structures. An explanation for the stabilization of the higher energy conformers was proposed[8] based on the effects of strong hydrogen bonding between the ring amine protons and Lewis bases present in the salts. This prediction was based on the observation that formation of a hydrogen bond to one of the axial amines in the Λδδδ conformation effectively blocks the remaining two protons and so the maximum number of hydrogen bonds can only be formed in the Λλλλ conformation. Of course, implicit in this observation is the assumption that the donor base be unable to form additional hydrogen bonds to the axial protons. For ions with geometries which allow simultaneous hydrogen-bond formation to all three axial protons, there is no reason to expect the higher energy λ conformation. Caughlan, *et al.*, have recently commented on this explanation in the structure report of $[Ni(en)_3][SO_4]$.[24] Two other recent structure reports have explicitly used the predictions of this model in explaining the observed conformations. The present structure determination supports this model, since in forming multiple hydrogen bonds to the axial protons, the basic premise of the model is denied and so the Λδδδ form is expected.

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The Crystal Structure of Pentacyanocobalt(III)-μ-cyano-pentaamminecobalt(III) Monohydrate

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The crystal structure of $(NH_3)_5CoNCCo(CN)_5 \cdot H_2O$ has been determined by single-crystal X-ray techniques. The space group is *Pbca*, and the lattice constants are $a = 17.359$ (5), $b = 12.187$ (3), and $c = 13.936$ (3) Å. The measured density is 1.66 (2) g cm^{-3}, and that calculated for eight molecules in the unit cell is 1.69 g cm^{-3}. Intensity data for 1791 reflections were collected with a Datex automated GE diffractometer using Co Kα radiation. Direct methods and full-matrix least-squares techniques were used to solve and refine the structure. The final *R* index is 0.044. The ligands form nearly regular octahedra about the cobalt atoms. Within each molecule there is no scrambling of ammonia and cyanide groups around the two cobalt centers. The two cobalt atoms are bridged by a cyanide group with the carbon atom of the group bonded to the cobalt atom with all the cyanide ligands. The average Co–N, Co–C, and C–N distances in the nonbridging groups are 1.959 (9), 1.893 (4), and 1.146 (7) Å, and for the bridging cyanide group the corresponding bond distances are 1.920 (3), 1.896 (4), and 1.152 (5) Å.

Introduction

Recently, de Castelló, Mac-Coll, Egen, and Haim[1] prepared the cyano-bridged binuclear compound $(NH_3)_5Co(CN)Co(CN)_5$ by thermal dehydration of the salt $[Co(NH_3)_5OH_2][Co(CN)_6]$. They were able to conclude that there was no scrambling of ammonia and cyanide ligands around the two cobalt centers, and while their spectroscopic measurements suggested that the compound should be formulated as $(NH_3)_5CoNCCo(CN)_5$, they could not rule out the isomer having the orientation of the bridging cyano group reversed.

We were particularly interested in this compound in connection with our studies on bridged dicobalt compounds. Besides wishing to verify the orientation of the bridging cyano group, we wished to study the exact geometry of the bridging group and its effect on the other ligands. Accordingly, we have carried out an X-ray diffraction analysis of the structure.

Experimental Section

Professor Haim kindly sent us some of his material. Recrystallization from water yielded orange, prismatic crystals. Oscillation and Weissenberg photographs of several of these crystals indicated at least two different modifications: an orthorhombic form, which was chosen for the structure analysis, and a tetragonal form, space group $P4_12_12$, with approximate cell dimensions $a = 11.2$ and $c = 28.7$ Å. No further work was done on the tetragonal crystals.

A prismatic crystal, elongated along *a*, with approximate dimensions 0.16 × 0.07 × 0.08 mm, was selected; it was completely coated with epoxy mounting cement and oriented with its *a* axis inclined by about 1° from the φ axis of a Datex automated General Electric quarter-circle diffractometer. Cell dimensions were obtained from a least-squares fit to 2θ values measured using cobalt radiation and an iron oxide filter. The density was measured by flotation in a mixture of chloroform and dibromomethane. Crystal data are given in Table I.

