putations. All calculations were performed on the IBM 360-91 computer operated by the UCLA Campus Computing Network.
(6) Numbers given in parentheses throughout this paper are the estimated standard deviations and refer to the last digit given.
(7) The conventional R index, $R_1 = \sum \| F_o| - |F_c\| / \sum |F_o|$, and the weighted residual factor, $R_2 = (\sum w \| F_o| - |F_c\|^2 / \sum |F_o|^2)^{1/2}$, where the weights are $w = 1/\sigma^2(F_o)$.
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Crystal Structure of μ-Thiocyanato-[pentaamminecobalt(III)]pentacyanocobalt(III) Monohydrate

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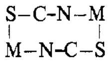
Received February 7, 1975 AIC50094F

The crystal structure of μ-thiocyanato-[pentaamminecobalt(III)]pentacyanocobalt(III) monohydrate, a binuclear cobalt complex containing a single thiocyanate bridge, has been determined by single-crystal X-ray diffraction techniques using counter-measured intensity data. Crystals of $(NH_3)_5CoNCSCo(CN)_5 \cdot H_2O$ are orthorhombic, space group *Pbca* with 8 formula units per unit cell; cell dimensions are a = 14.166 (4), b = 14.549 (4), and c = 15.187 (9) Å. Anisotropic least-squares refinement fitting 2453 unique data led to a final R index of 0.050. The binuclear molecule contains two octahedral Co(III) atoms bridged by a thiocyanate ligand bonded through the sulfur atom to the pentacyanocobalt group in the "bent" configuration, with a Co–S–C angle of 101°, and in a somewhat nonlinear fashion to the pentaamminecobalt group through the nitrogen atom, with a Co–N–C angle of 169°. This bending allows a contact between ligands on opposite ends of the molecule which is interpreted as an intramolecular N–H···N hydrogen bond. A shortening of the trans Co–NH_3 distance by greater than 0.04 Å relative to the cis distances is noted.

Introduction

The thiocyanate ion has been a subject of interest in recent times as a ligand because of its ambidentate nature. The ability to coordinate through the sulfur atom (thiocyanato) or through the nitrogen atom (isothiocyanato) or both leads to possibilities of linkage isomerism. Bridging thiocyanate ligands are common but usually occur in systems which place rigid restrictions upon the bridging geometry, such as dimers of the form



Recently, singly bridged dimers of the system $(NH_3)_5Co(SCN)Co(CN)_5$ have been prepared independently in two laboratories.[1,2] Both isomers were characterized by Buckley and Wardeska through elemental analysis, infrared spectra, electronic spectra, and conductivity measurements. We are interested in these compounds because of the unique single bridge in a discrete binuclear complex and in relation to our structural studies of the analogous cyano-bridged compounds.[3,4] The structure of the thiocyanato isomer[5] $(NH_3)_5CoNCSCo(CN)_5$ is reported here in an X-ray study of the monohydrate.

Experimental Section

Table I. Crystal Data

Formula	$(NH_3)_5CoNCSCo-(CN)_5 \cdot H_2O$	Vol	3130 (1) A^3
Formula wt	409.2	Z	8
$F(000)$	1664 electrons	ρ_{exptl}	1.77 (2) g cm^{-1}
Space group	*Pbca*	ρ_{calcd}	1.736 g cm^{-3}
a	14.166 (4) A	λ(Mo Kα)	0.71069 A
b	14.549 (4) A	μ(Mo Kα)	24.9 cm^{-1}
c	15.187 (9) A		

A sample of the compound was generously supplied by J. G. Wardeska in the form of an orange powder. Large single crystals were easily grown by dissolving this powder in 0.5 M $HClO_4$ at 50°, filtering the solution, and quickly cooling to 10°. Crystals were collected after 24 hr, washed with ethanol, and air-dried. The well-formed crystals are elongated with rectangular cross sections. Systematic extinctions judged from Weissenberg films are $0kl$ with k odd, $h0l$ with l odd, and $hk0$ with h odd. These extinctions uniquely determine the space group to be *Pbca*. The crystal chosen for data collection was elongated along c, and terminations at both ends were crumbled away to approximate a rectangular prism of dimensions 0.08 × 0.26 × 0.37 mm. This crystal was mounted with its c axis inclined about 0.5° from the ϕ axis of a Datex-automated General Electric quarter-circle diffractometer, and cell dimensions were determined by a least-squares fit using 2θ values measured for 20 reflections using graphite-monochromatized Mo Kα radiation (λ 0.71069 Å). The axial lengths, along with other pertinent crystal data, are listed in Table I. A density determination performed by flotation in a CCl_4–$CHBr_3$ mixture established that there are 8 formula units per cell and suggested that the complex is present in the crystal as the monohydrate.

