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Stereochemical Control of Valence. IV. Comparison of the Structures and Chemical Reactivities of Five- and Six-Coordinate Diarsine Complexes of the $\{CoNO\}^8$ Group

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Received July 31, 1974 AIC406984

Compounds of the type $Co(NO)(das)_2X_2$ (where das is *o*-phenylenebis(dimethylarsine), $C_6H_4[As(CH_3)_2]_2$, and X is a monoanion) exhibit markedly different coordination geometries and chemical behavior. The structures of $Co(NO)(das)_2(ClO_4)_2$ (**1**) and $Co(NO)(das)_2(NCS)_2$ (**2**) have been determined from single-crystal X-ray diffraction data obtained by counter methods. Compound **1** crystallizes in space group D_2^3-$P2_12_12_1$ with four molecules in a cell of dimensions $a = 12.565$ (9), $b = 12.639$ (9), and $c = 19.491$ (13) Å. The calculated and observed densities are 1.845 and 1.84 (1) g cm^{-3}, respectively. Compound **2** crystallizes in space group C_{2h}^3-$C2/m$ with four molecules in a cell of dimensions $a = 20.48$ (2), $b = 10.22$ (2), $c = 14.75$ (3) Å, and $\cos \beta = 0.2972$ (12). The observed and calculated densities are 1.725 and 1.72 g cm^{-3}, respectively. Full-matrix least-squares refinements of both structures using the data having $F_o^2 > 3\sigma(F_o^2)$ gave $R = 0.054$ for 1788 data for **1** and $R = 0.059$ for 1157 data for **2**. Structure **1** consists of $[Co(NO)(das)_2]^{2+}$ cations and uncoordinated ClO_4^- anions. The coordination geometry about the five-coordinate Co atom is approximately trigonal bipyramidal with the NO group occupying an equatorial position. The Co–N–O angle is 178 (2)° and the Co–N distance is 1.68 (3) Å. Structure **2** contains $[Co(NO)(das)_2NCS]^+$ cations and NCS^- anions. The six-coordinate cation is required to possess *m* symmetry by the space group. The NO and NCS ligands are trans to one another with Co–NO = 1.87 (1) Å and Co–NCS = 2.13 (1) Å. The Co–N–O angle is 132 (1)°. Analogs of **2** result from the addition of X^- (X = Cl, Br, I) to **1**. The $[Co(NO)(das)_2Br]^+$ cation reacts with protons in methanol to form $[Co(das)_2(HNO)Br]^{2+}$. Compound **1** is unreactive to $HClO_4$, but **1** does react with HBr to generate the $[Co(das)_2(HNO)Br]^{2+}$ ion *via* the $[Co(NO)(das)_2Br]^+$ intermediate. The pmr spectra of **1** are solvent and temperature dependent.

Introduction

The ability to modify specifically the structure and/or chemical reactivity of a coordinated group is an important feature of transition metal catalysts. Metal nitrosyl complexes should be excellent probes for studying the significant factors in the control of the structure and chemical reactivity of groups bound to transition metals because it is well established that mononitrosyl complexes of transition metals exhibit structures with MNO angles ranging from ~120 to 180°.[1] However, in spite of the voluminous literature in metal nitrosyl chemistry there has been no definitive example of the interconversion of linear and strongly bent nitrosyl groups, and the differences in the chemical reactivities of coordinated nitrosyl groups in these two limiting geometries has not been clearly demonstrated.

We have previously shown[1b,2-4] that the structures of mononitrosyl complexes can be understood by considering the behavior of the $\{MNO\}^n$ triatomic group[5] in ligand fields. This paper describes detailed studies of $\{CoNO\}^8$ complexes of the type $Co(NO)(das)_2X_2$ (where das is *o*-phenylenebis(dimethylarsine)) and presents the first definite evidence for the conversion of a linear MNO group into a strongly bent MNO group by a simple chemical reaction. It is further shown that both the *geometry* and *chemical reactivity* of the coordinated nitrosyl ligand are determined by the stereochemistry of the other ligands attached to the metal. The dynamics of the transformations of these $\{CoNO\}^8$ complexes have been explored by temperature-dependent pmr spectroscopy. A preliminary account of portions of this work has previously appeared.[6]

Experimental Section

Reagents. A dilute solution of hydrobromic acid in methanol, standardized by titration with NaOH, was used as the source of HBr. All operations were performed under electronic grade nitrogen using standard inert-atmosphere techniques.[7]

Compounds. $[Co(NO)(das)_2][ClO_4]_2$ and $Co(NO)(das)_2XY$ (where X and Y are monoanions) were prepared as previously described.[8]

$[Co(HNO)(das)_2Br][ClO_4]_2$. A slurry of 0.27 g (0.30 mmol) of $[Co(NO)(das)_2][ClO_4]_2$ in 25 ml of methanol was combined with 0.35 mmol of HBr in methanol. The mixture was stirred for 24 hr, and the resulting brown solid was isolated by filtration. After recrystallization by dissolving in dichloromethane, filtering, and adding diethyl ether, the dark brown crystals were removed by filtration, washed with diethyl ether, and dried *in vacuo*; ν_{NO} 1560 cm^{-1}. *Anal.* Calcd for $C_{20}H_{33}As_4BrCl_2CoNO_9$: C, 25.5; H, 3.5; N, 1.5. Found: C, 27.88; H, 3.73; N, 1.13.

Measurements. Infrared spectra were obtained on a Beckman IR-12 spectrophotometer. The samples were obtained as Nujol mulls and KBr pellets. Electronic absorption spectra were recorded in matched 1.0-cm cells on a Cary Model 14 spectrophotometer. Pmr spectra were obtained in DMSO-d_6, CD_3CN, and CD_2Cl_2 on Varian T-60 and HA-100 spectrometers. Photoelectron spectra were recorded on a McPherson ESCA-36 photoelectron spectrometer using Mg Kα radiation.

X-Ray Structure Determination. $[Co(NO)(das)_2][ClO_4]_2$. Red-orange single crystals were grown from methanol by evaporation. Preliminary precession photographs (Mo Kα) on a multifaceted crystal of approximate dimensions 0.1 × 0.1 × 0.1 mm showed *mmm* diffraction symmetry with conditions $h00$ ($h = 2n$), $0k0$ ($k = 2n$), and $00l$ ($l = 2n$). These conditions are consistent with the acentric orthorhombic space group D_2^3-$P2_12_12_1$. Cell parameters were obtained using Cu Kα (λ 1.54178 Å) radiation and a Picker FACS-I four-circle diffractometer. A least-squares refinement of the setting angles for eight reflections located in diverse regions of reciprocal space and having $2\theta \approx 25°$ gave $a = 12.565$ (9), $b = 12.639$ (9), and $c = 19.491$ (13) Å. The observed density of 1.84 (1) g cm^{-3}, determined by gradient technique in tetrabromethane–chloroform, agrees with the calculated density of 1.845 g cm^{-3} for four molecules per cell.

Data were collected by the θ–2θ scan technique using an incident beam monochromator to obtain Mo Kα radiation. The takeoff angle was 1.7°. The scan range was from $2\theta_{MoK\alpha_1} - 0.6°$ to $2\theta_{MoK\alpha_2} + 0.6°$. The scan rate was 1°/min, and the scintillation counter was 23 cm from the crystal with an aperature of 4 × 4 mm. The pulse height analyzer was set to admit ~90% of the Mo Kα peak. The intensities of three reflections in diverse regions of reciprocal space were monitored after every 50 reflections. None of these standards showed any systematic variation in intensity with time. The maximum variation of any standard from its mean value was ≤4%. A total of 2823 space group allowed reflections with $2\theta \leq 40°$ were recorded for the forms hkl and $\bar{h}\bar{k}\bar{l}$. The data were reduced to F^2 and $\sigma(F^2)$ by procedures similar to those previously described.[9,10] A value of 0.04 was assigned to p in the expression for $\sigma(F^2)$.[9]

The linear absorption coefficient for Mo Kα radiation is 52.6 cm^{-1}; however, sample absorption calculations[10] showed that for this crystal all transmission coefficients ranged within 0.58–0.62. Therefore, no absorption correction was made. Secondary extinction is not a problem in this crystal and no extinction correction was made.

