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Crystal Structure of *trans*-Bis(dimethylglyoximato)diamminecobalt(III) Bromide: Comments Concerning Cis and Trans Effects

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The crystal structure of *trans*-$[(NH_3)_2Co(dmgH)_2]Br$ has been determined. The complex crystallizes in the monoclinic system with $a = 8.4366$ (6) Å, $b = 9.7253$ (8) Å, $c = 9.340$ (5) Å, and $\beta = 99.02$ (1)° with space group $C2/m$. The structure, refined to $R_1 = 0.024$ and $R_2 = 0.027$, has nearly coplanar $dmgH^-$ ligands. The bridging hydrogen atoms are required by symmetry to be midway between the oxime oxygen atoms. The Co–NH_3 bond, 1.960 (2) Å, shows no evidence of a cis effect when compared to the structure of $[(NH_3)_6Co]Cl_3$. Comments on cases where cis effects from $dmgH^-$ ligands give rise to bond lengthening and bond shortening are included.

Introduction

We[1-7] and others[8-12] have determined the single-crystal structures of a large number of $[A_5CoX]^{n+}$ and $[(en)_2Co(A\text{-}X)]^{n+}$ complexes, where A is ammonia, X is a sulfur donor ligand, and A-X is a chelating ligand with ammine and sulfur donor moieties. These studies have clearly demonstrated the presence of a structural trans effect (STE) in cobalt(III) chemistry. The STE for these complexes is defined as the difference in bond lengths: [Co–N (trans to X)] − [Co–N (cis to X)] = STE. The STE is a highly reproducible property dependent on the chemical identity of X. The following STE series has been established: sulfito,[2] 0.089 (3) Å > sulfenato,[3,10] 0.073 (3) Å > sulfinato,[2,4,5] 0.054 (3) Å > thiolato,[1,8,9] 0.044 (2) Å > thiosulfato,[11] 0.019 (8) Å ~ thiocyanato,[12] 0.010 (4) Å ~ thiooxalato,[6] 0.010 (7) Å ~ disulfide,[6] 0.006 (5) Å ~ thioether,[7] 0.000 (7) Å. Further, we have shown in a limited case[2] that the STE correlates with a kinetic trans effect observed for $[A_5CoSO_3]^+$ and $[A_5CoSO_2C_6H_5]^{2+}$ substitution reactions. Difficulties which exist in the syntheses of $[A_5CoX]^{n+}$ complexes make further kinetic studies unlikely in the near future. However, syntheses[13,14] of complexes of the type *trans*-$[NH_3Co(dmgH)_2X]^{+,0,-}$, where $dmgH^-$ is the monoanion of dimethylglyoxime and X a variety of neutral and anionic ligands, appear more promising. In order to define a STE for these complexes, we have prepared and determined by X-ray methods the structure of $[(NH_3)_2Co(dmgH)_2]Br$, which we report here.

Experimental Section

Preparation. *trans*-Bis(dimethylglyoximato)diamminecobalt(III) bromide was prepared by simple metathesis of a hot solution of the chloride salt (prepared following literature methods[15]) with a saturated solution of lithium bromide. Crystals suitable for X-ray investigations were grown by recrystallization of a sample of the bromide salt on cooling of an aqueous solution. $[(NH_3)_2Co(dmgH)_2]Br$ crystallizes as yellow, nearly rectangular parallelepipeds. The IR spectra of the chloride and bromide salts are nearly identical with the exception that the water O–H stretch (3400 cm^{-1}, broad) in the chloride salt, $[(NH_3)_2Co(dmgH)_2]Cl\cdot5H_2O$, is absent in the anhydrous bromide salt, which has no absorption above 3300 cm^{-1}. IR spectra were determined as mineral oil mulls on KBr plates by using a Perkin-Elmer 599 spectrophotometer. The formulation of the complex as *trans*-$[(NH_3)_2Co(dmgH)_2]Br$ was confirmed by the X-ray analysis.