Intensity data were measured at room temperature using Mo Kα radiation, employing a θ–2θ scan technique and a proportional counter. All unique reflections having peak centers (the weighted mean of α_1 and α_2 lines) between the 2θ limits of 4° and 50° were scanned, and four standard reflections were remeasured every 100 measurements. Scanning widths varied linearly with 2θ, having values of 1.6° at 2θ = 7° and 1.9° at 2θ = 29°. All scans were performed at a constant

Table II. Positional and Anisotropic Thermal Parameters for the Heavy Atoms of $(NH_3)_5CoNCSCo(CN)_5 \cdot H_2O$[a]

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co(1)	5396 (0.4)	347 (0.4)	2278 (0.4)	23 (0.3)	18 (0.3)	17 (0.4)	0.8 (0.6)	−1.6 (0.6)	−6.7 (0.5)
Co(2)	7339 (0.4)	2538 (0.4)	4568 (0.4)	26 (0.3)	14 (0.3)	18 (0.4)	0.4 (0.6)	−7 (0.6)	−1.6 (0.6)
S	4678 (0.9)	1585 (0.9)	2990 (1)	22 (0.6)	29 (0.7)	31 (0.9)	9 (1)	−9 (1)	−26 (1)
C(1)	5559 (3)	1978 (3)	3587 (4)	26 (3)	19 (2)	24 (3)	7 (4)	8 (4)	−9 (4)
N(1)	6175 (3)	2242 (3)	4004 (3)	25 (2)	21 (2)	28 (3)	1 (4)	−3 (4)	−9 (4)
C(2)	5966 (4)	−634 (3)	1701 (4)	36 (3)	24 (3)	20 (3)	−4 (5)	10 (5)	−7 (5)
N(2)	6373 (4)	−1217 (3)	1372 (3)	54 (3)	41 (3)	39 (3)	10 (5)	14 (5)	−33 (5)
C(3)	6569 (3)	932 (3)	2249 (3)	27 (3)	25 (3)	17 (3)	5 (5)	−5 (4)	−10 (4)
N(3)	7282 (3)	1306 (3)	2193 (3)	35 (3)	33 (3)	42 (3)	−1 (5)	4 (5)	−23 (5)
C(4)	4221 (4)	−271 (4)	2230 (3)	35 (3)	29 (3)	15 (3)	−10 (5)	0 (5)	−12 (4)
N(4)	3523 (3)	−641 (3)	2188 (3)	40 (3)	49 (3)	47 (3)	−31 (5)	12 (5)	−43 (5)
C(5)	5107 (3)	945 (4)	1215 (4)	23 (3)	35 (3)	28 (3)	−4 (5)	2 (5)	5 (5)
N(5)	4930 (3)	1371 (4)	599 (3)	37 (3)	63 (4)	31 (3)	10 (5)	1 (5)	25 (5)
C(6)	5645 (4)	−216 (3)	3379 (4)	46 (3)	21 (3)	30 (4)	16 (5)	−4 (5)	−20 (5)
N(6)	5767 (4)	−549 (4)	4051 (4)	98 (4)	46 (3)	29 (3)	59 (6)	−7 (6)	12 (5)
N(7)	8521 (3)	2827 (3)	5139 (3)	32 (2)	23 (2)	31 (3)	−6 (4)	−25 (4)	0 (4)
N(8)	6904 (3)	3814 (3)	4734 (3)	36 (3)	19 (2)	30 (3)	7 (4)	−2 (4)	−4 (4)
N(9)	7742 (3)	1250 (3)	4393 (3)	35 (3)	19 (2)	30 (3)	4 (4)	7 (4)	0 (4)
N(10)	6788 (3)	2212 (3)	5721 (3)	45 (3)	27 (2)	21 (3)	2 (4)	5 (4)	0 (4)
N(11)	7877 (3)	2854 (3)	3408 (3)	31 (2)	22 (2)	24 (3)	−5 (4)	−3 (4)	3 (4)
O	3305 (3)	−65 (3)	4265 (3)	53 (3)	34 (2)	38 (3)	−9 (4)	17 (4)	2 (4)

[a] All values have been multiplied by 10^4. The anisotropic temperature factor is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. Estimated standard deviations are given in parentheses.