The structure was solved by direct methods using the MULTAN package[10] and the 202 reflections with $|E| \geq 1.50$. An E map based

Table I. Final Atomic and Group Parameters for $[Co(NO)(das)_2][ClO_4]_2$

Atom[a]	x	y	z	$10^3\beta_{11}$	$10^3\beta_{22}$	$10^3\beta_{33}$	$10^3\beta_{12}$	$10^3\beta_{13}$	$10^3\beta_{23}$
Co	.7370(3)	.4151(3)	.6765(2)	5.6(3)	4.5(3)	2.05(9)	0.8(2)	-0.1(1)	0.0(1)
As1	.7965(2)	.5293(2)	.5914(1)	7.1(3)	5.4(2)	2.24(9)	1.1(2)	0.5(1)	0.5(1)
As2	.7304(2)	.2682(2)	.6035(1)	5.7(2)	6.4(2)	2.53(9)	-0.2(2)	-0.3(1)	-0.8(1)
As3	.6876(2)	.2997(2)	.7641(1)	6.6(2)	5.2(2)	2.25(9)	0.0(2)	0.2(1)	0.2(1)
As4	.9170(2)	.4058(2)	.7099(1)	5.4(2)	4.7(2)	2.88(9)	0.3(2)	-0.7(1)	0.2(1)
N	.635(2)	.496(2)	.6931(9)	8(2)	5(2)	1.5(6)	-2(2)	-1(1)	1.3(9)
O1	.562(2)	.551(2)	.705(1)	9(2)	14(2)	7(1)	9(2)	1(1)	2(1)
C1	.540(2)	.319(2)	.795(1)	6(2)	10(3)	3.3(9)	1(2)	2(1)	3(1)
C2	.769(3)	.678(2)	.610(1)	15(3)	4(2)	4(1)	4(2)	-1(2)	0(1)
C3	.983(2)	.264(2)	.726(1)	13(3)	4(2)	4(1)	5(2)	0(2)	1(1)
C4	.850(2)	.235(2)	.541(1)	8(2)	11(3)	3.0(9)	0(2)	3(1)	-1(1)
C5	.748(2)	.512(2)	.495(1)	13(3)	10(3)	3.1(9)	2(2)	1(2)	3(1)
C6	.603(2)	.251(2)	.540(1)	6(2)	12(3)	3.7(9)	4(2)	-4(1)	-2(1)
C7	.765(2)	.300(2)	.851(1)	10(3)	9(3)	2.1(8)	-1(2)	-1(1)	2(1)
C8	.970(3)	.488(2)	.788(1)	13(3)	11(3)	2.6(9)	1(2)	0(2)	0(1)
Cl 1	.7073(7)	.6707(6)	.8402(4)	12.4(9)	7.6(7)	4.0(3)	0.2(6)	0.7(4)	0.4(3)
Cl 2	.5452(5)	.1172(5)	-.0090(4)	6.7(7)	8.0(7)	4.2(3)	-0.5(5)	0.1(4)	-0.1(4)

Group[a]	x_c	y_c	z_c	δ	ε	η	B_1	B_2	B_3	B_4	B_5	B_6
R1	.7041(7)	.0572(8)	.7057(5)	.270(16)	-2.262(9)	1.922(15)	2.8(5)	3.2(5)	4.2(6)	5.2(6)	4.7(6)	5.6(7)
R2	1.0599(10)	.5096(8)	.5821(5)	-3.212(20)	-2.176(9)	-3.112(20)	4.3(6)	4.1(6)	5.4(7)	5.8(7)	6.3(8)	5.3(7)
ClO_4-1	.7119(11)	.6753(9)	.8393(6)	-.609(13)	-2.733(10)	1.701(12)	11.3(4)[b]					
ClO_4-2a[c]	.546(2)	.118(2)	-.006(1)	.31(3)	-2.47(2)	3.13(3)	10.5(6)					
ClO_4-2b[c]	.545(3)	.121(2)	-.010(1)	1.69(5)	2.19(3)	-2.11(5)	10.5					

[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 deviation of the least significant figure is given in parentheses. x_c, y_c, and z_c are the fractional coordinates of the center of the group. The angles δ, ε, and η (in radians) bring about alignment except for translation of an internal coordinate system within the group with a fixed external coordinate system.[14] B_i is the isotropic thermal parameter (in Å^2) of atom i in the group. [b] Group thermal parameter for all four O atoms of a perchlorate anion. [c] ClO_4-2a and ClO_4-2b are the two orientations for the disordered perchlorate anion. The occupancy factor for ClO_4-2a is *0.56 (2)*. The group thermal parameters for these two orientations were constrained to be identical.

upon these reflections clearly revealed the four As atoms and the Co atom. A series of structure factor calculations, least-squares refinements and electron-density difference maps revealed all the non-hydrogen atoms of the formula unit.

Refinement of the complete structure was based upon F_o with $\sum w(|F_o| - |F_c|)^2$ being minimized; the weights were taken as $4F_o^2/\sigma^2(F_o^2)$. Atomic scattering factors for Co, As, and Cl were from Cromer and Waber;[12] the factors for C, N, and O were from the usual tabulation.[13] Two cycles of anisotropic refinement in which the Co, As, and Cl atoms were refined anisotropically and phenyl rings and perchlorate anions were treated as rigid groups[14] gave $R_1 = \sum||F_o| - |F_c||/\sum F_o = 0.061$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0.070$ for 1191 reflections with $F_o^2 \geq 3\sigma(F_o^2)$. However, the temperature factor for one of the perchlorate groups was 25 Å, suggesting that the group was disordered. A second orientation for the perchlorate was discerned from a difference electron density map based on the above model. Two additional cycles of full-matrix least-squares refinement assumed (1) anisotropic thermal motion for the Co, As, and Cl atoms, (2) isotropic thermal motion for methyl C atoms, (3) rigid-group behavior for the phenyl rings (D_{6h}-$6mmm$ symmetry, C–C = 1.392 Å) with a single isotropic thermal parameter, and (4) rigid-group behavior for the perchlorate oxygen atoms (T_d-$\bar{4}3m$ symmetry, Cl–O = 1.42 Å) with a variable occupancy factor for the disordered group. This refinement gave values which were essentially identical with the previous values for R_1 and R_2. The occupancy factor for the disordered ClO_4^- anion was 0.64 (2), and the thermal parameters for the O atoms of the ordered and disordered groups were 12 and 13 Å^2, respectively.

If the effects of anomalous dispersion are included, then $|F_{hkl}| \neq |F_{\bar{h}\bar{k}\bar{l}}|$ in space group $P2_12_12_1$. The correct enantiomer for the structure was established by including the effects of anomalous dispersion[15,16] for Co, As, and Cl and carrying out two additional cycles of refinement with anisotropic thermal parameters assumed for all nongroup atoms and individual isotropic thermal parameters for the C atoms of the phenyl rings (199 variable parameters). Both hkl and $\bar{h}\bar{k}\bar{l}$ data were used in these calculations. The enantiomer which had been arbitrarily selected by the choice of phases in the initial direct-methods solution converged to $R_1 = 0.059$ and $R_2 = 0.067$ for the 1789 unique data having $F_o^2 \geq 3\sigma(F_o^2)$. The alternative enantiomer converged to $R_1 = 0.054$ and $R_2 = 0.061$ and was concluded to be the correct conformation. No hydrogen atoms could be located in the difference electron density map calculated from the final structure factors for the correct enantiomer. The largest peak in this map (1 e/Å^3) could be assigned to a residual of one of the O atoms of a ClO_4^- anion. The standard deviation of an observation of unit weight was 1.22. An analysis of the weighting scheme showed that $w(\Delta F)^2$ was not a function of $|F_o|$ or $(\sin\theta)/\lambda$. Final structural parameters appear in Table I, and Table II shows the derived fractional coordinates for the group atoms. A list of $10|F_o|$ and $10|F_c|$ is available.[17]

[Co(NO)(das)$_2$NCS][NCS]. A red-brown plate of approximate dimensions 0.75 × 0.20 × 0.05 mm was selected from the bulk sample and mounted parallel to the long axis of the crystal. Preliminary photographs (Cu Kα) indicated that the crystals were monoclinic with diffraction condition hkl ($h + k = 2n$). These conditions are consistent with space groups C_2^3-$C2$, C_s^3-Cm, and C_{2h}^3-$C2/m$. Cell parameters were obtained from a least-squares refinement of the setting angles of 10 reflections that had been centered automatically on a Picker FACS-I diffractometer using Mo Kα radiation (λ 0.71069 Å). These reflections had 2θ values ranging from 18 to 27° and gave $a = 20.48$ (2), $b = 10.22$ (2), $c = 14.75$ (3) Å, and $\cos\beta = -0.2972$ (12). The calculated density of 1.725 g cm^{-3} for four formula weights per cell agrees well with the observed density of 1.72 g cm^{-3}.