TABLE I
CRYSTAL DATA

Space group *Pbca*	$(NH_3)_5CoNCCo(CN)_5 \cdot H_2O$
$a = 17.359$ (5) Å	Formula weight 376.86
$b = 12.187$ (3) Å	$F_{000} = 1501$
$c = 13.936$ (3) Å	Co Kα_1 1.78892 Å
$Z = 8$	Co Kα_2 1.79278 Å
$d_m = 1.66$ (2) g cm^{-3}	No. of reflections 1791
$d_x = 1.69$ g cm^{-3}	

Intensities were measured, also with Co Kα radiation, using a θ–2θ scan technique, at a scan speed of 1°/min (in 2θ). The scan range varied from 1.5° at 2θ = 10° to 2.6° at 2θ = 100°. Background was counted for 40 sec at both extremes. Two check reflections were measured periodically during the data collection; they showed no appreciable changes in intensity. The recorded counts were corrected for background and for Lorentz and polarization effects but not for absorption; the maximum value of μR is approximately 0.32, so that neglect of absorption

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[1] R. A. de Castelló, C. P. Mac-Coll, N. B. Egen, and A. Haim, *Inorg. Chem.*, **8**, 699 (1969).

TABLE II

Positional and Thermal Parameters of the Heavy Atoms[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co(1)	12,987 (4)	66,829 (5)	2,130 (4)	155 (2)	252 (5)	178 (3)	0 (6)	4 (5)	39 (7)
Co(2)	11,817 (3)	38,530 (5)	26,488 (4)	153 (2)	257 (5)	198 (4)	2 (6)	−10 (5)	12 (7)
C(1)	10,418 (21)	57,144 (34)	12,191 (27)	145 (15)	397 (33)	241 (22)	−3 (36)	−25 (28)	−60 (46)
N(1)	9,666 (18)	50,780 (27)	18,235 (23)	201 (13)	377 (27)	244 (19)	−62 (31)	−23 (26)	110 (41)
C(2)	16,164 (22)	76,280 (33)	−7,818 (28)	168 (15)	313 (31)	274 (23)	83 (36)	16 (30)	−8(47)
N(2)	18,425 (21)	81,919 (30)	−13,855 (26)	332 (16)	430 (30)	446 (24)	35 (37)	104 (33)	340 (48)
C(3)	11,142 (21)	55,670 (32)	−7,005 (27)	164 (15)	327 (30)	229 (21)	−2 (36)	−8 (30)	79 (46)
N(3)	10,151 (20)	49,252 (31)	−12,865 (25)	305 (17)	515 (32)	385 (23)	23 (37)	−57 (30)	−193 (48)
C(4)	14,758 (22)	78,316 (35)	11,001 (27)	158 (16)	407 (33)	293 (23)	64 (39)	15 (30)	−5 (50)
N(4)	15,833 (21)	85,395 (30)	16,256 (26)	319 (16)	533 (33)	430 (24)	−31 (37)	−1 (32)	−310 (48)
C(5)	23,311 (23)	61,882 (32)	3,295 (25)	201 (17)	310 (30)	197 (21)	−97 (36)	10 (28)	12 (44)
N(5)	29,611 (20)	58,972 (29)	3,630 (26)	207 (15)	500 (30)	502 (25)	29 (36)	40 (30)	8 (45)
C(6)	2,775 (25)	71,977 (33)	653 (25)	230 (17)	372 (31)	175 (22)	25 (37)	23 (30)	−48 (45)
N(6)	−3,260 (21)	75,373 (31)	−362 (23)	236 (15)	724 (35)	334 (24)	214 (39)	−40 (29)	−108 (45)
N(7)	14,649 (20)	25,893 (28)	34,121 (23)	272 (15)	448 (29)	367 (21)	−30 (34)	−145 (29)	222 (41)
N(8)	7,462 (19)	46,348 (27)	37,602 (22)	217 (14)	398 (29)	306 (20)	38 (32)	26 (26)	−17 (38)
N(9)	16,029 (19)	31,243 (29)	15,097 (25)	225 (14)	578 (33)	424 (23)	−19 (34)	1 (29)	−349 (46)
N(10)	1,673 (18)	31,886 (27)	23,716 (23)	183 (14)	439 (27)	347 (20)	−56 (30)	9 (26)	18 (42)
N(11)	21,837 (18)	45,108 (26)	29,328 (23)	192 (13)	341 (27)	323 (20)	4 (30)	−67 (25)	−115 (38)
O(1)	7,275 (17)	8,302 (23)	18,075 (20)	316 (13)	519 (26)	436 (19)	62 (30)	15 (25)	204 (36)

Positional Parameters Assigned to Hydrogen Atoms[b]

