)₂Cr. More recent ¹⁹F NMR studies by Fletcher and McGlinchey[6] have also provided evidence that the electronic environment in substituted arenechromium tricarbonyls is considerably different from that of the corresponding bis(arene) complexes.

Recent developments in synthetic techniques[7-9] have now made it possible to prepare a variety of substituted bis(arene) complexes for a few of the transition metals. We have initiated a program to learn more about the effects of substitutent groups on the stereochemistry and bonding involved in bis(arene) systems. The present study deals with the solid-state structure of bis(1,4-difluorobenzene)vanadium(0).

Experimental Section

The compound was prepared as described previously[9] and dark amber crystals were obtained by sublimation. In order to check for air sensitivity, several crystals were mounted in thin-walled glass capillaries under argon and several were mounted under atmospheric conditions. The crystals were unaffected by brief air exposure. The crystal selected for data collection was cut from a larger crystal, under atmospheric conditions, to the approximate dimensions 0.40 mm × 0.32 mm × 0.47 mm and was secured in the capillary with a small amount of petroleum jelly.

Photographic examination with Cu Kα radiation led to an *I*-centered monclinic cell, chosen for the convenience of the β angle, having systematic absences consistent with a *c*-glide plane ($h0l$, $l = 2n + 1$) thus limiting the possible choices of space groups to $I2/c$ or Ic. Final lattice constants were determined on our Picker automatic diffractometer using Mo Kα₁ radiation (λ 0.7093 Å) from the least-squares refinement[10] of the setting angles of 20 carefully centered reflections. The resulting lattice constants are a = 13.850 (6), b =