Data were collected using Mo Kα radiation as described for $Co(NO)(das)_2(ClO_4)_2$, with the following modifications: takeoff angle of 2.0°; scan range of $2\theta_{MoK\alpha_1} - 0.8°$ to $2\theta_{MoK\alpha_2} + 0.8°$; open scintillation counter aperature. None of the three standard reflections

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

Group[a]	Atom	*x*	*y*	*z*
R1	C1	0.719 (1)	0.144 (1)	0.6630 (7)
	C2	0.695 (1)	0.1592 (9)	0.7320 (7)
	C3	0.680 (1)	0.0724 (9)	0.7747 (5)
	C4	0.689 (1)	−0.030 (1)	0.7485 (8)
	C5	0.713 (1)	−0.0448 (9)	0.6795 (8)
	C6	0.728 (1)	0.042 (1)	0.6367 (6)
R2	C1	0.950 (1)	0.520 (1)	0.5832 (9)
	C2	1.001 (1)	0.461 (1)	0.6335 (7)
	C3	1.111 (1)	0.450 (1)	0.6323 (8)
	C4	1.170 (1)	0.499 (2)	0.581 (1)
	C5	1.119 (2)	0.559 (1)	0.5307 (8)
	C6	1.009 (2)	0.569 (1)	0.5318 (7)
ClO_4-1	O1	0.749 (2)	0.703 (1)	0.7731 (7)
	O2	0.616 (1)	0.731 (1)	0.853 (1)
	O3	0.789 (1)	0.703 (2)	0.8891 (9)
	O4	0.693 (2)	0.565 (1)	0.842 (2)
ClO_4-2a[b]	O1	0.653 (2)	0.153 (3)	−0.007 (2)
	O2	0.543 (3)	0.007 (2)	−0.016 (2)
	O3	0.489 (3)	0.169 (3)	−0.060 (1)
	O4	0.500 (3)	0.144 (3)	0.058 (1)
ClO_4-2b[b]	O1	0.461 (3)	0.169 (4)	0.027 (2)
	O2	0.607 (4)	0.200 (3)	−0.042 (2)
	O3	0.504 (4)	0.051 (4)	0.060 (2)
	O4	0.610 (4)	0.063 (4)	0.037 (2)

[a] The estimated standard deviations are derived from those of the group parameters and are meant to be used in error analysis on inter-ring distances. The intra-ring C–C is 1.392 Å. The Cl–O distance is 1.42 Å. [b] One of the orientations of the disordered perchlorate.

showed any systematic variation in intensity during data collection. The maximum variation of any standard from its mean value was ≤5%. A total of 1484 unique data with $2\theta \leq 40°$ were obtained, of which 1157 had $F_o^2 \geq 3\sigma(F_o^2)$.

The positions of the Co and As atoms were readily determined from a three-dimensional Patterson function. A sequence of structure factor calculations (assuming space group $C2/m$) followed by difference electron density maps revealed the positions of the remaining nonhydrogen atoms. Two cycles of full-matrix least-squares refinement of the nonhydrogen atoms gave $R_1 = 0.122$ and $R_2 = 0.157$ for the data with $F_o^2 \geq 3\sigma(F_o^2)$. The refinement was based upon F_o as described above using the same scattering factors plus those for S.[12]

The morphology of the crystal results in transmission coefficients ranging from 0.40 to 0.76 for $\mu = 54.6$ cm^{-1}. The plate face of the crystal was identified as {001}. Other faces included {20$\bar{1}$}, {$\bar{1}\bar{1}$2}, and ($\bar{2}$02). The crystal was carefully measured and the data were corrected for absorption.[10]

Refinement was continued assuming anisotropic thermal parameters for all atoms. Two cycles gave $R_1 = 0.059$ and $R_2 = 0.099$. A difference electron density map had no peak greater than 0.75 e/Å^3 and revealed reasonable positions for several H atoms, further substantiating the choice of the space group as $C2/m$. Positions were calculated for the remaining H atoms and all H atoms were included as fixed contributions in subsequent calculations.[18] A structure factor calculation on all 1484 reflections gave $R_1 = 0.091$ and $R_2 = 0.093$, and no data with $F_o^2 < \sigma(F_o^2)$ had $|F_c| \geq |3\sigma(F_o)|$. At this point it was discovered that the As atoms had been erroneously assigned Co scattering factors. Two final cycles of least-squares refinement (163 variables) with correct scattering factors assigned to all atoms gave $R_1 = 0.038$ and $R_2 = 0.053$. The standard deviation of an observation of unit weight was 1.72. An analysis of the weighting scheme as a function of $(\sin\theta)/\lambda$ and $|F_o|$ showed that the weak reflections were slightly overweighted. A table of $10|F_o|$ and $10|F_c|$ is available.[17] The final structural parameters appear in Table III.

Results

Description of the Structures. Figure 1 shows the coordination geometry of the $Co(NO)(das)_2^{2+}$ ion (**1**) and Figure 2 shows the $Co(NO)(das)_2(NCS)^+$ ion (**2**). Important distances and angles are shown in these figures and in Tables IV–VI. The coordination geometry about the Co atom in compound **1** is best described as trigonal bipyramidal with the NO group occupying an equatorial position. No symmetry is imposed upon the cation by the space group. Cation **2** exhibits trans six-coordinate geometry about the Co atom. The ion is required to possess m-C_s symmetry by the space group. The mirror plane contains the Co atom and the NO and NCS ligands and bisects each of the das ligands.

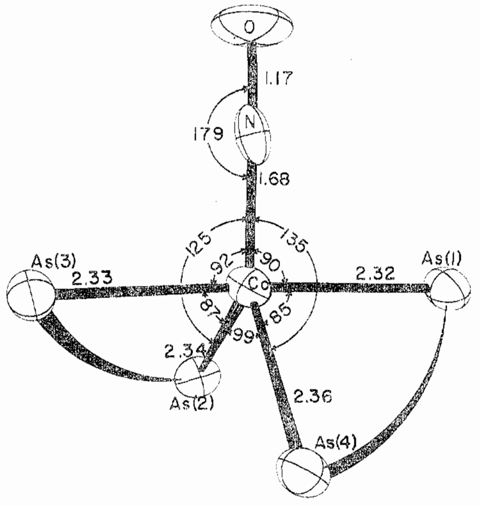


Figure 1. View of the coordination sphere of the $[Co(NO)(das)_2]^{2+}$ cation. Hydrogen atoms have been omitted for clarity.

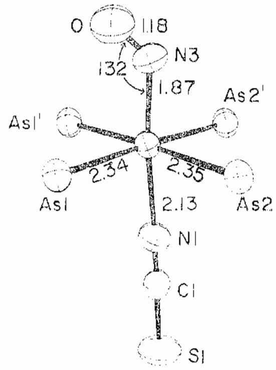


Figure 2. The coordination sphere of the $[Co(NO)(das)_2(NCS)]^+$ ion. Primed atoms are related to unprimed atoms by a mirror plane in the plane of the paper. The chelate rings join As1 with As1′ and As2 with As2′.

The geometries of the CoNO group are strikingly different for the two compounds. Compound **1** (Figure 1) has a Co–N–O angle of 178 (2)° and a Co–N distance of 1.68 (3) Å. This is the shortest distance observed to date for a five-coordinate complex containing the $\{CoNO\}^8$ group.[1] Compound **2** (Figure 2) exhibits a Co–N–O angle of 132 (1)° and a Co–NO distance of 1.85 (1) Å. This distance is not significantly different from that in the isoelectronic six-coordinate complexes $[Co(NH_3)_5(NO)]^{2+}$,[19] $[Co(en)_2(NO)Cl]^+$,[20] and $[Co(en)_2(NO)(ClO_4)]^+$.[21] The Co–N–O angles in the latter compounds range from 119 to 124°.

