bond (C_2–C_2') that is coordinated to manganese is significantly longer than the uncoordinated bond. This increase in the length of a double bond upon coordination with a metal is most likely due to a decrease in the π-bond order.

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The Structure of Tris(ethylenediamine)chromium(III) Hexacyanocobaltate(III) Hexahydrate, $[Cr(C_2H_8N_2)_3][Co(CN)_6]\cdot 6H_2O$

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The structure of tris(ethylenediamine)chromium(III) hexacyanocobaltate(III) hexahydrate, $[Cr(C_2H_8N_2)_3][Co(CN)_6]\cdot 6H_2O$, has been determined from three-dimensional X-ray data collected by counter methods. The final R factor on F for the 1035 F^2 values above $\sigma(F^2)$ is 9.4%, and for the 735 reflections above $3\sigma(F^2)$ it is 6.1%. The material crystallizes with four molecules in space group C_{2h}^5-I2/a of the monoclinic system in a cell of dimensions a = 16.745 (20), b = 10.546 (15), c = 14.331 (20) Å, β = 96.9 (1)°. The measured and calculated densities are both 1.46 g/cm³. The site symmetry at Co is $\bar{1}$; that at Cr is 2. The structure consists of discrete $Cr(C_2H_8N_2)_3^{3+}$ cations and $Co(CN)_6^{3-}$ anions. Hydrogen bonding connects the anions, cations, and water molecules. The $Cr(C_2H_8N_2)_3^{3+}$ cation has its expected coordination geometry. For a Λ configuration of the cation the conformation of the complex is $\Lambda\lambda\lambda\lambda$. The average Cr–N, N–C, and C–C distances are 2.081 (5), 1.481 (12), and 1.489 (9) Å. The $Co(CN)_6^{3-}$ anion has its expected octahedral geometry. The average Co–C distance is 1.869 Å, although the three independent Co–C distances appear to differ slightly. The average C–N distance is 1.155 (8) Å.

Introduction

The successful isolation of the pentacyanonickelate(II) ion[1] prompted attempts[2] to isolate the $HCo(CN)_5^{3-}$ ion and the $Co(CN)_5^{3-}$ ion by precipitation with a large counterion of charge +3. The decomposition of $Co(CN)_5^{3-}$ ion in aqueous solutions is apparently catalyzed by $Cr(en)_3^{3+}$ (en = $NH_2CH_2CH_2NH_2$ = $C_2H_8N_2$).[3] Attention was therefore focused on the $HCo(CN)_5^{3-}$ ion.[4] Yellow crystals of what was believed to be the $Cr(en)_3^{3+}$ salt of $HCo(CN)_5^{3-}$ were isolated. Chemical analysis of this compound did not definitely distinguish among the $Co(CN)_5(OH)^{3-}$, $HCo(CN)_5^{3-}$, and $Co(CN)_6^{3-}$ salts, particularly since the exact number of waters of hydration was uncertain to within $\pm 1/2 H_2O$.

An infrared band at 2030 cm^{-1}, which disappeared upon deuteration, was interpreted as a Co–H stretching mode. The $Cr(en)_3^{3+}$ salts of $Co(CN)_5(OH)^{3-}$ and $Co(CN)_6^{3-}$ were prepared by combining their aqueous solutions at room temperature. In both cases the infrared spectra of the resulting compounds were very different from what was believed to be the hydride salt. At this point, in an attempt to supplement the chemical and spectroscopic information at hand, we undertook a rapid X-ray determination of the structure of the compound. This determination proved that the material is $[Cr(en)_3][Co(CN)_6]\cdot 6H_2O$. This salt has subsequently been made by the more direct method of combining aqueous $[Cr(en)_3]Cl_3$ and $K_3[Co(CN)_6]$ solutions. The hexahydrate is obtained only at low temperatures and rapidly effloresces when opened to the air. The infrared spectrum of the compound prepared in this way is identical, including the band at 2030 cm^{-1}, with that of what was initially characterized as the hydride. When the first few waters of hydration are lost, this band disappears, and those bands which correspond to C–N stretching vibrations change markedly.