Table III. Coordinates ($\times 10^3$) Assigned to the Hydrogen Atoms

Atom	x	y	z
7H(1)	890	226	519
7H(2)	839	312	573
7H(3)	889	329	473
8H(1)	731	411	516
8H(2)	623	379	491
8H(3)	695	413	412
9H(1)	846	124	444
9H(2)	753	106	379
9H(3)	745	87	488
10H(1)	720	173	599
10H(2)	614	198	560
10H(3)	679	280	609
11H(1)	852	307	351
11H(2)	746	333	315
11H(3)	786	222	304

rate of 1°/min with backgrounds counted for 30 sec at each extreme of the scan. Total decline in the intensities of standard reflections amounted to only 0.5% in the 200 hr required for data collection. The 86 most intense reflections were remeasured with the intensity of the incident X-ray beam decreased; the four strongest reflections had suffered from coincidence losses to the extent of about 0.5%. These four intensities and their weights were adjusted to correct for this. Of 2703 unique reflections measured, 171 had negative values of F_o^2. Corrections were made for Lorentz and polarization effects, but absorption corrections were deemed insignificant. The linear absorption coefficient μ(Mo Kα) is 24.9 cm^{-1}, leading to maximum and minimum transmission coefficients of 0.91 and 0.83. Observational variances were computed from the equation $\sigma(I) = [S + [B_1 + B_2)(t/60)^2 + (0.02S)^2]^{1/2}$ where S is the scan count, t is the scan time, and B_1 and B_2 are the background counts. The value 0.02 has been typical of this apparatus in the past but may be underestimated for this particular data set.

Derivation and Refinement of the Structure

The intensity data were placed on an approximately absolute scale by the method of Wilson.[6] A three-dimensional Patterson map was calculated, from which two cobalt atoms in general positions were easily located. Successive Fourier syntheses revealed the positions of all ligand atoms and the oxygen atom of the water molecule. A structure factor calculation based upon this unrefined structure yielded an R index ($R = \sum|F_o - |F_c||/\sum F_o$) of 0.38. This model was refined by full-matrix least squares, allowing thermal parameters to refine anisotropically after a few cycles. The quantity minimized in the least-squares calculations was $\sum w(F_o^2 - F_c^2)^2$, where the weights are $w = 1/\sigma^2(F_o^2)$. All reflections measured were used in the refinement. Machine calculations were carried out on an IBM 370/155 computer using the CRYM crystallographic computing system. Scattering factors for Co, S, C, N, and O were taken from ref 7, the curve for neutral cobalt being corrected for the real term of anomalous dispersion. Hydrogen scattering factors were those of Stewart, Davidson, and Simpson for bonded hydrogen.[8] Ammine hydrogen atoms were located by difference syntheses in the expected planes. They were assigned isotropic temperature factors with $B = 5.0$ Å^2, and their positions were adjusted during the refinement on the basis of difference maps; their parameters were not refined for economic reasons. Near the end of the refinement, a number of reflections distributed widely in intensity but closely in reciprocal space were noted to be calculated systematically considerably larger than their observed F values. Examination of the raw data indicated that these reflections were all collected close together in real time. Standard reflections for this phase of the data collection procedure appeared mostly normal; however, several strings of "bad" reflections were noted occurring between measurements of standards, consecutively in the order of data collection. We believe that this problem is due to fluctuations of some portion of the apparatus on a time scale which was short with respect to the remeasurement of the standards, which occurred about every 6 hr. A consecutive string of data consisting of 250 reflections was therefore given zero weight in further refinement, indiscriminately with regard to individual agreements with calculated F values.