The Co–N1 distance of 2.12 (1) Å in **2** is significantly longer than the Co–N distance of 1.98 (1) Å found for a five-coordinate isothiocyanato complex of Co(II).[22] There appear to be no previous determinations of the Co–N distance for a six-coordinate isothiocyanato complex. A substantial lengthening of the bond trans to a strongly bent nitrosyl group has also been observed in other six-coordinate cobalt complexes.[19-21]

The Co–As distances are similar for the five-coordinate complex **1** and the six-coordinate complex **2**. In **1** the mean distances are Co–As$_{eq}$ = 2.327 (3) Å and Co–As$_{ax}$ = 2.348 (3) Å. The average Co–As distance in **2** is 2.343 Å. These distances also agree with Co–As distances found for other das complexes of cobalt.[23,24]

Table III. Final Atomic Parameters for $[CoNO(das)_2(NCS)][NCS]$

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	0.10666(8)	0	0.24849(12)	14.8(5)	84(2)	34(1)	0	7.7(6)	0
As1	0.01928(4)	0.1557(1)	0.21935(6)	16.3(3)	87(1)	44.3(7)	0.7(5)	8.4(3)	-3.8(7)
As2	0.19429(4)	0.1572(1)	0.28557(7)	16.6(3)	91(1)	45.4(7)	-1.3(5)	9.2(3)	-2.0(7)
S1	0.1280(2)	0	0.5889(3)	50(2)	130(6)	41(3)	0	20(2)	0
S2	0.3583(2)	0	0.1507(4)	36(2)	129(6)	96(4)	0	25(2)	0
N1	0.1180(6)	0	0.3959(9)	26(4)	124(17)	42(9)	0	14(5)	0
N2	0.3718(8)	0	-0.031(1)	24(5)	163(22)	109(14)	0	13(7)	0
N3	0.1058(6)	0	0.1224(9)	26(4)	150(19)	32(8)	0	6(5)	0
C1	0.1219(6)	0	0.475(1)	18(4)	69(18)	47(11)	0	6(6)	0
C2	0.3655(8)	0	0.042(2)	15(4)	90(21)	124(18)	0	7(8)	0
C3	0.0000(5)	0.235(1)	0.3263(7)	23(3)	153(16)	63(7)	3(6)	9(4)	-31(10)
C4	0.0239(5)	0.303(1)	0.1387(8)	20(3)	135(17)	89(9)	9(6)	7(4)	31(10)
C5	0.1905(5)	0.301(1)	0.3689(8)	28(3)	133(17)	83(8)	3(7)	23(4)	-29(10)
C6	0.2196(5)	0.246(1)	0.1852(7)	26(3)	150(16)	65(7)	1(6)	16(4)	34(9)
O	0.0676(7)	0	0.061(1)	41(5)	801(60)	43(10)	0	16(6)	0
R1C1	-0.0658(4)	0.0651(9)	0.1555(6)	15(3)	95(12)	36(5)	1(4)	3(3)	-2(7)
R1C2	-0.1258(5)	0.138(1)	0.1113(7)	22(3)	113(15)	53(7)	6(6)	10(4)	-6(8)
R1C3	-0.1846(4)	0.0681(9)	0.0661(6)	14(3)	123(13)	46(6)	-1(5)	5(3)	-7(7)
R2C1	0.2781(4)	0.0662(9)	0.3541(6)	17(3)	116(13)	35(6)	-5(5)	13(3)	-13(7)
R2C2	0.3382(5)	0.137(1)	0.3977(7)	17(3)	109(14)	61(7)	-10(6)	10(4)	-22(8)
R2C3	0.3974(5)	0.067(1)	0.4427(7)	22(3)	194(18)	47(7)	-9(6)	10(4)	-14(8)

Table IV. Selected Interatomic Distances (Å) and Angles (deg) in $[Co(NO)(das)_2][ClO_4]_2$

Distances

N-O	1.16 (2)	As1-C2	1.95 (2)
Co-N	1.68 (3)	As2-C6	2.03 (2)
Co-As1	2.322 (4)	As2-C4	1.98 (2)
Co-As2	2.340 (4)	As3-C1	1.96 (2)
Co-As3	2.331 (4)	As3-C7	1.96 (2)
Co-As4	2.357 (4)	As4-C8	1.95 (3)
As1-As4	3.171 (4)	As4-C3	1.99 (2)
As2-As3	3.202 (4)	As1-R2C1	1.94 (1)
As1-As2	3.411 (4)	As2-R1C1	1.96 (1)
As2-As4	3.581 (4)	As3-R1C2	1.89 (1)
As3-As4	3.350 (4)	As4-R2C2	1.96 (1)
As1-C5	1.99 (3)		

Angles

Co-N-O	178 (2)	Co-As3-C7	120.2 (8)
As1-Co-N	90.3 (6)	Co-As4-C8	120.8 (9)
As2-Co-N	125.2 (7)	Co-As4-C3	119.0 (8)
As3-Co-N	92.1 (6)	C5-As1-C2	103 (1)
As4-Co-N	135.5 (7)	C6-As2-C4	101.7 (9)
As1-Co-As4	85.3 (1)	C1-As3-C7	102 (1)
As2-Co-As3	86.6 (2)	C8-As4-C3	102 (1)
As1-Co-As2	94.0 (2)	Co-As1-R2C1	110 (1)
As1-Co-As3	176.6 (2)	Co-As2-R1C1	106 (1)
As2-Co-As4	99.3 (2)	Co-As3-R1C2	109 (1)
As3-Co-As4	91.2 (1)	Co-As4-R2C2	108 (1)
Co-As1-C5	120.6 (8)	As1-R2C1-R2C2	116 (1)
Co-As1-C2	114.0 (9)	As2-R1C1-R1C2	119 (1)
Co-As2-C6	118.7 (7)	As3-R1C2-R1C1	117 (1)
Co-As2-C4	121.0 (8)	As4-R2C2-R2C1	118 (1)
Co-As3-C1	113.4 (7)		

Table V. Selected Interatomic Angles in $[Co(NO)(das)_2(NCS)][NCS]$

Atoms	Angle, deg	Atoms	Angle, deg
Co-N3-O	132.3 (14)	Co-As2-R2C1	106.7 (3)
Co-N1-C1	177.8 (12)	C5-As2-C6	101.8 (5)
N1-C1-S1	179.7 (13)	As1-R1C1-R1C1′	118.3 (3)
N1-Co-N3	174.5 (5)	As1-R1C1-R1C2	120.0 (7)
As1-Co-As2	93.9 (1)	R1C1′-R1C1-R1C2	121.7 (5)
As1-Co-As1′	85.8 (1)	R1C1-R1C2-R1C3	117.3 (9)
As2-Co-As2′	86.3 (1)	R1C2-R1C3-R1C3′	121.0 (6)
N1-Co-As1	91.9 (2)	As2-R2C1-R2C1′	118.5 (3)
N1-Co-As2	85.3 (2)	As2-R2C1-R2C2	120.4 (7)
N3-Co-As1	92.1 (3)	R2C1′-R2C1-R2C2	121.0 (6)
N3-Co-As2	90.7 (3)	R2C1-R2C2-R2C3	118.0 (9)
Co-As1-C3	118.1 (3)	R2C2-R2C3-R2C3′	120.9 (6)
Co-As1-C4	117.8 (3)	C3-As1-R1C1	103.0 (4)
Co-As1-R1C1	106.9 (3)	C4-As1-R1C1	105.8 (4)
C3-As1-C4	103.6 (5)	C5-As2-R2C1	103.2 (4)
Co-As2-C5	119.7 (3)	C6-As-R2C1	103.0 (4)
Co-As2-C6	120.1 (3)	N2-C2-S2	178.5 (18)

Table VI. Selected Interatomic Distances in $[Co(NO)(das)_2(NCS)][NCS]$

Atoms	Distance, Å	Riding model	Atoms	Distance, Å
N3-O	1.00 (1)	1.18 (2)	As2-R2C2	1.949 (9)
Co-N3	1.85 (1)	1.87 (1)	R1C1-R1C1′	1.33 (2)
Co-N1	2.12 (1)	2.13 (1)	R1C1-R1C2	1.42 (1)
N1-C1	1.15 (2)		R1C2-R1C3	1.39 (1)
C1-S1	1.65 (2)	1.68 (2)	R1C3-R1C3′	1.39 (2)
Co-As1	2.337 (3)	2.340 (3)	R2C1-R2C1′	1.35 (2)
Co-As2	2.349 (3)	2.352 (3)	R2C1-R2C2	1.41 (1)
As1-C3	1.916 (10)	1.932 (10)	R2C2-R2C3	1.39 (1)
As1-C4	1.938 (12)	1.956 (12)	R2C3-R2C3′	1.37 (2)
As1-R1C1	1.951 (8)		N2-C2	1.12 (2)
As2-C5	1.927 (11)	1.946 (11)	C2-S2	1.66 (2)
As2-C6	1.930 (10)	1.948 (10)		

The distances and angles in Figure 1 and Table IV show that cation **1** deviates significantly from idealized 2-C_2 symmetry. In particular the As2–Co–N and As4–Co–N angles are 125.2 (7) and 135.5 (7)°, respectively. The As2–Co–As4 angle of 99.3 (2)° is also significantly smaller than the value of 120° expected for an idealized trigonal bipyramid. A stereoview of the entire cation is shown in Figure 3 and a view of the packing in the unit cell appears in Figure 4.