Even though the material prepared was not the one hoped for, we persisted with the refinement of the structure for the following reasons. First, we found earlier that the conformations of the two independent tris(ethylenediamine)chromium(III) ions in the pentacyanonickelate(II) salt were different[5] from that found previously (and generally believed to be most stable). We postulated that hydrogen bonding specifically favors these different conformers. Since the present hexahydrate salt should exhibit considerable hydrogen bonding, it seemed of interest to determine the conformation of the tris(ethylenediamine)chromium(III) in the present structure. Second, there are no reliable data for any of the hexacyanides[6] and it was therefore

(1) K. N. Raymond and F. Basolo, *Inorg. Chem.*, **5**, 949 (1966).

(2) K. N. Raymond and F. Basolo, Proceedings of the Nara Meeting on Synthetic and Stereochemical Aspects of Coordination Chemistry, Nara, Japan, 1967, p 17.

(3) F. Basolo, *Coord. Chem. Rev.*, in press.

(4) See M. G. Burnett, P. J. Connolloy, and C. Kemball, *J. Chem. Soc., A*, 800 (1967), and references therein.

(5) K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *Inorg. Chem.*, **7**, 1362 (1968).

(6) D. Britton in "Perspectives in Structural Chemistry," Vol. 1, J. D. Dunitz and J. A. Ibers, Ed., John Wiley and Sons, Inc., New York, N. Y., 1967, p 109.

of interest to complete this structure in order to provide such information.

Unit Cell Data and Collection of Intensities

On the basis of precession photographs taken with Mo Kα radiation from a crystal sealed in a capillary, the material was assigned to the monoclinic system. The systematic absences found on the $h0l$–$h2l$ and the $hk0$–$hk2$ photographs are: hkl, $h + k + l \neq 2n$; $h0l$, $h \neq 2n$. These extinctions are consistent with the space groups C_{2h}^6-I2/a and C_s^4-Ia. The cell parameters, as determined from these photographs, are a = 16.745 (20), b = 10.546 (15), c = 14.331 (20) Å, β = 96.9 (1)°. The cell parameters were obtained at 25°; the wavelength of Mo Kα was taken as 0.7107 Å. The errors are estimates based on consistencies among the various photographs. The density observed by flotation in carbon tetrachloride–toluene solutions was 1.46 (2) g/cm^3. The density calculated for the final composition is 1.46 g/cm^3 for four molecules in the unit cell. The order of I2/a, the space group confirmed by the successful structure analysis, is 8. Thus the site symmetry of the metal atoms must be 2 or $\bar{1}$. The Cr of the tris(ethylenediamine) ion could lie on the twofold axis. Packing considerations eliminate the possibility that the Co could also lie on the twofold axis, and so it must, of necessity, lie at the center of symmetry. If the complex had contained the $HCo(CN)_5^{3-}$ ion, as we had hoped, this ion would necessarily have been disordered.

A needlelike crystal approximately 0.9 mm long and of cross section 0.16 × 0.14 mm was mounted approximately along the needle axis (a) on a eucentric goniometer head. Data were collected with Mo Kα radiation by methods previously described[7,8] on a Picker four-circle automatic X-ray diffractometer. The pulse-height analyzer was set to admit about 90% of the Mo Kα window. The diffracted beams were filtered through 3.0 mils of Zr foil. The counter aperture, a square 7 mm on an edge, was placed 30 cm from the crystal. The takeoff angle was 1.5°. Data were collected by the θ–2θ scan technique. The peaks were scanned from −0.8 to +1.7° in 2θ from the Bragg angle. The scan rate was 2°/min. Background counts at each end of the scan were taken for 4 sec. Intensity data were collected for a single set of the 1592 unique reflections within the range θ(Mo Kα) $\leq$ 20°. Intensities of four standard reflections were monitored during the run; there was no change in their intensities. The entire process of data collection required only 2.5 days.