Convergence was fairly rapid. Refinement was discontinued when all shifts were smaller than half their standard deviations. Final values of R are 0.050 for the 2305 data with $F_o > 0$ and 0.039 for the 1847 data having $F_o > 3\sigma(F_o)$. The "goodness of fit" (GOF = $[\sum w(F_o^2 - F_c^2)^2/(m - s)]^{1/2}$) is 2.33 for $m = 2453$ observations and $s = 190$ parameters. It is possible that the empirical correction term we used in estimating the esd's of the structure factors (0.02) should have been chosen larger; this would have improved the GOF. However the factor 0.02 has been adequate for this equipment in the past; the high value of the GOF is probably related to the instrumental fluctuations noted earlier. A three-dimensional difference Fourier synthesis calculated at the conclusion of the refinement indicated no discrepancies greater than ±0.8 e Å^{-3}. One of the more outstanding features of the map is a toroid of electron density of about 0.3–0.7 e Å^{-3} around the position of the oxygen atom of the water molecule, for which discrete hydrogen positions were never assigned. A table of final observed and calculated structure factors is available.[9]

Results and Discussion

Our structural study confirms Buckley and Wardeska's formulation of this compound as a singly bridged, nonionic binuclear complex containing the thiocyanate bridging ligand in the more favorable isomeric configuration, with the hard nitrogen end of the thiocyanate coordinated to the hard pentaamminecobalt(III) group and the softer sulfur end coordinated to pentacyanocobalt(III). Refined coordinates and anisotropic thermal parameters are given in Table II;

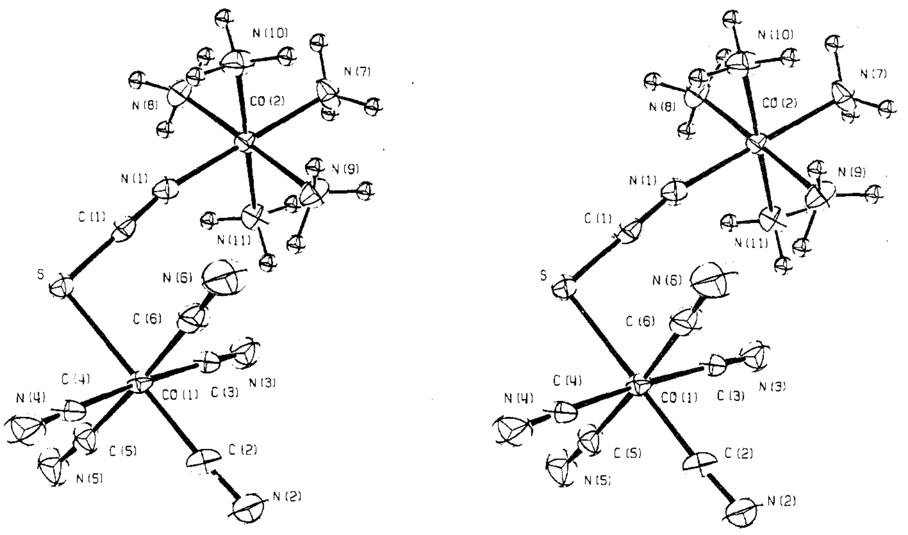


Figure 1. An ORTEP representation of the $(NH_3)_5CoNCSCo(CN)_5$ molecule. Thermal ellipsoids are drawn at the 40% probability level, and hydrogen atoms are represented by spheroids of arbitrary radius.

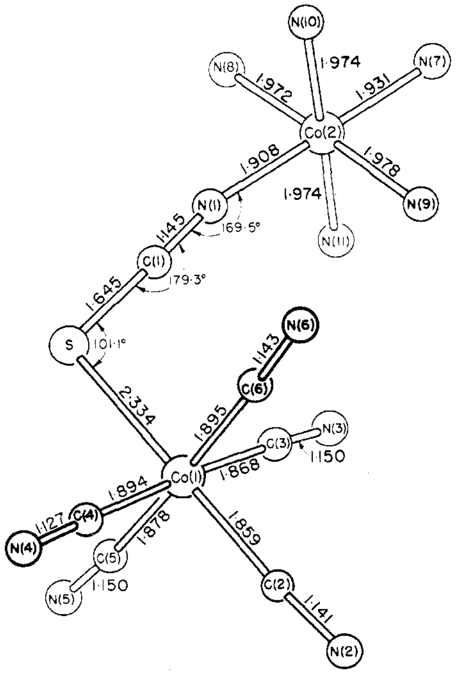


Figure 2. Interatomic distances and some important angles in the molecule. Esd's are 0.002 Å for Co–S, 0.004 Å for Co–N, 0.005 Å for Co–C and S–C, and 0.007 Å for C–N.