The $Co(das)_2$ unit of cation **2** shows significant deviations from planarity as is apparent from Figure 5, a packing diagram of the unit cell. The phenyl rings make dihedral angles of ~15° with the $CoAs_4$ plane. The same type of molecular distortion has been observed for other complexes with two trans

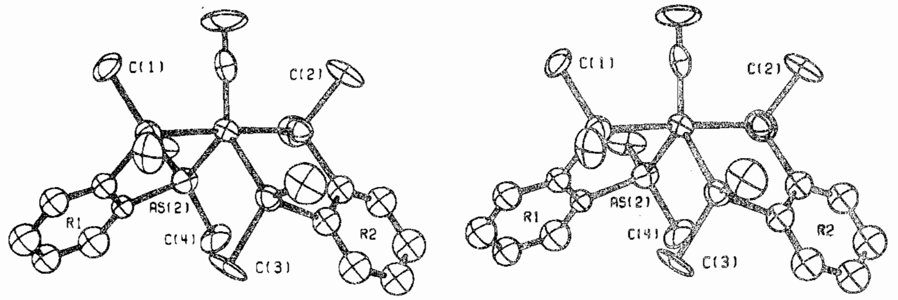


Figure 3. Stereoview of the $[Co(NO)(das)_2]^{2+}$ cation. The identity of the unlabeled items can be determined by reference to Figure 1 and the tables. Hydrogen atoms have been omitted for clarity.

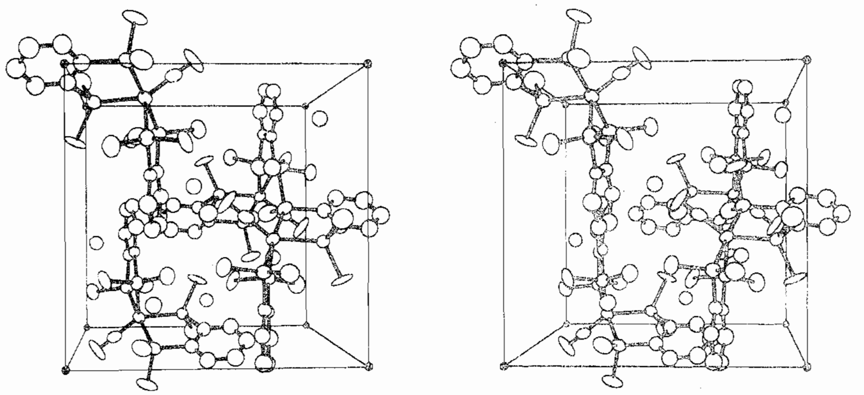


Figure 4. Stereoview of the packing for $[Co(NO)(das)_2][ClO_4]_2$. The ClO_4^- ions have been represented by a single open circle. The positive direction of the *c* axis of the unit cell is up out of the plane of the paper; the positive direction of the horizontal *a* axis is toward the right.

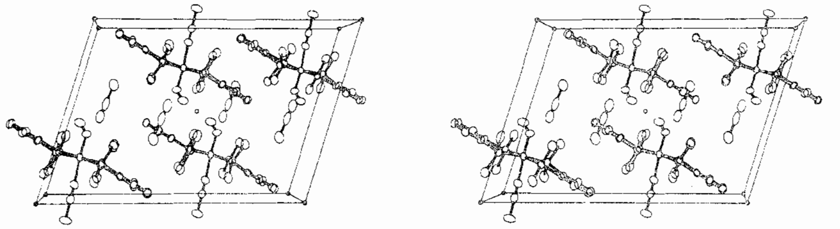


Figure 5. Stereoview of the packing for $[Co(NO)(das)_2(NCS)][NCS]$. The positive direction of the *b* axis of the unit cell is up out of the plane of the paper; the positive direction of the horizontal *a* axis is toward the left.

das ligands.[23–25] Space-filling molecular models show that this molecular geometry, achieved by rotation about the Co–As bonds, minimizes the steric interactions of the methyl groups. Thus, it appears that intramolecular methyl–methyl interactions rather than interactions between the methyl groups and the axial ligands[24] are primarily responsible for the geometry of the phenyl rings.

The C–C distances of the phenyl rings of **2** show systematic variations of marginal significance. In the most precise structural determination for a das complex all C–C distances are within one standard deviation (~0.01 Å) of the average C–C distance of 1.383 Å.[24] Thus, the treatment of the phenyl rings of **1** as rigid groups in order to minimize the number of variables is justified. However, it may have been preferable to use an effective C–C distance slightly shorter than the spectroscopic distance of 1.392 Å.

Several of the atoms of cations **1** and **2** show highly anisotropic thermal motion. The rms amplitudes of vibration are shown in Tables VII and VIII and the relative directions of the motion can be inferred from the Figures 1–5. For cation **1** (Figure 3) the O atom and the methyl C atoms show the expected wagging motion. The orientation of the ellipsoid for the N atom approximately parallel to the Co–N bond is unusual, although it has been observed in at least one other trigonal-bipyramidal metal nitrosyl complex.[26] In **2** the O atom of the nitrosyl group shows a large amplitude normal to the mirror plane. This corresponds to a torsional motion of the bent Co–N–O group about the Co–N bond. Such a low-energy motion also leads to an unreasonably short N–O distance of 1.00 Å. Correction of this distance for thermal motion assuming a riding model gives a chemically reasonable distance of 1.18 (2) Å. Other distances are not substantially affected by correction for thermal motion (Table VI).

Table VII. Root-Mean-Square Amplitudes of Vibration (Å) in $[Co(NO)(das)_2][ClO_4]_2$

Atom	Min	Intermed	Max
Co	0.182 (6)	0.198 (5)	0.220 (5)
As1	0.193 (5)	0.204 (5)	0.255 (4)
As2	0.195 (5)	0.218 (4)	0.247 (4)
As3	0.201 (4)	0.210 (4)	0.232 (4)
As4	0.188 (5)	0.204 (5)	0.245 (4)
N	0.13 (5)	0.20 (3)	0.28 (4)
O	0.14 (5)	0.34 (3)	0.42 (3)
C1	0.16 (5)	0.23 (4)	0.34 (4)
C2	0.16 (5)	0.28 (4)	0.37 (4)
C3	0.10 (8)	0.28 (4)	0.35 (4)
C4	0.14 (6)	0.29 (4)	0.33 (4)
C5	0.19 (5)	0.29 (4)	0.35 (4)
C6	0.06 (9)	0.25 (4)	0.38 (4)
C7	0.16 (5)	0.27 (4)	0.31 (4)
C8	0.22 (4)	0.30 (4)	0.33 (4)
Cl1	0.244 (11)	0.274 (11)	0.319 (11)
Cl2	0.229 (12)	0.257 (11)	0.283 (10)

Infrared and Photoelectron Spectra. The infrared and X-ray photoelectron spectra for complexes **1** and **2** and their analogs

Table VIII. Root-Mean-Square Amplitudes of Vibration (Å) in $[Co(NO)(das)_2(NCS)][NCS]$