X-ray Characterization. Preliminary precession photographs of a crystal of $[(NH_3)_2Co(dmgH)_2]Br$ mounted about a nonprincipal axis indicated[16] a *C*-centered monoclinic unit cell. A crystal (0.18 × 0.19 × 0.45 mm) was mounted and optically centered on a Syntex $P\bar{1}$ diffractometer (Mo Kα, λ 0.71069 Å, graphite monochromator). Precise cell constants obtained from least-squares analysis of 16 pairs of reflections measured at both $+2\theta$ and -2θ values in the region 18–30° are $a = 8.4366$ (6) Å, $b = 9.7253$ (8) Å, $c = 9.340$ (5) Å, $\beta = 99.02$ (1)°, $V = 756.86$ Å^3, $Z = 2$, $\rho_{obsd} = 1.767$ g cm^{-3}, $\rho_{calcd} = 1.769$ g cm^{-3} (neutral buoyancy, $CHCl_3/CHBr_3$), space group $C2/m$, $C2$, or Cm, and μ(Mo Kα) = 3.99 mm^{-1}. Intensities were measured for 1434 reflections of the types hkl and $hk\bar{l}$ in the region $2.5° \le 2\theta \le 60°$. From these, 1044 unique, observed reflections ($I \ge 2\sigma(I)$) were obtained[18] by averaging. Absorption corrections were applied with transmission coefficients varying from 0.403 to 0.506. Other details of data collection were as follows: scan method, $\theta/2\theta$; scan rate, 1–6.0°/min; scan range, 0.7° below Kα_1 peak to 0.8° above Kα_2 peak in 2θ; max *h*, 13; max *k*, 14; max *l*, 14.

Examination of the intensity data revealed no conditions limiting possible reflections other than those due to the *C* centering. A Patterson map yielded locations for all nonhydrogen atoms in agreement with the space group[19] $C2/m$, No. 12. The bromine atom was placed at 0, 0, 0 ($2/m$ symmetry) and the cobalt atom at 0, 0, $^1/_2$ ($2/m$ symmetry). This model refined without difficulty. Two acentric space groups[19] ($C2$, No. 5; Cm, No. 8) are also possible and attempts were made to refine the structure in these lower symmetries. Correlation coefficients between variables related by the higher symmetry were high (>0.8) and refinement produced nonpositive definite anisotropic temperature parameters. It appeared that our normal weighting scheme, with the ignorance factor[1] $p = 0.03$, was overemphasizing a relatively small group of middle intensities and causing additional difficulty in the low symmetry refinement which requires nearly twice the number of variables. The adoption of unit weights for all subsequent calculations allowed straightforward re-

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Table I. Fractional Atomic Positional Parameters[a, b]

	x	y	z
Co	0.0	0.0	0.5
Br	0.0	0.0	0.0
N(1)	0.1544 (2)	0.0	0.3635 (2)
N(2)	0.1281 (2)	0.1271 (1)	0.6207 (1)
O	0.1100 (2)	0.2641 (1)	0.6038 (1)
C(1)	0.2309 (2)	0.0758 (2)	0.7243 (2)
C(2)	0.3376 (3)	0.1588 (3)	0.8334 (2)
H(1)	0.0	0.273 (4)	0.5
H(2)	0.111 (5)	0.0	0.277 (5)
H(3)	0.222 (3)	0.072 (3)	0.371 (3)
H(4)	0.288 (3)	0.252 (3)	0.827 (3)
H(5)	0.337 (3)	0.116 (3)	0.925 (3)
H(6)	0.438 (3)	0.188 (3)	0.798 (3)

[a] The estimated error in the last digit is given in parentheses. Those values without errors correspond to symmetry fixed positions. [b] The numbering scheme is shown in Figure 1.