Table IV. Bonding Angles[a]

Atoms	Angle, deg	Atoms	Angle, deg
S-Co(1)-C(2)	179.5	N(1)-Co(2)-N(7)	179.5
S-Co(1)-C(3)	92.7	N(1)-Co(2)-N(8)	90.0
S-Co(1)-C(4)	90.1	N(1)-Co(2)-N(9)	88.5
S-Co(1)-C(5)	86.9	N(1)-Co(2)-N(10)	90.1
S-Co(1)-C(6)	90.3	N(1)-Co(2)-N(11)	89.2
C(2)-Co(1)-C(3)	87.3	N(7)-Co(2)-N(8)	90.5
C(2)-Co(1)-C(4)	90.0	N(7)-Co(2)-N(9)	90.9
C(2)-Co(1)-C(5)	92.6	N(7)-Co(2)-N(10)	89.9
C(2)-Co(1)-C(6)	90.2	N(7)-Co(2)-N(11)	90.9
C(3)-Co(1)-C(4)	176.3	N(8)-Co(2)-N(9)	178.5
C(3)-Co(1)-C(5)	87.9	N(8)-Co(2)-N(10)	89.4
C(3)-Co(1)-C(6)	93.0	N(8)-Co(2)-N(11)	90.9
C(4)-Co(1)-C(5)	89.8	N(9)-Co(2)-N(10)	90.3
C(4)-Co(1)-C(6)	89.5	N(9)-Co(2)-N(11)	89.4
C(5)-Co(1)-C(6)	177.1	N(10)-Co(2)-N(11)	179.2
Co(1)-C(2)-N(2)	175.3	Co(1)-S-C(1)	101.1
Co(1)-C(3)-N(3)	176.8	S-C(1)-N(1)	179.3
Co(1)-C(4)-N(4)	178.9	C(1)-N(1)-Co(2)	169.5
Co(1)-C(5)-N(5)	174.9		
Co(1)-C(6)-N(6)	177.9		

[a] Esd's are 0.1° for angles involving S and Co, 0.2° for angles between lighter ligands coordinated to cobalt, and 0.3° for Co–C–N.

coordinates assigned to the hydrogen atoms are listed in Table III. An ORTEP representation of the molecule is shown in Figure 1, and interatomic distances are given in Figure 2.

The most striking feature of the molecule is its overall bending. The coordination angle at the sulfur atom is 101°, and at the bridging nitrogen atom it is 169°. Deviations from linearity of greater than 10° are not uncommon for N-bonded thiocyanate, and angles at sulfur have been observed in S-bonded thiocyanate complexes over a range of 90–109°.[10] This range probably reflects more the steric differences between various complexes than relative stabilities due to hybridization of sulfur orbitals. In $(NH_3)_5CoSCN^{2+}$, which exhibits a Co–SCN angle of 104.9°, the thiocyanate carbon atom makes close contacts with ammine ligands, preventing a smaller angle.[10] In the square-pyramidal copper complex Cu(trien)SCN^+, which has a Cu–SCN angle of 89.5°, no such close contacts exist.[11] The present case is sterically intermediate between the two examples cited, and the angle at sulfur is also intermediate. Nonbonded contacts with the thiocyanate carbon atom C(1) to cyanide carbon atoms are 2.91 Å to C(3) and 3.21 Å to C(6); a smaller angle at sulfur would lead to severe nonbonded repulsions.

Molecular bending was also noted in the closely related complexes $(NH_3)_5CoNCCo(CN)_5$ and $(NH_3)_5CoCNCo(CN)_5$ and attributed to electrostatic attraction between the positively charged pentaammine end and the negatively charged pentacyano end of the molecules.[3,4] In the thiocyanate complex, more flexibility is possible, and the bending manifests itself in an intramolecular hydrogen bond. Ammine ligand N(11) donates to cyanide ligand N(3) through hydrogen atom 11H(3). The hydrogen bond is reasonably strong, having an N···N distance of 3.03 Å and an N–H···N angle of 154°. An adjacent ammine ligand N(9) also has a close contact to N(3), with an N···N distance of 3.40 Å.