	Atom	x	y	z
N(7)	H(1)	1972	2524	3420
	H(2)	1290	2677	4010
	H(3)	1260	1982	3150
N(8)	H(4)	1116	5007	4060
	H(5)	543	4148	4173
	H(6)	387	5096	3567
N(9)	H(7)	1227	2990	1089
	H(8)	1827	2485	1681
	H(9)	1954	3555	1232
N(10)	H(10)	−69	3546	1904
	H(11)	−129	3209	2899
	H(12)	225	2480	2197
N(11)	H(13)	2531	4293	2505
	H(14)	2335	4313	3524
	H(15)	2150	5244	2907
O(1)	H(16)	1060	590	1530
	H(17)	840	570	2300

[a] The temperature factors are of the form $\exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$. All values have been multiplied by 10^5. [b] All values have been multiplied by 10^4. All hydrogen atoms were assigned isotropic temperature factors, $B = 5.0$ Å^2.

effects could have led to errors in the relative values of the structure factors amounting to about 4% in the extreme case. Observational variances $\sigma^2(I)$ were computed from counting statistics with an additional term $(0.02S)^2$, where S is the scan count, which we have found to be appropriate in these laboratories.[2] Two octants of data—those with k both positive and negative—were collected and averaged together to give a set of 1791 independent reflections with 2θ less than 140°. The F values were brought to an approximately absolute scale using Wilson's method.[3]

Determination and Refinement of the Structure

At the beginning, attempts were made to solve the structure by heavy-atom methods. A three-dimensional Patterson map quickly yielded the coordinates of the cobalt atoms; however, subsequent electron density maps failed to indicate the positions of the lighter atoms. Moreover, a number of severe discrepancies between observed and calculated F values made us doubt that the assignment of cobalt positions was correct; in particular, the contribution of the cobalt atoms to the extremely strong 620 reflection was almost zero. Since no other interpretation of the Patterson map was apparent, we turned our attention to direct methods of phasing.

The phase determination was carried out using the symbolic addition method[4] as applied by Long,[5] based on 255 reflections with $E \geqq 1.5$. Of the 16 solutions generated by assigning arbitrary signs to four reflections, one was outstanding, converging the most rapidly (5 cycles) and having the highest consistency index (0.85). An E map based on these signs revealed the locations of all the Co, C, and N atoms, and the initial R index $(=\Sigma|F_o - |F_c||/\Sigma F_o)$ was 0.32. A difference map then indicated an additional atom, presumably a water of hydration.

Refinement was by least squares, interspersed with difference maps from which the coordinates of the hydrogen atoms were obtained. The quantity minimized was $\Sigma w(F_o^2 - (1/k^2)F_c^2)^2$, where weights w were taken equal to the reciprocals of the observational variances $\sigma^2(F_o^2)$ (see Experimental Section). Convergence was rapid. During the last four least-squares cycles, a total of 182 parameters—a scale factor, a secondary extinction parameter,[6] and positional and anisotropic temperature parameters of all the nonhydrogen atoms—were included in a single matrix. The positions of the hydrogen atoms were adjusted

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twice on the basis of difference maps but were not included in the least-squares refinement; the hydrogen atoms were assigned isotropic temperature factors with $B = 5.0$. All calculations were carried out on an IBM 360-75 computer under the crystallographic computing system CRYM. Form factors for Co, C, N, and O were taken from ref 7, the value for cobalt being reduced by 2.19 electrons to take account of the real component of anomalous dispersion; form factors for hydrogen were from Stewart, Simpson, and Davidson.[8]

The final R index is 0.044 and the goodness of fit, $(\Sigma w(F_o^2 - F_c^2)^2/m - s)^{1/2}$, is 1.32. In the final least-squares cycle, no parameter shifted by as much as 5% of its standard deviation. The final parameters and their standard deviations are given in Table II; observed and calculated structure factors are available as indicated in ref 9. The final value for the extinction parameter g^6 was 1.12 (6) × 10^{-5}.

We note that the parameters for the cobalt atoms that we derived from the Patterson map were essentially correct and that, if we had had more courage in our convictions, we undoubtedly could have derived the complete structure by continued pursual of the heavy-atom method. In assessing the poor agreement between F_o and F_c for the $hk0$ reflections (Table III), we had underestimated the possible influence of the lighter atoms. As an example, in Figure 1 we show a structure factor map of the 620 reflection—the second strongest reflection. Whereas the cobalt atoms lie in regions of very small contribution, essentially all of the other atoms lie in regions of large negative contribution.