Table II. Interatomic Distances (Å) and Angles (deg)

Co–N(1)	1.960 (2)	Co–N(2)	1.893 (1)
N(2)–O	1.347 (2)	N(2)–C(1)	1.294 (2)
C(1)–C(2)	1.487 (3)	C(1)–C(1)[a]	1.474 (3)
O–H(1)	1.235 (3)	N(1)–H(2)	0.837 (43)
N(1)–H(3)	0.896 (29)	C(2)–H(4)	0.997 (32)
C(2)–H(5)	0.953 (29)	C(2)–H(6)	0.993 (29)
		O–O[b]	2.465 (2)
N(1)–Co–N(2)	90.69 (6)	N(2)–Co–N(2)[b]	98.48 (6)
N(2)–Co–N(2)[a]	81.52 (6)	C(1)–N(2)–O	121.3 (1)
Co–N(2)–C(1)	116.5 (1)	Co–N(2)–O	122.2 (1)
N(2)–C(1)–C(1)[a]	112.7 (1)	N(2)–C(1)–C(2)	124.4 (2)
C(2)–C(1)–C(1)[a]	122.9 (2)	H(2)–N(1)–Co	113 (3)
H(3)–N(1)–Co	116 (2)	H(2)–N(1)–H(3)	104 (3)
H(3)–N(1)–H(3)[a]	102 (3)	H(4)–C(2)–C(1)	104 (2)
H(5)–C(2)–C(1)	107 (2)	H(6)–C(2)–C(1)	112 (2)
H(4)–C(2)–H(5)	123 (2)	H(4)–C(2)–H(6)	95 (3)
H(5)–C(2)–H(6)	123 (2)	O–H(1)–O[b]	172 (4)

[a] Transformed to $x, -y, z$. [b] Transformed to $-x, y, 1-z$.

Table III. Root-Mean-Square Displacements (Å)

atom	min	mean	max	atom	min	mean	max
Co	0.114	0.115	0.139	N(1)	0.132	0.146	0.156
N(2)	0.131	0.141	0.155	O	0.125	0.169	0.196
C(1)	0.130	0.158	0.171	C(2)	0.148	0.201	0.229
Br	0.140	0.192	0.213				

finement of four different models to convergence. Each refinement was based on nonhydrogen atoms only and involved positional and anisotropic thermal parameters only. The results were as follows: $C2/m$, $R_1 = 0.031$,[20] $R_2 = 0.042$; $C2$, $R_1 = 0.030$, $R_2 = 0.041$; $C2$ (enantiomer), $R_1 = 0.030$, $R_2 = 0.041$; Cm, $R_1 = 0.031$, $R_2 = 0.043$. Although a Hamilton R-factor ratio test[21] indicated that the $C2$ model was marginally superior, the bond lengths and angles did not differ significantly from those of the $C2/m$ model. We chose to continue with the simpler model. Hydrogen atoms were located from a difference electron density map and given arbitrary isotropic temperature parameters ($B = 4.0$ Å^2). Final convergence was reached (unit weights, $R_1 = 0.024$, $R_2 = 0.027$) by refining all positional parameters and anisotropic thermal parameters for nonhydrogen atoms. In the final cycle the maximum shift was 0.1 esd and the average shift was 0.01 esd. A final difference map was essentially featureless, the highest peak occurring near the bromine atom and representing less than 0.25 e Å^{-3}. Neutral atom scattering factors[22,23] were used with Co and Br corrected[24] for anomalous dispersion. Table A[25] listing final values of $|F_o|$ and F_c is available. Final atomic positional parameters are presented in Table I. Bond lengths and angles derived therefrom are listed in Table II. Root-mean-square displacements (Table III) have been calculated from the anisotropic thermal parameters which are available (Table B[25]), as are the calculated ligand planes (Table C[25]).

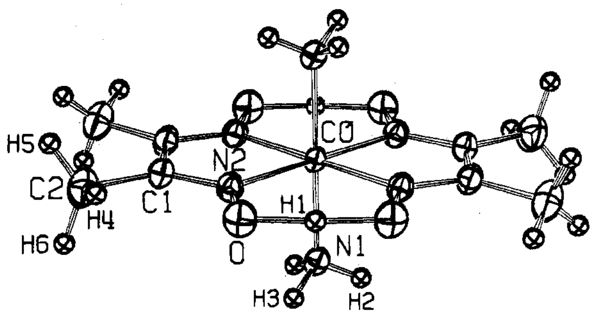

Figure 1. Perspective view of the title complex cation with 50% probability thermal ellipsoids. Hydrogen atoms are shown as spheres of 0.1 Å radius at their refined positions.