The data were processed in the manner previously described.[7,8] The value of p used in the estimation of standard deviations of the intensities was 0.05. Of the 1592 reflections, 1035 had $I \geq \sigma(I)$, and 735 had $I \geq 3\sigma(I)$. The linear absorption coefficient for Mo Kα radiation is 11.69 cm^{-1}. After the composition of the material had been established from solution of the structure, tests were made to determine the possible effects of absorption on the data. Transmission coefficients of selected reflections ranged from 0.83 to 0.87 and so no absorption correction was applied.

Solution and Refinement of the Structure

A three-dimensional Patterson function was computed.[9] A suitable interpretation of the function involved the assumption of space group I2/a, rather than Ia, with one metal atom placed at the origin (center of symmetry) and another metal atom placed on the twofold axis at $^1/_4$, y, $^1/_2$ with y nearly zero. The general positions of space group I2/a are: $(0, 0, 0; {}^1/_2, {}^1/_2, {}^1/_2) \pm (x, y, z; {}^1/_2 - x, y, \bar{z})$. This model was refined by least-squares methods. In this and subsequent calculations the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes. The weights w were taken as $4F_o^2/\sigma^2(F_o^2)$. The atomic scattering factors tabulated by Ibers[10] for O, N, and C were used; those of Cromer and Waber[11] were used for Cr and Co and those of Stewart, *et al.*,[12] for H. The effects of anomalous dispersion were included in F_c;[13] the values of f' and f'' calculated by Cromer[14] for Cr and Co were employed. This refinement of the two metal atoms along with the over-all scale factor converged to values of R_1 and R_2 of 41 and 46% for the 1035 reflections above $\sigma(I)$, where $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and where the weighted R factor or $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2}$.

A difference Fourier map computed at this point clearly showed the positions of all remaining nonhydrogen atoms. To our disappointment the anion appeared to be $Co(CN)_6^{3-}$, rather than a disordered $HCo(CN)_5^{3-}$ anion. Subsequent refinements were carried out on the 735 reflections above $3\sigma(I)$. Refinement of all nonhydrogen atomic positions and isotropic thermal parameters converged to values of R_1 and R_2 of 10.0 and 12.6%. A subsequent difference Fourier map clearly indicated that no heavy atoms remained to be found and that those atoms already found were vibrating anisotropically. A subsequent refinement in which these atoms were allowed to vibrate anisotropically converged to values of R_1 and R_2 of 7.3 and 9.6%. The calculated hydrogen positions[5] on the ethylenediamine rings were next included as fixed contributions to the structure factors. An isotropic thermal parameter of 3 Å^2 was assigned to these hydrogen atoms. Subsequent refinement of the nonhydrogen parameters converged to values of R_1 and R_2 of 6.2 and 7.4%. A difference Fourier map computed at this point showed peaks up to 0.74 e$^-$/Å^3. The positions of some of the hydrogen atoms of the water molecules could be predicted from geometrical considerations. Indeed, the difference

(7) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

(8) R. J. Doedens and J. A. Ibers, *ibid.*, **6**, 204 (1967).

(9) In addition to various local programs for the CDC 3400 computer, local modifications of the following programs were employed: Zalkin's FORDAP Fourier program, the Levy–Busing ORFLS least-squares and ORFFE error function programs, and the Johnson ORTEP thermal ellipsoid plotting program.

(10) J. A. Ibers, "International Tables for X-Ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England, 1962, Table 3.3.1A.

(11) D. T. Cromer and J. T. Waber, *Acta Cryst.*, **18**, 104 (1965).