TABLE III

SOME F_c VALUES BASED ON FINAL PARAMETERS OF THE Co ATOMS ALONE

h k l	F_o	F_c	*h k l*	F_o	F_c
4 0 0[a]	377.86	298.31	10 2 0	153.91	22.09
4 2 0	9.63	62.55	0 4 0	62.08	213.28
6 2 0[b]	326.74	18.32	2 4 0	91.33	8.26
8 2 0	65.66	47.41			

[a] Strongest reflection. [b] Second strongest reflection.

Results and Discussion

In Figure 2 is shown a drawing of the molecule, including the bond distances. Bond angles are given in Table IV. A stereoscopic view of the molecule is shown in Figure 3.

Our results confirm that there is no mixing of NH_3 and CN ligands around the two cobalt atoms and that the bridging CN group is oriented with its carbon atom bonded to the cobalt atom with five other CN ligands. This latter result is confirmed not only by the final bond distances and temperature factors but also by difference maps and least-squares calculations carried out at various stages of the refinement. Interchange of the C

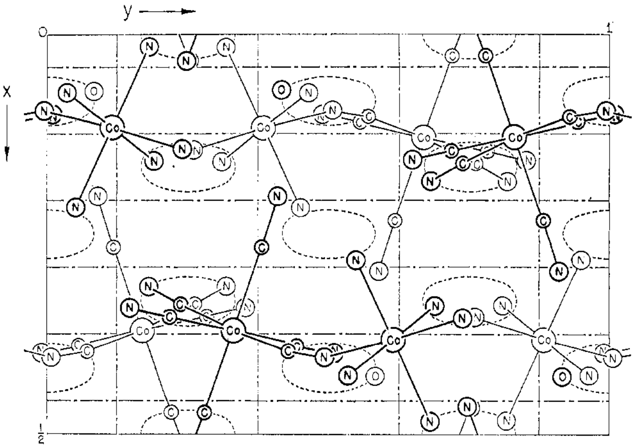

Figure 1.—Structure factor diagram of reflection 620 with a projection of the structure contents along the c axis. The ellipsoidal dashed lines represent the contours of $\cos 2\pi\ (6x) \cos 2\pi\ (2y) = -\,^1/_2$.

TABLE IV

BOND ANGLES

Atoms	Angle, deg	Atoms	Angle, deg
C(1)-Co(1)-C(2)	176.6 (2)	N(1)-Co(2)-N(7)	175.5 (1)
C(1)-Co(1)-C(3)	90.6 (2)	N(1)-Co(2)-N(8)	91.2 (1)
C(1)-Co(1)-C(4)	90.9 (2)	N(1)-Co(2)-N(9)	86.6 (1)
C(1)-Co(1)-C(5)	87.8 (2)	N(1)-Co(2)-N(10)	91.6 (1)
C(1)-Co(1)-C(6)	93.8 (2)	N(1)-Co(2)-N(11)	88.6 (1)
C(2)-Co(1)-C(3)	89.7 (2)	N(7)-Co(2)-N(8)	92.9 (1)
C(2)-Co(1)-C(4)	88.9 (2)	N(7)-Co(2)-N(9)	89.4 (1)
C(2)-Co(1)-C(5)	88.9 (2)	N(7)-Co(2)-N(10)	90.4 (1)
C(2)-Co(1)-C(6)	89.5 (2)	N(7)-Co(2)-N(11)	89.4 (1)
C(3)-Co(1)-C(4)	178.3 (2)	N(8)-Co(2)-N(9)	177.7 (1)
C(3)-Co(1)-C(5)	89.4 (2)	N(8)-Co(2)-N(10)	90.6 (1)
C(3)-Co(1)-C(6)	90.4 (2)	N(8)-Co(2)-N(11)	89.1 (1)
C(4)-Co(1)-C(5)	91.5 (2)	N(9)-Co(2)-N(10)	89.3 (1)
C(4)-Co(1)-C(6)	88.7 (2)	N(9)-Co(2)-N(11)	91.0 (1)
C(5)-Co(1)-C(6)	178.4 (2)	N(10)-Co(2)-N(11)	179.6 (1)
Co(1)-C(1)-N(1)	172.4 (3)	Co(1)-C(4)-N(4)	178.9 (4)
Co(1)-C(2)-N(2)	177.1 (3)	Co(1)-C(5)-N(5)	177.4 (3)
Co(1)-C(3)-N(3)	176.7 (3)	Co(1)-C(6)-N(6)	177.8 (4)
Co(2)-N(1)-C(1)	159.8 (3)		
H(16)-O-H(17)	95.8	H(17)-O···H(5)	105.6
H(16)-O···H(5)	105.6	H(17)-O···H(11)	105.0
H(16)-O···H(11)	139.3	H(5)···O···H(11)	94.4