Results

The crystal structure is built from sheets of anions ($z = 0$) and intervening layers of cations ($z = {}^1/_2$). Most contacts between anions and cations appear normal van der Waals type. There is a hydrogen bond between an ammine hydrogen atom, H(2), and the bromide ion, H(2)–Br, 2.61 Å, with an angle, N(1)–H(2)–Br, of 172°. There is also a hydrogen bond between cations joining the second amine hydrogen atom to an oxygen atom on the dimethylglyoxime complex at ${}^1/_2, {}^1/_2, {}^1/_2$ (H(3)–O, 2.13 Å; N(1)–H(3)–O, 177 (2)°).

The site symmetry ($2/m$) of the cobalt atom requires a trans complex as shown in Figure 1. The ammine nitrogen atoms lie on the mirror plane which bisects each $dmgH^-$ ligand as well. One $dmgH^-$ ligand is related to the other by the twofold rotation axis, which also passes through H(1), the oxime hydrogen atom, and requires H(1) to be midway between the oxygen atoms of the two $dmgH^-$ ligands. The $dmgH^-$ ligands are essentially planar and slightly bent out of the plane of the cobalt and four imine nitrogen atoms (2.3°) presumably by packing forces. The details of the $dmgH^-$ ligand structure are normal and are within the range of those found previously.[26,27]

Discussion

The major thrust of this study was to precisely determine the $Co-NH_3$ bond length in *trans*-$[(NH_3)_2Co(dmgH)_2]Br$ and to discover whether this distance is the same as that observed for NH_3 trans to NH_3 in a variety of $[A_5CoX]^{n+}$ complexes. Since the complex was recrystallized from water, it is important to determine that no substitution of water for ammonia has taken place. The relevant observations are as follows. First, the IR spectrum of the crystals studied shows no O–H stretch. Second, the ammine nitrogen temperature parameters are in good agreement with those of the oxime nitrogen atom, whereas, if the oxygen atom of water were present, these temperature parameters would be significantly smaller. Third, the Co–N bond length, 1.960 (2) Å, is in the range expected[1-12] for nitrogen bonding, whereas a Co–O bond should be ~0.1 Å longer. Partial substitution of water for ammonia should result in elongation of the thermal ellipsoids along the $Co-NH_3$ bond. Fourth, the successful location and refinement of the *three* hydrogen atoms of ammonia preclude water substitution. Thus, we are confident that the value of 1.960 (2) Å for the $Co-NH_3$ bond is not only precise but also chemically meaningful, establishing that the conversion of cobalt from the "hard" center of the pentaammine complexes to the "soft"

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(20) $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.

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center of a cobaloxime does not significantly modify the length of the Co–NH_3 bond (vide infra).

Proton Shifts. Recent articles[26,27] concerning bis(dimethylglyoximato)cobalt complexes have suggested that these species often should be represented as complexes of one neutral dimethylglyoxime ligand ($dmgH_2$) and one dianionic dimethylglyoximato ligand (dmg^{2-}). Palenik and co-workers[26] have postulated a ligand-induced proton shift (LIPS) in which the proton shift results from the stabilizing π interaction between the phenyl ring of an aniline ligand and a dmg^{2-} ligand, giving the asymmetrical formulation $[(dmg)(dmgH_2)CoXY]$. Bresciani-Pahor et al.[27] suggest that such asymmetry often occurs for other reasons as well. In the case studied here, no such asymmetry is likely; the two equivalent $dmgH^-$ ligands are related by the twofold axis and the proton lies on this axis midway between the oxygen atoms. Even if the symmetry is lower than that required by the choice of *C*2/*m* space group, the preferred lower symmetry space group *C*2 (vide supra) maintains the twofold axis and requires equivalent $dmgH^-$ ligands. The *Cm* space group allows inequivalence between the dimethylglyoxime ligands. However, a Hamilton test[21] indicated that this space group was an inferior choice and in the refined model all comparable ligand bond lengths agreed within three estimated standard deviations.