The bridging thiocyanate ligand is essentially linear with interatomic distances typical of those found in both coordinated and free thiocyanate ions. The Co–S bond has a length of 2.334 (2) Å, which is significantly longer than the essentially identical distances of 2.272 (7) and 2.284 (6) Å found in pentaamminecobalt(III) complexes of –SCN and $-S_2O_3$, respectively.[10,12] This lengthening of the Co–X bond in

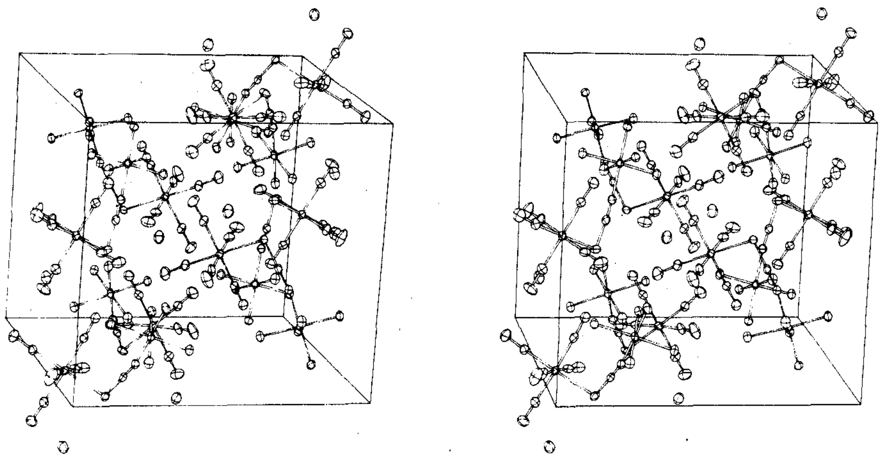


Figure 3. A stereoscopic representation of the contents of the unit cell. Atoms are represented by thermal ellipsoids enclosing 40% probability. The origin of the coordinate system is at the lower left (foreground). The *a* axis is vertical, and the *b* axis is horizontal.

Table V

Intermolecular N· · ·N Contacts Less Than 3.3 A

A–H· · ·B	A· · ·B, A	H· · ·B, A	Angle, deg
N(7)–7H(1)· · ·N(2)	3.00	2.38	120
N(7)–7H(1)· · ·N(5)	3.12	2.29	141
N(7)–7H(3)· · ·N(6)	3.05	2.04	161
N(8)–8H(3)· · ·N(4)	3.08	2.12	153
N(8)–8H(2)· · ·N(5)	3.10	2.13	165
N(9)–9H(3)· · ·N(2)	3.26	2.86	104
N(9)–9H(1)· · ·N(5)	3.11	2.09	172
N(10)–10H(1)· · ·N(2)	3.14	2.23	150
N(10)–10H(3)· · ·N(3)	3.18	2.23	154
N(11)–11H(2)· · ·N(4)	3.09	2.11	171
N(11)–11H(1)· · ·N(6)	3.17	2.39	136

Close Contacts to the Water Molecule

Ammine A–H	N· · ·O, A	H· · ·O, A	Angle, deg	Cyanide N	N· · ·O, A
N(8)–8H(1)	3.09	2.16	161	N(3)	3.31
N(9)–9H(3)	3.05	2.05	171	N(4)	3.28
N(10)–10H(1)	3.13	2.55	116	N(6)	3.01

$(CN)_5Co–X$ systems vs. $(NH_3)_5CoX$ systems has been previously observed for bridging ligands O_2^{2-}, O_2^-, and –NC.[4,13,14] It is perhaps surprising that the Co–S bond is shorter (and thus presumably stronger) for the pentaammine complex than for the pentacyano complex, due to the observed relative stabilities to isomerization of the nonbridging thiocyanato complexes; however, the important consideration is the relative stability of each complex with respect to its own linkage isomer.

The Co–NCS distance of 1.908 (4) Å is indistinguishable from the value of 1.921 (5) Å found for Co–NC in $(NH_3)_5CoNCCo(CN)_5$. Distances within the $Co(NH_3)_5$ fragment are given in Figure 2, and angles are given in Table IV. All equatorial Co–N distances are identical with an average value of 1.975 (2) Å. The axial $Co–NH_3$ bond is 0.044 Å shorter than this average; this difference is formally 10σ and is considered quite significant. This trans influence is thought to arise from competition between $–NH_3$ and –NCS for σ-bonding e_g orbitals of the cobalt atom, in which NH_3 is the better competitor. We think it worthwhile to point out the close correspondence between this pentaamminecobalt grouping and that found in the corresponding cyano-bridged complex $(NH_3)_5CoNCCo(CN)_5$. As stated earlier, the cobalt to bridging nitrogen distances in the two molecules are indistinguishable, as are the trans distances 1.931 (4) and 1.935 (5) Å. The equatorial distances average 1.965 Å in the cyano-bridged structure, quite close to the value found here. Apparently "inserting" a neutral sulfur atom into the bridge three atoms distant from the cobalt center has no detectable effect upon the overall bonding to the cobalt atom.