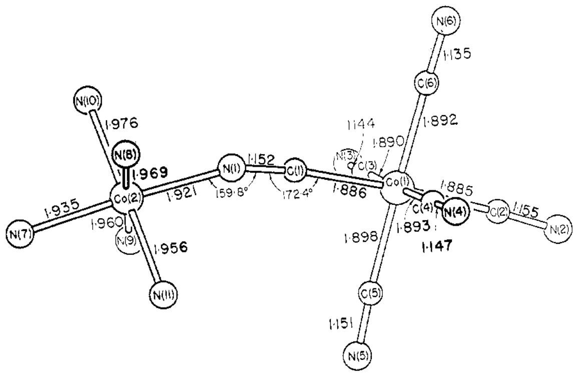

Figure 2.—A perspective drawing and the numbering scheme of the molecule of pentacyanocobalt(III)-μ-cyano-pentaamminecobalt(III).

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(7) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p 202.

(8) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(9) A listing of structure factor amplitudes will appear immediately following this article in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth Street, N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit $3.00 for photocopy or $2.00 for microfiche.

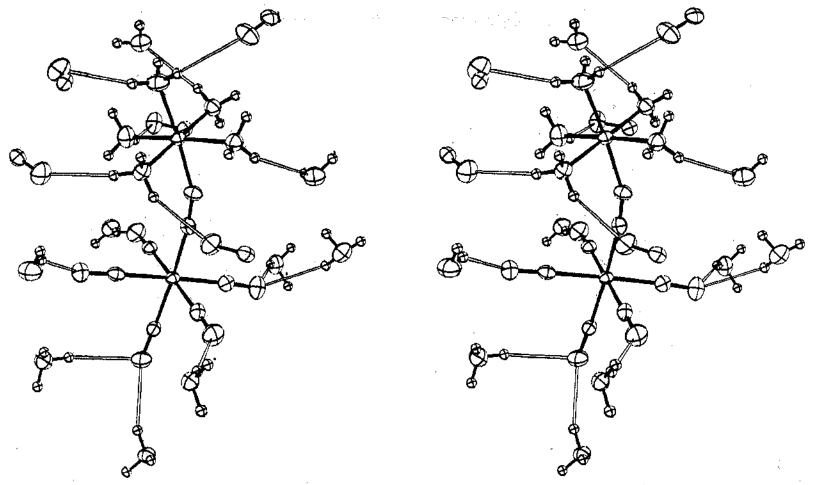

Figure 3.—A stereodrawing of the molecule and its closest neighbors (C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965). Thermal ellipsoids of the heavy atoms are drawn at the 50% probability level; the hydrogen atoms are represented as spheres of arbitrary radius $R = 0.1$ Å.

and N atoms of the bridging group invariably led to unrealistic values of the temperature factors and to residual regions of positive and negative electron density in the difference maps.

The bridging C–N distance, 1.152 (5) Å, is not significantly different from the terminal C–N bond distances, which range from 1.135 (5) to 1.154 (5) Å and average 1.146 Å; the standard deviation of a single observation is 0.007 Å. The average C–N distance, 1.147 Å, agrees well with the typical values of 1.158 Å found for the gaseous cyanides[10] and 1.14 Å for lithium cyanide[11] and with C–N distances in some of the transition metal cyanides—for example, 1.16 (2) Å in $NaFe(CN)_5NO \cdot 2H_2O$,[12] 1.15 (5) Å in $Ni(CN)_2 \cdot NH_3 \cdot {}^1/_4H_2O$,[13] and 1.15 Å in $K_3Co(CN)_6$.[14]

The six independent Co–C bond distances range from 1.884 (4) to 1.898 (4) Å and average 1.890 Å; the standard deviation of a single observation is 0.004 Å. The standard deviation is the same as that of an individual Co–C distance as estimated from the inverse matrix. The average Co–C bond distance agrees well with the result (1.89 Å) obtained from the two-dimensional neutron diffraction data on $K_3Co(CN)_6$.[14] However it is about 0.17 Å shorter than that observed in another polymorphic form of $K_3Co(CN)_6$[15] and in $Cd_3[Co(CN)_6]_2$,[16] where the Co–C distances are 2.07 and 2.05 Å, respectively (Table V).