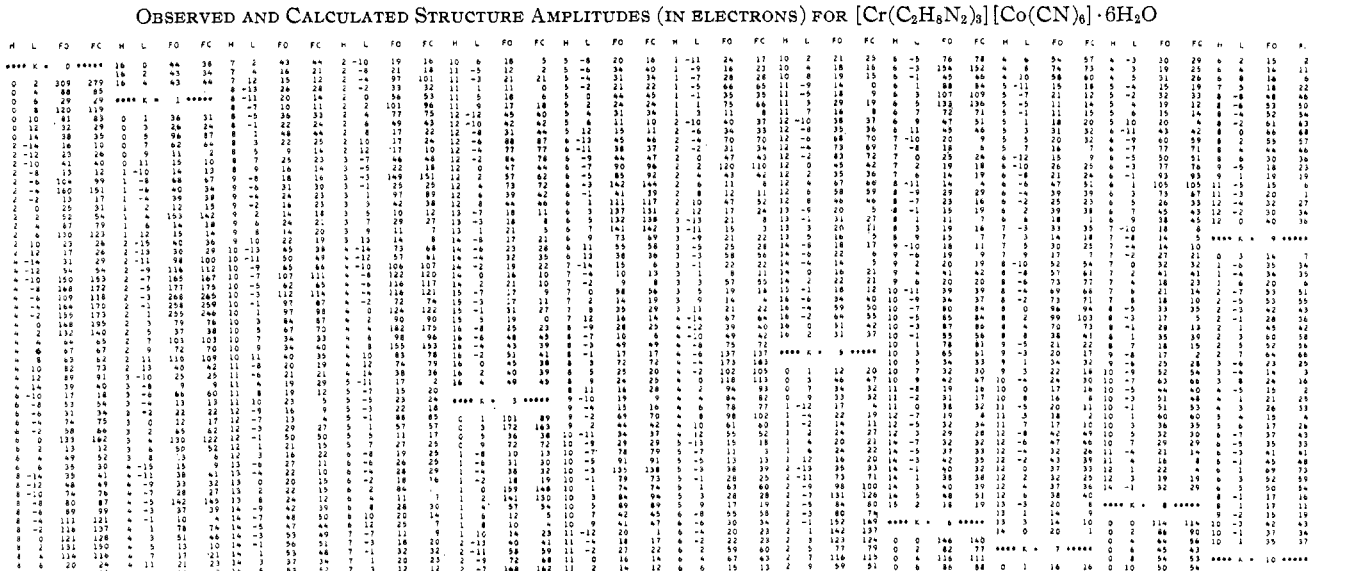
(12) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(13) J. A. Ibers and W. C. Hamilton, *Acta Cryst.*, **17**, 781 (1964).

(14) D. T. Cromer, *ibid.*, **18**, 17 (1965).

TABLE I

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (IN ELECTRONS) FOR $[Cr(C_2H_8N_2)_3][Co(CN)_6]\cdot 6H_2O$



map showed peaks corresponding to some of these predicted positions. Five of the six hydrogen atoms on the three independent water molecules were located by this process and their positions were idealized for subsequent calculations. The second hydrogen atom on water molecule O_2 could not be located. Its position was not evident when bond distance and angle calculations involving the 20 highest peaks on this difference map were made. Apparently this hydrogen does not enter into hydrogen bonding.

When the fixed contributions to the structure factors of these five hydrogen atoms of the water molecules were included in the calculations, the refinement converged to values of R_1 and R_2 of 6.1 and 7.2%. In a final round of calculations all 1035 intensities above $\sigma(I)$ were included. There were no significant shifts from the parameters found using only those data above $3\sigma(I)$, but the standard deviations on the parameters were slightly lower. The final values of R_1 and R_2 are 9.4 and 8.2%. This increase in the value of R_2 suggests that we may have overweighted the weaker reflections. No change of weights was made, as we do not feel this is justified, since the data set was collected as rapidly as possible and without the benefit of dependent reflections that would enable better weights to be assigned. The final value of the error in an observation of unit weight is 1.94; clearly the weights are not on an absolute scale.

In Table I we list the values of $|F_o|$ and $|F_c|$, in electrons, for those reflections above $\sigma(I)$. Table II lists the final atomic parameters. Table III lists the hydrogen atom positions used in the calculations. Table IV lists the root-mean-square amplitudes of vibration of the nonhydrogen atoms.