Atom	Min	Intermed	Max
Co	0.167 (3)	0.186 (3)	0.211 (3)
As1	0.176 (2)	0.206 (2)	0.220 (2)
As2	0.177 (2)	0.212 (2)	0.221 (2)
S1	0.191 (7)	0.262 (6)	0.312 (6)
S2	0.247 (6)	0.261 (6)	0.312 (6)
N1	0.192 (20)	0.227 (19)	0.256 (18)
N2	0.214 (23)	0.294 (20)	0.337 (20)
N3	0.179 (23)	0.231 (18)	0.282 (18)
C1	0.186 (23)	0.191 (25)	0.224 (24)
C2	0.169 (26)	0.218 (25)	0.365 (26)
C3	0.208 (16)	0.219 (17)	0.315 (16)
C4	0.191 (16)	0.249 (17)	0.327 (15)
C5	0.196 (18)	0.253 (16)	0.315 (16)
C6	0.200 (17)	0.229 (15)	0.315 (15)
O	0.202 (23)	0.281 (19)	0.651 (25)
R1C1	0.165 (16)	0.204 (14)	0.226 (14)
R1C2	0.201 (17)	0.226 (15)	0.255 (16)
R1C3	0.165 (16)	0.217 (15)	0.258 (13)
R2C1	0.150 (17)	0.191 (16)	0.255 (14)
R2C2	0.174 (18)	0.216 (16)	0.275 (15)
R2C3	0.203 (16)	0.214 (16)	0.324 (15)

Table IX. Infrared[a] and Photoelectron[b] Spectra of the $\{CoNO\}^8$ Complexes

Compd	ν_{NO}, cm^{-1}	Binding energy, eV	
		N(1s)	Co(2p$_{3/2}$)
$[Co(NO)(das)_2][ClO_4]_2$	1852	402.3	781.5
$[Co(NO)(das)_2(NCS)][NCS]$	1587, 1561		
$[Co(NO)(das)_2Br]Br$	1565, 1550	400.5	780.5

[a] The infrared spectra were obtained as Nujol mulls between KBr disks. [b] The photoelectron spectra were obtained using the McPherson ESCA 36, Varian, and Hewlett-Packard spectrometers.

are shown in Table IX. There is a qualitative correlation between N(1s) binding energy and ν_{NO}, as has been pointed out previously.[27] The N(1s) binding energies decrease by ~1.5 eV in going from the five-coordinate cations to the six-coordinate cations. Attempts to obtain the infrared spectra of complexes in noncoordinating solvents have been unsuccessful. Solution spectra of **1** show disappearance of the band at 1852 cm^{-1} and a new peak at 1550 cm^{-1}. The new peak is presumably due to analogs of **2** formed by abstraction of halide ions from the cell windows. Polyethylene cell windows cannot be used because of interfering absorptions in this region.

Pmr Spectra. The maximum possible symmetry for **1** is 2-C_2. If the cation adopts this symmetry in solution, then it will possess four distinct types of methyl groups and a 1:1:1:1 pattern should be observed in the methyl region of the pmr spectrum. In CD_3CN, the pmr spectrum of **1** consists of two singlets of equal intensity at τ 8.1 and 8.2 (11.1-Hz separation). Varying the temperature of a CD_3CN solution of **1** from −44 to +76° causes the CH_3 peak at τ 8.2 to shift downfield and the peak separation to decrease from 16.7 to 5.0 Hz. The pmr spectrum of **1** in DMSO-d_6 behaves similarly (Figure 6). At 20° the methyl region consists of two peaks of equal intensity at τ 7.9 and 8.1. As the temperature is increased, the peak at τ 8.1 shifts downfield until the two peaks coalesce into a single broad peak (51°). Further increases in the temperature cause the single peak to narrow and to continue to shift downfield.

The observations in DMSO indicate that at least two dynamic processes are important in this temperature range: a slow process which averages the environment of all of the methyl groups of the das ligand and a fast process which causes a downfield shift of the position of all of the methyl protons. The pmr spectra of **1** are best explained by Scheme I.

Species "*d*" has the structure of the chiral cation **1** and should exhibit four CH_3 resonances of equal intensity. However, rapid solvent exchange (reaction 1) will result in two CH_3 peaks of equal intensity by interconverting the "*d*" and "*l*" enantiomers *via* intermediate *s*. The change in the relative concentration of *s* with respect to "*d*" and "*l*" accounts for the average downfield shift of these two single peaks. The coalescing of these two single peaks at 51° is indicative of either a turnstile rotation[28] (reaction 2) or psuedorotations.[29] Since the only reasonable psuedorotation which $Co(NO)(das)_2{}^{2+}$ can undergo results in a square pyramid with the NO group in the basal plane, we prefer the turnstile mechanism. Holmes[29] came to similar conclusions regarding five-coordinate phosphorus compounds with two bidentate ligands. The energy of activation of reaction 2, 7.5 ± 2 kcal mol^{-1}, was evaluated from the temperature dependence of the pmr spectrum between 20 and 51° (Figure 6). This value is within the range expected for the rearrangement of a five-coordinate TP complex.[28,29] The estimated equilibrium constant obtained for reaction 1 from the pmr spectrum (Figure 6) has a large uncertainty associated with it, but the magnitude of the constant suggested that it might be possible to observe *s* of Scheme I directly by employing a more rapid spectroscopic technique.

Electronic spectra of **1** were obtained in DMSO as a function of temperature between 25 and 40°. The spectra show an

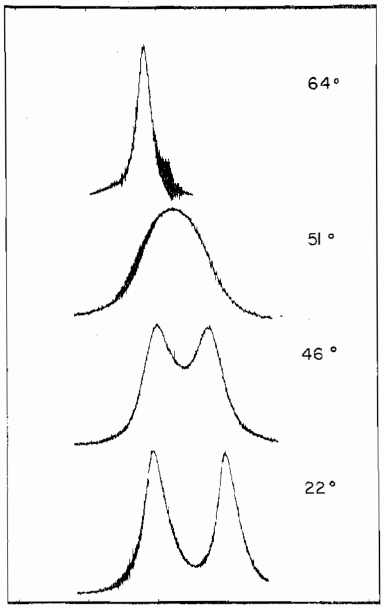
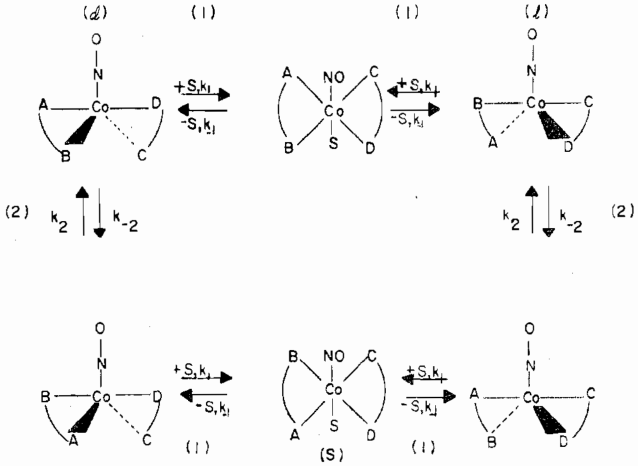
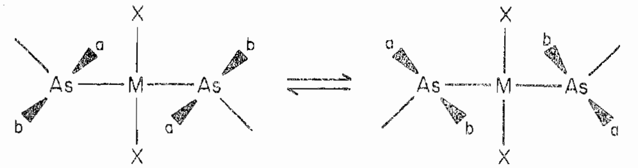


Figure 6. The temperature dependence of the pmr spectrum of $[Co(NO)(das)_2]^{2+}$ in DMSO-d_6. An activation energy of 7.5 kcal mol^{-1} was calculated for the process which equilibrates all of the methyl groups of this complex using the method described by H. S. Gutowski and C. H. Holm, *J. Chem. Phys.*, **25**, 1226 (1956).

Scheme I



Scheme II



absorption maximum at 20.0 kK with a shoulder at 13.9 kK. The shoulder at 13.9 kK is absent in the reflectance spectrum of solid samples of this five-coordinate complex, but the six-coordinate complexes all have absorption maxima near 13.5 kK.[8] Increasing the temperature of solutions of **1** in DMSO results in an increase in intensity of the shoulder at 13.9 kK relative to the more intense absorption band at 20.0 kK. Cooling solutions of **1** from 40 to 25° results in a decrease of the relative intensity of the shoulder at 13.9 kK. This temperature dependence of the visible spectrum of **1** indicates that at least two species are present in solution. The shoulder at 13.9 kK is assigned to an electronic transition of a six-coordinate complex, while the intense absorption maximum at 20.0 kK is an electronic transition of the five-coordinate complex which has an absorption maximum near 20.0 kK in its reflectance spectrum. Thus, the increase in the relative intensity of the shoulder at 13.9 kK with increasing temperature is consistent with equilibrium 1 of Scheme I and suggests that the six-coordinate complex is favored at higher temperature. Slow decomposition of the solutions precludes a quantitative determination of the concentrations of the five- and six-coordinate complexes in DMSO.