Table V

Summary of Co–C and C–N Bond Distances in Cobalt(III) Hexacyanides

	Co–C, Å	C–N, Å	Method	Ref
$K_3Co(CN)_6$	1.89	1.15	Neutron	15
$K_3Co(CN)_6$	2.07	1.16	X-Ray	16
$Cd_3[Co(CN)_6]_2$	2.05	1.18	X-Ray	17
$(NH_3)_5CoNCCo(CN)_5$	1.890 (4)	1.146 (7)	X-Ray	This work

Such a large variation in the observed Co–C bond length among different crystals is unlikely to be correct. Considering the trend of the size variation from Fe to Co to Ni, it is unlikely that the Co–C distance should be very much different from the Fe–C and Ni–C distances. The observed Fe–C distance is 1.85 Å in $Fe(CNCH_3)_6Cl \cdot 3H_2O$,[17] 1.80 Å in *trans*-$Fe(CNCH_3)_4(CN)_2$,[18] and 1.90 (2) Å in $NaFe(CN)_5NO \cdot 2H_2O$;[12] the Ni–C distance is 1.76 Å in $Ni(CN)_2 \cdot NH_3 \cdot C_6H_6$[19] and 1.86 Å in $Ni(CN)_2 \cdot NH_3 \cdot {}^1/_4H_2O$.[13] Although some of these results are not of high accuracy, they nevertheless indicate the range of an M–C bond distance. Therefore, we believe that the distance 1.89 Å is more reasonable than 2.07 Å for a Co–C bond.

The six Co–N bonds in this structure range in length from 1.920 (3) to 1.975 (3) Å. The shortest one is the bridging Co–N bond. This bond is expected to be shorter because this nitrogen atom uses sp hybridization rather than sp^3 hybridization. Among the five Co–NH_3 bonds the axial Co–NH_3 bond (the one trans to the bridging bond), 1.935 (3) Å, is significantly shorter than the nonaxial Co–NH_3 bonds which have an average value of 1.965 (9) Å. This average value agrees well with the Co–N distance found in some other cobalt complexes—for example, 1.96 ± 0.02 Å in cobalt(III) hexamines,[20] 1.962 Å in $[(NH_3)_5Co(O_2)Co(NH_3)_5](SO_4)_2 \cdot 4H_2O$[21] and $[(NH_3)_4Co(NH_2)(O_2)Co(NH_3)_4](NO_3)_4$,[22] and 1.968 Å in $[Co(NH_3)_5Cl]Cl_2$,[23] $[Co(NH_3)_5N_3](N_3)_2$,[24] and $[Co(NH_3)_6][ZnCl_4]Cl$.[25]

The shortening of the axial Co–NH_3 bond is worth comment. We believe that this shortening (more than $3\sigma_{av}$) is outside of experimental error and is significant. X-Ray diffraction studies[23,24,26] of complexes of $Co(NH_3)_5X^{n+}$, where $X^- = Cl^-$, N_3^-, or NO_2^-, do not indicate any significant shortening or lengthening of the axial Co–N bond, as might be caused by an octa-

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TABLE VI

INTERMOLECULAR N–N OR N–O DISTANCES LESS THAN 3.2 Å

From atom A	Through	To atom B	At	Distance A···B, Å	Distance H···B, Å	Angle A–H···B, deg
N(7)	H(1)	N(2)	$^1/_2 - x, 1 - y, ^1/_2 + z$	3.10	2.25	161
	H(3)	N(3)	$x, ^1/_2 - y, ^1/_2 + z$	3.19	2.49	135
	H(2)	N(6)	$\bar{x}, -^1/_2 + y, ^1/_2 - z$	3.01	2.21	149
N(8)	H(5)	N(6)	$\bar{x}, -^1/_2 + y, ^1/_2 - z$	3.20	2.33	162
	H(6)	O(1)	$x, ^1/_2 - y, -^1/_2 + z$	3.05	2.19	163
N(9)	H(9)	N(4)	$^1/_2 - x, -^1/_2 + y, z$	3.19	2.60	125
	H(7)	N(6)	$\bar{x}, 1 - y, \bar{z}$	3.13	2.24	174
N(10)	H(12)	O(1)	x, y, z	3.13	2.26	164
N(11)	H(15)	N(2)	$x, ^3/_2 - y, ^1/_2 + z$	3.02	2.21	149
	H(13)	N(4)	$^1/_2 - x, -^1/_2 + y, z$	3.05	2.17	170
O(1)	H(17)	N(3)	$x, ^1/_2 - y, ^1/_2 + z$	2.86	2.08	170
	H(16)	N(4)	$x, -1 + y, z$	3.17	2.66	127
	H(16)	N(5)	$^1/_2 - x, -^1/_2 + y, z$	3.04	2.38	147