Description of the Structure

The structure consists of the packing of discrete $Cr(en)_3^{3+}$ and $Co(CN)_6^{3-}$ ions. A packing diagram of the cations and anions is shown in Figure 1. The packing approximates a primitive cubic lattice array. Both cations and anions are surrounded by an approximately cubic array of eight oppositely charged ions. The Co atom, with $\bar{1}$ (C_i) site symmetry, has Cr atoms 6.68, 6.78, 7.85, and 8.72 Å away. The Cr atom, with 2 (C_2) site symmetry, has, of course, Co atoms at the same distances.

The $Cr(en)_3^{3+}$ and $Co(CN)_6^{3-}$ ions are linked by hydrogen bonds. The three independent water molecules also take part in hydrogen bonding. These hydrogen bonds are listed in Table V. A stereoscopic drawing of the hydrogen-bonding scheme is shown in Figure 2. All twelve of the $Cr(en)_3^{3+}$ amine hydrogen atoms participate in hydrogen bonds. The $Co(CN)_6^{3-}$ ions are linked together by water oxygen atoms O_1 and O_3. As mentioned earlier, apparently one of the hydrogen atoms on water oxygen O_2 does not participate in hydrogen bonding, as O_2 has only one distance to a possible base that is less than 3.31 Å. The $Co(CN)_6^{3-}$ ions uppermost in Figure 2 are 6.68 Å from the central $Cr(en)_3^{3+}$ ion. The lower $Co(CN)_6^{3-}$ ions are at a dis-

TABLE II

POSITIONAL AND THERMAL PARAMETERS FOR $[Cr(C_2H_8N_2)_3][Co(CN)_6]\cdot 6H_2O$[a]

Atom	x	y	z	β_{11}[b]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	0	0	0	284 (9)	553 (24)	333 (13)	−11 (16)	24 (8)	−60 (19)
Cr	1/4	−61 (3)	1/2	375 (12)	514 (29)	318 (15)	0	30 (10)	0
O_1	2264 (5)	−6 (9)	−2298 (5)	550 (42)	1810 (126)	426 (49)	303 (69)	36 (34)	53 (81)
O_2	617 (5)	−1129 (9)	−3703 (5)	816 (55)	1724 (142)	551 (60)	23 (74)	112 (47)	−210 (76)
O_3	988 (9)	2019 (10)	2725 (7)	2267 (128)	1153 (138)	967 (92)	240 (104)	−759 (79)	−218 (88)
N_1	601 (7)	251 (12)	−1882 (8)	536 (56)	1974 (200)	605 (78)	−105 (85)	123 (55)	97 (112)
N_2	610 (7)	2669 (11)	533 (9)	486 (60)	899 (143)	1151 (103)	−203 (77)	116 (60)	−168 (102)
N_3	1609 (6)	−1040 (11)	814 (7)	412 (54)	1199 (155)	767 (85)	125 (77)	−110 (56)	−261 (92)
C_1	366 (7)	144 (13)	−1160 (9)	421 (57)	1126 (173)	521 (81)	−21 (95)	86 (56)	83 (130)
C_2	375 (6)	1669 (12)	321 (8)	174 (46)	814 (163)	572 (83)	−226 (76)	−39 (48)	25 (92)
C_3	988 (7)	−634 (11)	521 (9)	333 (59)	661 (139)	591 (91)	40 (80)	205 (64)	−116 (91)
N_4	1265 (5)	−178 (8)	4605 (6)	342 (39)	684 (117)	523 (58)	26 (61)	41 (39)	−83 (76)
N_5	2492 (6)	−1415 (8)	6048 (6)	498 (51)	517 (114)	378 (61)	47 (60)	−19 (45)	12 (65)
N_6	2350 (5)	1432 (8)	5920 (6)	539 (52)	627 (119)	263 (55)	107 (61)	4 (43)	−71 (64)
C_4	1091 (7)	−863 (12)	3712 (9)	418 (60)	908 (166)	574 (89)	−214 (84)	−103 (59)	−29 (100)
C_5	1692 (8)	−1911 (11)	3693 (9)	563 (71)	692 (146)	595 (89)	−230 (88)	47 (63)	−369 (93)
C_6	2627 (8)	2648 (10)	5513 (7)	628 (73)	377 (131)	512 (76)	−5 (80)	43 (65)	−112 (77)