The pmr spectra of six-coordinate complexes related to **2** have also been obtained in solution. Since the solid-state structure of **2** has m-C_s symmetry, four singlets with intensity ratios 1:1:1:1 would be expected in the CH_3 region. However, in solvents in which the compounds do not decompose two sharp singlets are observed. For example, the pmr spectrum of *trans*-$[Co(das)_2(NO)Cl][ClO_4]$ in CD_3CN shows two singlets of equal intensity at τ 8.01 and 8.28. The separation between these singlets decreases only slightly (4 Hz) between 35 and 51° and provides little insight into dynamic processes which could lead to the simple spectrum observed. However, consideration of the solid-state structures and pmr data for other six-coordinate complexes (*vide infra*) containing the *trans*-$M(das)_2$ fragment does lead to an understanding of the simple pmr spectra for analogs of **2**.

Pmr spectra of *trans*-$[Co(das)_2X_2]^+$ cations have been previously studied[30] and show only a single methyl resonance. In the solid state, however, such trans complexes have only $2/m$-C_{2h} symmetry[23,24] and therefore should ideally exhibit *two* methyl resonances in solution. The presence of only a single resonance indicates that there is rapid interconversion between the two "chair" conformations of the trans complexes thereby averaging the two different types of methyl groups of the C_{2h} complex (Scheme II). This process also accounts for the observation of only two methyl peaks[31] (1:1 intensity ratio) in *trans*-$MXY(das)_2$ complexes such as $[Ru(NO)Cl(das)_2]^{2+}$. Likewise, the pmr results for analogs of **2** (*vide supra*) can be explained by rapid interconversion of chair conformers by Scheme II and concomitant rapid rotation of the bent Co–N–O group.

Chemical Reactions. Both the pronounced differences in geometry and in the other physical properties of the $\{CoNO\}^8$ group in **1** and **2** suggest that the chemical reactivity of the five- and six-coordinate species should be quite dissimilar. This surmise has been verified by some simple chemical reactions as outlined below.

The complexes *trans*-$[Co(das)_2(HNO)Br]XY$ ($X^- = Br^-$, $Y^- = ClO_4^-$; $X^- = Y^- = ClO_4^-$) have been prepared from the reactions in methanol of $HClO_4$ with *trans*-$[Co(das)_2NOBr]Br$ and of HBr with $[Co(das)_2NO][ClO_4]_2$. The fact that no reaction is observed between $[Co(das)_2NO][ClO_4]_2$ and $HClO_4$ in methanol indicates that the protonation reaction of the NO group proceeds through the six-coordinate complex

$$[Co(das)_2NO]^{2+} + Br^- \rightarrow [Co(das)_2NOBr]^+ \tag{3}$$

$$[Co(das)_2NOBr]^+ + H^+ \rightarrow [Co(das)_2(HNO)Br]^{2+} \tag{4}$$

The protonation reaction, (4), proceeds rapidly, allowing the six-coordinate complex to be titrated spectrophotometrically at 625 nm. The results of this titration show that 1 equiv of H^+ is consumed per mole of $[Co(das)_2NOBr]^+$.

The pmr spectrum of $[Co(das)_2(HNO)Br][ClO_4]_2$ has been recorded in DMSO-d_6. The methyl region of this spectrum consists of two singlets at τ 7.97 and 8.40 which integrate in a 3:1 ratio, respectively. Two multiplets at τ 2.1 and 1.7 are observed in the phenyl region of this spectrum. Careful integration of this region revealed a 4.9:4.0 ratio, respectively. NH protons in coordinated ligands have been identified[32] by decoupling ^{14}N. Several attempts were made to observe effects on the multiplets at τ 2.1 and 1.7 by irradiating at the ^{14}N frequency. Unfortunately, no effects of decoupling could be observed due to the overlapping signals of the aromatic protons. However, addition of a small amount of $Eu(fod)_3$ nmr shift reagent[33] to the sample produced a change in appearance in the multiplet at τ 2.1 and changed the integration ratio of the multiplet at τ 2.1 and 1.7 to 4.0:4.0 as would be expected for the aromatic protons of das. When the same experiment was performed on unprotonated $[Co(das)_2NOCl]ClO_4$, the integration ratio of these multiplets was 4.0:4.0 both before and after the addition of $Eu(fod)_3$.

On this basis the HNO resonance is assigned to the region of τ 2.1. This assignment is consistent with that for the NH proton (τ −5.1) in the related complex $[p\text{-}FC_6H_4N{=}N\text{-}(H)Pt(PEt_3)_2Cl]BF_4$.[34] A thorough search was made for additional proton signals at higher and lower fields ($\tau < 0$ and $\tau > 10$), but none were observed. The NO stretching frequency of $[Co(das)_2(HNO)Br]^{2+}$ is 1560 cm^{-1} (KBr pellet, Nujol mull); this absorption band is not significantly shifted from that of $[Co(das)_2NOBr]^+$ (1565, 1550 cm^{-1}) but is considerably less intense. The NO stretching frequency of a previously reported osmium HNO complex is 1410 cm^{-1}.[35]

Although $[Co(das)_2(HNO)Br][ClO_4]_2$ is stable for short periods of time in dichloromethane, DMSO, and acetonitrile, the HNO group is rapidly displaced by methanol, producing the $[Co(das)_2(MeOH)Br][ClO_4]_2$ complex. The latter complex may be generally useful as a starting material for the synthesis of complexes of the type $[Co(das)_2XY]Z$ which presently are difficult to prepare.

Discussion

It is generally accepted that the bonding in the MNO fragment of metal nitrosyl complexes is highly covalent. We have pointed out that considerable insight into mononitrosyl complexes can be obtained by investigating the behavior of the $\{MNO\}^n$ group[1b,2-4] in ligand fields. A detailed discussion of the bonding in complexes like **1** and **2** which are derivatives of the $\{CoNO\}^8$ group was presented elsewhere.[1b,2-4] Here it is sufficient to emphasize that the conversion of a linear $\{CoNO\}^8$ group of **1** into the strongly bent $\{CoNO\}^8$ of **2** requires a change in the nature of the highest occupied molecular orbital (HOMO) of the complex. Specifically, the formation of **2** from **1** entails the transfer of a pair of electrons from an orbital mainly localized on the metal (d_{z^2}) to a totally antibonding π-type molecular orbital which has a large component from $\pi^*(NO)$. The essential features of the process are shown in Figure 7. The substantially different electronic structures for **1** and **2** result in the vastly different geometries and chemical reactivities which are observed. Thus, the NO group of **2** readily protonates because one of the highest lying