hedral trans effect. [A possible exception to this statement is the compound $(NH_3)_5CoO_2Co(NH_3)_5(SO_4)_2 \cdot 4H_2O$. In the cation the Co–N bond trans to the bridging O_2^{2-} group is just 3σ *longer* than the average of the other four Co–N bonds (1.983 (9) and 1.956 (9) Å).[21]] The shortening of the Co–N bond in this case indicates that there is some donation of metal dπ electrons to the vacant π^* 2p nitrogen orbital on the cyanide group; thus the metal d-electron cloud is shifted toward the cyanide group and the repulsion between the d electrons and the axial ammonia ligand is reduced. It is very likely, in this case, that the nitrogen end of the CN^- group is able to accept some dπ-electron density from a metal ion because the formal negative charge on the group has been reduced due to the coordination of the carbon end of the group to another positive metal ion. An example of this change of dπ-bonding character with the formal charge of the ion is the isocyanide group RNC, which is isoelectronic with CO and CN^- but resembles the former rather than the latter in its tendency to form π-bonding complexes with metals in a low oxidation state.

The existence of π bonding between the carbon end of a cyanide group and a metal ion has been studied by a semiempirical MO calculation[27] and was confirmed more directly by close analysis of the vibrational spectra of cyanide complexes.[28] However, X-ray measurements of metal–ligand bond lengths have never provided impressive evidence for π bonding owing to the lack of information on the length that the bond would have if it were exclusively σ in character. Also, many structural results reported are of dubious accuracy as shown by the wide spread of some of the observed bond lengths (*e.g.*, the Co–C distances as listed in Table V) and hence comparisons among different structural results are sometimes unreliable. The bridging CN^- group between two cobalt atoms in the present structure offers a good opportunity for a qualitative evaluation of the bond order between Co–NC and Co–CN bonds. The Co–CN bond is about 0.04 Å shorter than the Co–NC bond. This is opposite to what one would expect for single covalent bonds. Therefore, the bond order in Co–CN is higher than that in Co–NC which has a normal σ bond and some possible d–pπ bonding. This then is an example of crystallographic evidence for the existence of d–pπ bonding in the Co–CN bond.

One of the interesting findings in this investigation is that the Co–N–C–Co group is nonlinear. The bond angles at carbon and nitrogen are 173 and 160°, respectively. Bending of the bond around the nitrogen and/or carbon atom has been observed in numerous metal and nonmetal cyanides—for example, in the structures of $KCu_2(CN)_3 \cdot H_2O$[29] (average angle at C, 174.4°; at N, 176.7°); $Se(CN)_2$[30] (average angle 177°), and $P(CN)_3$[31] (average angle at C, 171.6°; at N, 148–155°). Except in the structure of $P(CN)_3$, most of the M–C–N or M–N–C angles are rather small. In the structure of $P(CN)_3$ the nonbonded P–N distance (2.93 Å) is shorter than the van der Waals distance (3.4 Å) and the bending at the carbon atom is said to be due to the nonlinear external interaction. The bridging cyanide in the present structure is tightly bonded to the two cobalt centers, a different situation from that in $P(CN)_3$. Thus, the large bending of this bridging bond raises a question as to whether this represents some change of the bonding character in the bridge cyanide, *i.e.*, whether there is a contribution of a structure such as $:C{=}\ddot{\bar{N}}:^-$ in addition to the structure $:\bar{C}{\equiv}N$, or whether this bending is solely due to external molecular interactions. The former possibility is not likely to be significant because it would involve a lengthening of the C–N distance. It is more likely that this bending is a result of an attempt of the molecules to achieve optimum intramolecular interactions. Contrary to most dicobalt species, the present dicobalt unit is a neutral species but with asymmetrical charge distribution (for emphasis one may write it as $(NH_3)_5Co^{3+}{-}NCCo(CN)_5^{3-}$). For electrostatic reasons alone, one might expect that these molecules would prefer a bent Co–N–C–Co grouping, so that the oppositely charged ends of the molecule could be closer together. Of course, intermolecular forces may also contribute to the bending of the molecule. It is interesting to note, though, that among the largest distortions from octahedral coordination about the Co atoms are the N(1)–Co–N(9), N(1)–Co–N(11), and C(1)–Co–C(5) angles, and these are in such a sense as to further decrease the distance between the C(5)–N(5) group and the ammonia groups N(9) and N(11) (see Figure 2).