[a] The positional parameters and their estimated standard deviations have been multiplied by 10^4; the thermal parameters and their estimated standard deviations have been multiplied by 10^5. [b] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

TABLE III

CALCULATED POSITIONS OF HYDROGEN ATOMS[a]

Atom	10^3x	10^3y	10^3z	Atom	10^3x	10^3y	10^3z
N_4H_1	103	73	453	C_5H_2	159	−264	420
N_4H_2	101	−64	513	C_6H_1	237	344	584
N_5H_1	290	−213	419	C_6H_2	328	271	565
N_5H_2	271	−100	337	O_1H_1	175	1004	789
N_6H_1	268	125	655	O_1H_2	260	967	821
N_6H_2	175	151	600	O_2H_1	61	933	695
C_4H_1	114	−24	313	O_3H_1	82	294	293
C_4H_2	50	−127	366	O_3H_2	82	217	202
C_5H_1	166	−233	301				

[a] An isotropic thermal parameter of 3 Å^2 was assigned to these fixed hydrogen atoms in the structure factor calculations.

TABLE IV

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (Å) ($\times 10^3$)

Atom	Min	Inter-med	Max	Atom	Min	Inter-med	Max
Co	167 (5)	193 (4)	201 (3)	C_1	220 (22)	246 (17)	258 (23)
Cr	170 (5)	181 (4)	230 (4)	C_2	109 (31)	228 (19)	260 (18)
O_1	208 (12)	247 (13)	345 (12)	C_3	159 (23)	207 (20)	268 (20)
O_2	224 (14)	320 (13)	339 (12)	N_4	189 (17)	219 (13)	238 (13)
O_3	233 (16)	264 (15)	621 (16)	N_5	169 (19)	194 (16)	271 (13)
N_1	237 (16)	276 (15)	338 (16)	N_6	156 (18)	188 (17)	282 (13)
N_2	197 (19)	277 (16)	347 (16)	C_4	174 (23)	239 (20)	293 (18)
N_3	216 (17)	232 (18)	330 (15)	C_5	127 (28)	271 (17)	300 (19)
				C_6	138 (26)	234 (17)	298 (17)

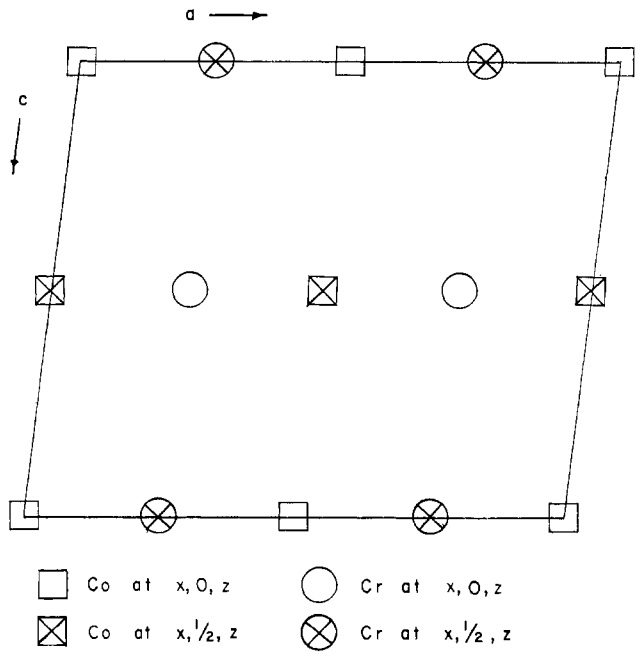


Figure 1.—Packing diagram of $Cr(en)_3^{3+}$ cations and $Co(CN)_6^{3-}$ anions in $[Cr(en)_3][Co(CN)_6]\cdot 6H_2O$.

tance of 6.78 Å from this ion. For visual clarity only a few of the symmetry-related water oxygens are shown in Figure 2. The positions of others are easily visualized since the Co atoms lie at centers of symmetry and the Cr atom lies on a twofold axis. Nonoxygen atoms in Figure 2 may be identified by reference to Table V.