Dimensions of the $Co(CN)_5$ fragment of the molecule may be found in Figure 2 and Table IV. The Co–C bond lengths range from 1.859 (5) to 1.895 (6) Å, with the shortest being trans to the bridging ligand. While the trans distance is 0.025 Å shorter than the equatorial average and significantly shorter than most of the equatorial distances, statistically significant differences exist also among the equatorial distance themselves. For this reason we cannot conclude that we are definitely observing a bona fide trans influence. Our average Co–C distance is 1.879 Å, which agrees satisfactorily with the typical value of 1.890 Å found in cobalt(III) cyanide complexes. All C–N distances of the cyanide ligands are statistically indistinguishable, averaging 1.142 Å, which is in good agreement with the value of 1.149 Å typical of cobalt cyanides.[13] All cyanide groups coordinate linearly to within about 5°; variations such as these are generally found for terminal cyanide ligands.

The arrangement of molecules within the unit cell is represented in Figure 3. This molecule would be expected to employ much hydrogen bonding in the crystalline state, since one end of the complex is composed of good donor ligands (ammines) and the other end is a cluster of good acceptor ligands (cyanides). The packing does indeed appear to be determined by hydrogen bonding. Intramolecular hydrogen bonding has been previously discussed. Table V lists intermolecular N···N contacts, many of which should be considered to be hydrogen bonds. The water molecule, which can act as both donor and acceptor, is located in the vicinity of three ammine ligands and three cyanide ligands; this geometry is summarized in Table V. It is clear that the water molecule has several orientations to choose from, and it is not surprising that no discrete positions were determined for its hydrogen atoms, which are no doubt statically disordered in several orientations. Another close intermolecular contact involves the sulfur atom and the trans ammine N(7). The S–N distance is 3.39 Å, and the N–H···S angle is 126°, which places the hydrogen atom 2.7 Å from the sulfur atom, as compared to a van der Waals distance of 3.05 Å.

Acknowledgment. We wish to thank Dr. Jeff G. Wardeska for the gift of a sample of the compound. This work was supported in part by the National Science Foundation through Grant GP-25730, for which we are grateful. We thank Dr. Sten Samson for his construction and maintenance of the X-ray diffraction equipment.

Registry No. $(NH_3)_5CoNCSCo(CN)_5 \cdot H_2O$, 55493-58-8.

Supplementary Material Available. A listing 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 $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC50094F-9-75.

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Crystal and Molecular Structure and the Kinetics of Ligand Exchange of Tris(*N*,*N*-dimethyldithiocarbamato)thallium(III)

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Received March 6, 1975 AIC50169F

The crystal structure of tris(*N*,*N*-dimethyldithiocarbamato)thallium(III) monohydrate, $Tl(Me_2dtc)_3 \cdot H_2O$, has been solved from three-dimensional counter data in order to determine the detailed structural parameters of the TlS_6 core. The structure was determined because ligand-exchange kinetic studies by PMR and solution infrared data suggested that the coordination number may be less than 6. The space group is $P2_1/c$ with lattice constants $a = 9.143$ (5) Å, $b = 19.201$ (16) Å, $c = 12.429$ (7) Å, $\beta = 109.1$ (1)°, and $Z = 4$. The data were refined by least-squares to a conventional R of 0.080. The average Tl–S distance is 2.659 Å and all six Tl–S distances are within 0.046 Å or 5σ of the average; hence the Tl atom is six-coordinate. The geometry of the TlS_6 core is typical of other $M(dtc)_3$ complexes in that a geometry intermediate between trigonal antiprismatic and trigonal prismatic is found with approximate D_3 symmetry. The average twist angle, ϕ, and the average propeller pitch angle, ψ, are 33.2 and 26.5°, respectively. In addition a significant C_2 distortion is superimposed on the trigonally twisted geometry of the TlS_6 core. The geometry of the TlS_6 core is compared to other $M(dtc)_3$ complexes and is analyzed in light of Kepert's electrostatic repulsive potential calculations of ground-state geometry for $\sim D_3$ M(bidentate)$_3$ complexes as a function of ligand bite angle. Several short intermolecular contacts are found: S–S of 3.43 (2) Å and methyl–methyl of 3.32 (6) Å but these do not appear to affect the geometry of the TlS_6 core. A total line shape analysis of exchange broadened PMR spectra for $Tl(Me_2dtc)_3$ has also been carried out. The coalesence of the methyl doublet (J(Tl–H) = 10 Hz at −50°) results from a first-order dissociative ligand-exchange reaction with $\Delta H^{\ddagger} = 6.2 \pm 1.0$ kcal/mol and $\Delta S^{\ddagger} = -28 \pm 10$ eu.