The function of the water molecule appears to be to bridge between the positive and negative ends of the molecules whenever the geometry or arrangement does

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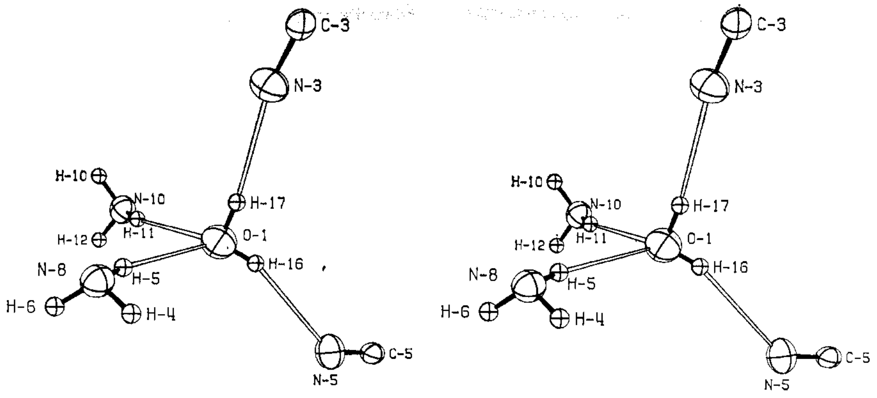

Figure 4.—A stereodrawing showing the water molecule and its closest neighbors.

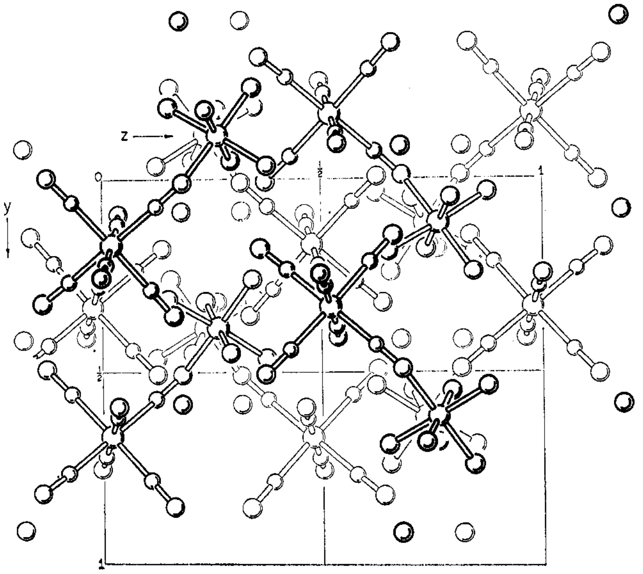

Figure 5.—A projection of the contents of one unit cell viewed along the *a* axis.

not allow them to have direct contact. As can be seen in Figure 4 the water molecules have been centered nicely in a tetrahedral environment of two cyanide and two ammonia ligands. As a result each terminal ligand of the molecule involves at least one close contact with other molecules and each molecule participates in 14 hydrogen bonds to neighboring groups. The hydrogen bonding system is described in Table VI.

Figure 5 shows a projection of the contents of one unit cell down the *a* axis.

The thermal motion of the molecule and its associated water is represented in Figure 3. Here one can see that, while all the atoms vibrate anisotropically, the motions are nowhere extreme. The cobalt atoms have small motions which are nearly isotropic. The ligand nitrogen atoms vibrate more strongly, but the major axis of vibration is nearly always roughly perpendicular to the Co–N bond. The carbon atoms have smaller amplitudes of motion but their orientation is more random. The nitrogen atoms attached to the carbon atoms vibrate more, and again the major axis is usually about perpendicular to the C–N bond. The motion of the bridging C–N group is somewhat less than that of the five cyanide ligands, as one might expect. The oxygen atom of the water molecule has nearly the largest motion of any atom in the structure but this motion is reasonably isotropic, in keeping with the fairly symmetric hydrogen bonding about it.

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