Trans and Cis Effects. Intuitively, a trans effect is the ability of a ligand to moderate some property (length, strength, reactivity, etc.) of a trans metal–ligand bond and, similarly, a cis effect is the ability to change some property of a cis bond. Due to the symmetry of the metal orbitals involved in transmission of these effects, trans effects may depend on both σ and π interactions between metal and ligands, while cis effects depend primarily on π interactions. Thus, a probe ligand such as ammonia which is a pure σ donor may exhibit trans effects but not cis effects. That the Co–NH_3 bond length is insensitive to variation in cis ligands is shown by a comparison of the structure of $[(NH_3)_6Co]Cl_3$[28] with that of the title complex where four cis ammonia moieties have been replaced by two $dmgH^-$ ligands. The average Co–NH_3 distance, 1.966 (9) Å, in the hexaammine is in good agreement with the value of 1.960 (2) Å in the $dmgH^-$ complex. The relative insensitivity of the Co–NH_3 bond length to variation in cis ligands is demonstrated further by the average cis Co–NH_3 lengths for the following classes[1-12] of $[A_5CoX]^{n+}$ complexes: sulfito, 1.966 (2) Å; sulfenato, 1.971 (2) Å; sulfinato, 1.969 (5) Å; thiolato, 1.966 (3) Å. Thus, any changes found in Co–NH_3 lengths in complexes of the type $[(NH_3)Co(dmgH)_2X]$ should be pure trans effects and are expected to parallel those observed already for $[A_5CoX]^{n+}$ and $[(en)_2Co(A\text{-}X)]^{n+}$.

When the probe ligand also is capable of π interactions with the metal center, both cis and trans effects are expected to determine the bond length between the metal and probe ligand donor atoms. The trans effects can be eliminated by comparing Co–Cl bond lengths in *trans*-$[Cl(dmgH)_2CoNH_3]$[29] and *trans*-$[ClCo(NH_3)_5]Cl_2$,[30] since in both complexes Cl^- is trans to NH_3. The expected cis effect on the Co–Cl bond is that for the replacement of four cis NH_3 groups by two $dmgH^-$ ligands. The four cis NH_3 ligands are pure σ donors and thus are expected to have no π interaction with the cobalt, and consequently the Co–Cl bond, 2.286 (2) Å, should show no cis effect. Since Cl^- is thought[31] to be a π donor and $dmgH^-$ a π acceptor, a synergistic cis effect results in shortening the Co–Cl bond in *trans*-$[Cl(dmgH)_2CoNH_3]$ to 2.251 (2) Å.

A similar comparison may be made of Co–NO_2 bond lengths in *trans*-$[(NO_2)_2Co(NH_3)_4]CH_3CO_2$,[32] 1.937 (6) Å, and *trans*-$Na[(NO_2)_2Co(dmgH)_2]$,[27] 1.946 (4) Å. Here NO_2^- is trans to NO_2^- in both complexes, excluding any difference in trans effect between the two complexes. When NO_2 is cis to four ammonia ligands, there should be no cis effect. When NO_2^- (a π acceptor) is cis to $dmgH^-$ (also a π acceptor), the cis effect should be antagonistic, in agreement with the marginally longer Co–NO_2 bond length for the $dmgH^-$ complex.

Thus, considerable consistency is beginning to emerge in the study of structural cis and trans effects. The choice of NH_3 as a probe ligand allows the determination of "pure" trans effects while other probes are sensitive to both cis and trans effects. Further studies will attempt to analyze these mixed effects.

Registry No. $[(NH_3)_2Co(dmgH)_2]Br$, 72121-29-0.

Supplementary Material Available: Tables A–C containing lists of structure factors, anisotropic thermal parameters, and ligand planes (5 pages). Ordering information is given on any current masthead page.

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