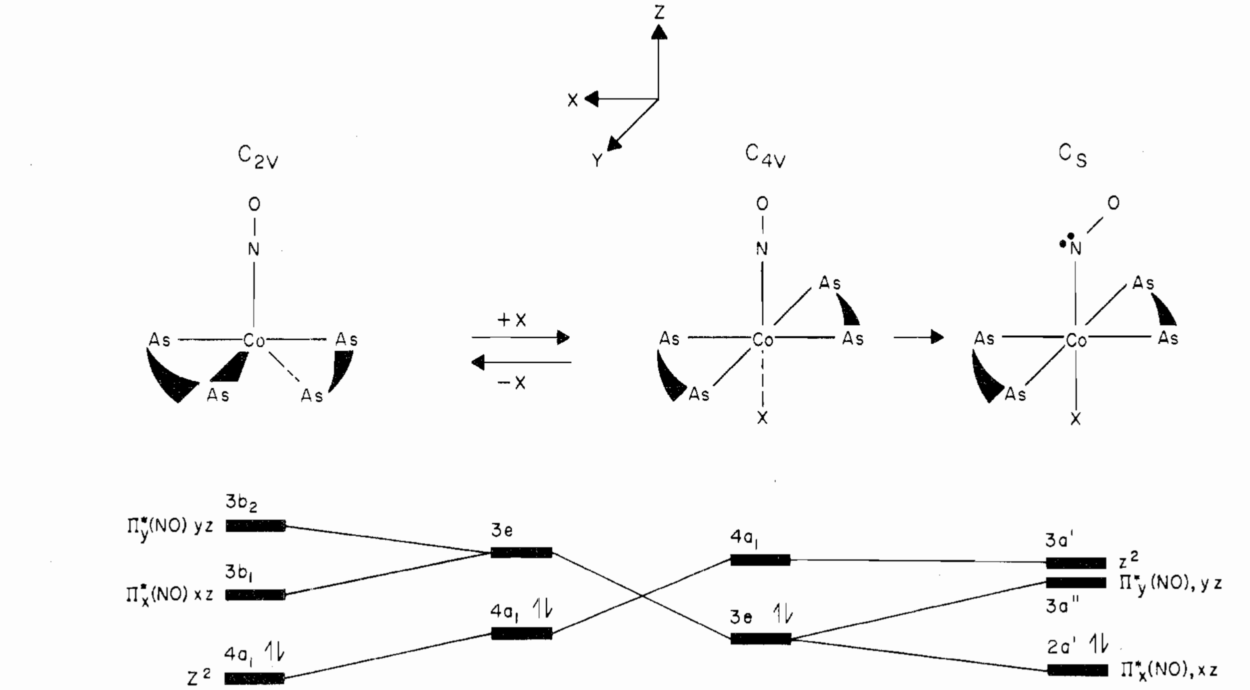


Figure 7. A molecular orbital correlation diagram of the highest occupied and lowest unoccupied molecular orbitals of the $\{CoNO\}^8$ group in ligand fields with C_{2v} and C_s symmetries.

molecular orbitals is primarily an sp^2-type orbital located mainly on the bent NO group. In complex **1**, however, the highest lying orbital is primarily d_{z^2}, a nonbonding orbital located on cobalt. Therefore, complex **1** does *not* readily protonate. Complex **1** can be protonated by first allowing it to react with a good coordinating ligand such as Br^- to generate **2**, the chemically reactive six-coordinate complex with a strongly bent CoNO group (reaction 3).

Similar results have been obtained with four- and five-coordinate complexes of the $\{IrNO\}^8$ group, $[Ir(NO)(P(C_6H_5)_3)_2Cl]^+$ and $[Ir(NO)(P(C_6H_5)_3)_2Cl_2]$.[36] Although $[Ir(NO)(P(C_6H_5)_3)_2Cl]^+$ has not been structurally characterized, its properties are most consistent with square-planar geometry and a linear Ir–N–O group. The coordination of a second chloride results in a five-coordinate complex with tetragonal-pyramidal geometry and a bent (123°) Ir–N–O group in the axial position.[37] While protonation of the bent Ir–N–O group of $[Ir(NO)(P(C_6H_5)_3)_2Cl_2]$ has not yet been accomplished, the related five-coordinate osmium complex $Os(NO)(CO)(P(C_6H_5)_3)_2Cl$ adds HCl, but the site of protonation has not been established with certainty.[35] Finally, the $\{ReNO\}^8$ group in $Re(CO)_2(NO)(P(C_6H_5)_3)_2$ has been reported to react with HCl to form a six-coordinate complex with a protonated NO group, $Re(CO)_2(HNO)(P(C_6H_5)_3)_2Cl$.[38] However, no pmr spectra have been reported for any of these complexes.

In summary, the addition of a sixth ligand to **1** raises the energy of the d_{z^2} orbital of the metal and leads to **2**. The transformation of **1** into **2** can also be *formally* described[6] as a two-electron reduction of a coordinated ligand (here NO^+ to NO^-) which is initiated by a change in the stereochemistry about the metal.

Conclusions

Several discussions of the relationship between the structure and bonding of metal nitrosyls have appeared in recent years.[1,2-4,39] In this paper we have shown that the structure, bonding, and chemical reactivity of the $\{CoNO\}^8$ group are controlled by the stereochemistry of the other ligands coordinated to the metal and that a change in the stereochemistry about the metal will markedly change the distribution of the valence electrons of the $\{CoNO\}^8$ group.[40] The principles of stereochemical control of valence electrons are generally applicable to metal nitrosyl complexes.[1b,2-4] Moreover, we contend that these principles are key features in the reactions of all ligands coordinated to transition metals.[6]

Acknowledgment. We thank Mr. E. Valente for growing crystals of **1**. Professor R. Hoffmann kindly provided a preprint of ref 40. A generous allocation of computer time from the University of Arizona Computer Center is gratefully acknowledged. This research was supported by the National Science Foundation.

Registry No. $[Co(NO)(das)_2][ClO_4]_2$, 53495-87-7; $[Co(NO)(das)_2NCS][NCS]$, 53495-89-9; $[Co(NO)(das)_2Br]Br$, 53495-90-2; $[Co(das)_2(HNO)Br][ClO_4]_2$, 53586-49-5.

Supplementary Material Available. Listings of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number AIC406984.

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Crystal and Molecular Structure of [Ag(P(OMe)$_3$)$_2$NO$_3$]$_2$. A Case of Symmetric Nitrate–Oxygen Bridging

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Received August 6, 1974 AIC40545G

The crystal and molecular structure of tetrakis(trimethyl phosphite)-di-μ-nitrato-disilver(I), [Ag(P(OMe)$_3$)$_2$NO$_3$]$_2$, has been determined by single-crystal X-ray diffraction methods. The compound crystallizes in the orthorhombic P_{bca} space group with four molecules per unit cell of which the dimensions are a = 9.146 (3), b = 16.769 (4), and c = 20.689 (6) Å. The structure was solved by the heavy-atom method and refined by least-squares calculations to a final R of 0.048 with 1233 independent reflections. While the molecule is a centrosymmetric dimer in the crystalline state with an Ag–Ag bond distance of 4.095 (2) Å, molecular weight determinations indicate the presence of extensive dissociation in solution. The geometry around the silver atom in the solid state is a greatly distorted tetrahedron with an OAgO angle of 67.0 (3)° and a PAgP angle of 133.8 (1)°. The bridging oxygens are equidistant (2.456 (8) and 2.454 (8) Å) from both silvers.

Introduction

In a recent review[2] on nitrate coordination, the authors sort the known structures into three classes: bidentate, unidentate, and bridging nitrate systems. The bidentate class is subdivided into a symmetric group, wherein both metal–oxygen distances are the same, and an unsymmetric group, in which they differ by 0.2–0.7 Å. If this difference is greater than 0.7 Å, the nitrate is considered to be unidentate. Unidentate coordination may also be subclassified as symmetrical if the two metal to noncoordinated oxygen distances are equal or unsymmetrical if these distances are not equal. Many crystal structures of coordinated nitrate complexes have been reported. Classification is not unambiguous inasmuch as some nitrates fall into more than one category[3] and some of the complexes have more than one type of coordinated nitrate.[4,5]

Of the more than 50 compounds containing coordinated nitrate whose structures are known,[2,5-8] about half possess one or more symmetrical bidentate nitrate groups, about 20% have a unidentate nitrate, and approximately 15% have an unsymmetrical bidentate nitrate, leaving almost 15% containing bridging nitrates. The preferred coordination mode of a bridging nitrate utilizes two oxygens, one bound to each metal. The cases in which one nitrate oxygen is coordinated to more than one metal are limited. There is evidence for one oxygen being coordinated to three metal atoms[9] in $Cu_4(NO_3)_2(OH)_6$ although further refinement would be desirable in view of the high R factor (0.30). To our knowledge there are only two cases in which only one oxygen is coordinated to two metal atoms[3,4] and in both cases the two metal–oxygen distances are significantly different. Here we report the first example of a bridged nitrate complex in which the bridging occurs *via* one oxygen which is equidistant from both metal atoms.

Experimental Section

The silver complex was prepared as previously described.[10a] Crystals were grown by dissolving about 2 g in 20 ml of acetone, adding 20 ml of ether, and then adding pentane until slightly cloudy. Slowly cooling the solution to −78° produced clear, colorless, nearly cubic crystals. Inasmuch as they are sensitive to prolonged exposure to atmospheric conditions, one of them was mounted in a 0.3-mm sealed Lindemann capillary tube. Data were collected at room temperature using an automated four-circle diffractometer designed and built in the Ames Laboratory. The upper full circle was purchased from STOE and is equipped with encoders (Baldwin Optical) and drive motors. The design of the base allows the encoders to be directly connected to the main θ and 2θ shafts, using solid and hollow shaft encoders, respectively. The diffractometer is interfaced to a PDP-15 computer in a real-time mode and is equipped with a scintillation counter. The χ, ω, and 2θ angles of 13 reflections were tuned and these values were used to calculate[10b] the reduced cell. This cell was