Introduction

During our investigation of the dynamic stereochemistry of tris(*N*,*N*-disubstituted-dithiocarbamato)metal complexes, $M(R_1R_2dtc)_3$,[1-4] some new analogs were synthesized where M = thallium(III) and found to have several unusual properties in solution. The PMR spectrum of $Tl(Me_2dtc)_3$[5] in various noncoordinating solvents showed a well-separated methyl doublet below ca. −38°. This doublet which is due to $^{(203)205}Tl-^1H$ coupling[6,7] with J = 10 Hz in CD_2Cl_2 solution at −50° collapses into a sharp singlet at ca. 0°. Rapid ligand exchange best accounts for the coalescence of the doublet because the exchange-broadened spectra were accurately computer simulated using this model (vide infra). In addition the rate of ligand exchange which is independent of complex concentration ($k_1 = 15 \pm 1$ sec^{-1} at −19°) probably results from ligand dissociation. Such fast dissociative ligand-exchange rates are unusual for chelated dithiocarbamato complexes[1-4,8] and possibly suggest a coordination number lower than 6. Further support for this possibility comes from CS_2 and CH_2Cl_2 solution infrared data which show a splitting of the band between 950 and 1000 cm^{-1} which has often been attributed to monodentate coordination of the dithiocarbamato ligand.[9,10] The analogous six-coordinate $Fe(Me_2dtc)_3$ complex does not show such a splitting in CS_2 solution. In the solid (KBr disk), however, $Tl(Me_2dtc)_3$ does not show a distinct split band in this region which suggests a coordination number change between the solution and solid phase. It was decided to undertake an X-ray analysis of this new complex in order to establish the mode of coordination in the solid state. In addition it should be of interest to see how the MS_6 core of a tris(dithiocarbamato) complex of a sixth-row metal is distorted relative to other $M(dtc)_3$ complexes. A trend has recently been established for this type of complex which shows that the smaller the bite angle the larger the distortion from trigonal-antiprismatic toward trigonal-prismatic geometry.[1,11] $Tl(Me_2dtc)_3$ is expected to have the smallest bite angle of any $M(dtc)_3$ complex thus far examined.

Experimental Section

Preparation of the Complex. Tris(*N*,*N*-dimethyldithiocarbamato)thallium(III) monohydrate, $Tl(Me_2dtc)_3 \cdot H_2O$, was synthesized by the reaction of thallium trichloride (3.1 g in ca. 25 ml of acetonitrile) with $Me_2dtcNa \cdot xH_2O$ (5.0 g in ca. 50 ml of absolute ethanol). The yellow precipitate which formed immediately on mixing the two solutions was filtered and washed with ethanol. Yellow crystals were obtained after several crystallizations from CH_2Cl_2–heptane solution. The product was vacuum-dried and stored under nitrogen.

The infrared spectrum of the solid (KBr disk) was very similar to other six-coordinate $M(Me_2dtc)_3$ complexes but the CS_2 and CH_2Cl_2 solution spectra revealed a splitting of the band at ca. 975 cm^{-1} which is characteristic of a monodentate dtc ligand;[9,10] the analysis of the vacuum-dried anhydrous complex is as follows. Anal. Calcd for $TlC_9H_{18}N_3S_6 \cdot H_2O$: C, 19.53; H, 3.46. Found: C, 19.01; H, 3.11. The experimental average molecular weight by vapor pressure osmometry in $CHCl_3$ solvent is 558 in the concentration range 1 × 10^{-2}