The $Cr(en)_3^{3+}$ cation is shown in Figure 3. Important bond distances and angles, together with standard deviations estimated from the inverse matrix, are given in Table VI. Since the space group is centrosymmetric, optically active $Cr(en)_3^{3+}$ ions of the Λ and Δ configurations occur in equal numbers in the structure. The ion shown in Figure 3 is arbitrarily chosen to have the Λ configuration. The conformation of the cation rings is ΛΛΛ. According to the calculations of Corey and Bailar[15] this particular conformer should be the highest in energy. Elsewhere we discuss the role of hydrogen bonding in stabilizing this and other high-energy conformers.[16] The Cr–N distances do not differ significantly and they average 2.081 (5) Å. This may be compared with the average Cr–N distance of 2.075 (3) Å from the two independent $Cr(en)_3^{3+}$ ions in the $Ni(CN)_5^{3-}$ salt.[5] Similarly the N–C and C–C distances found here agree very well with those reported for the $Ni(CN)_5^{3-}$ salt.[5] The comparative values are N–C = 1.481 and 1.490 Å; C–C = 1.489 and 1.502 Å. Since the conformations of these three ring systems are different, it appears that the bond distances within the rings

(15) E. J. Corey and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **81**, 2620 (1959).
(16) K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *Inorg. Chem.*, **7**, 842 (1968).

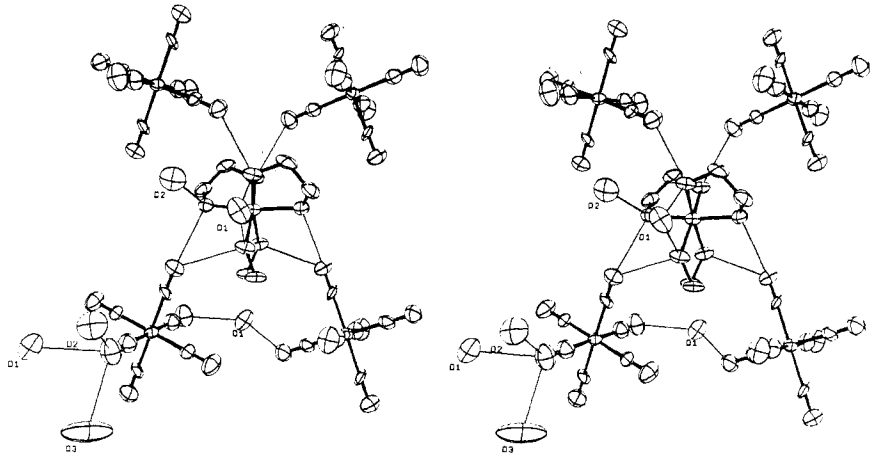


Figure 2.—Stereoscopic pair showing the hydrogen bonds in $[Cr(en)_3][Co(CN)_3]\cdot 6H_2O$. The horizontal axis is *a;* the vertical axis is *b*. The two $Co(CN)_6^{3-}$ anions uppermost in the drawing are one cell translation along *b* above the lower anions. The twofold axis relates the $Co(CN)_6^{3-}$ anions on the left to those on the right.

TABLE V

POSSIBLE A–H···B BONDS WITH A···B DISTANCES LESS THAN 3.21 Å

A	B	H	A–B	Angle around H, deg
N_4	O_2	H_2	2.948 (12)	165
N_4	N_2	H_1	3.213 (13)	137
N_5	O_1	H_2	2.862 (12)	160
N_5	N_3	H_1	3.063 (13)	155
N_6	O_1	H_1	2.988 (12)	125
N_6	N_2	H_2	3.050 (13)	148
O_1	N_1	H_1	2.930 (14)	172[a]
O_1	N_3	H_2	2.883 (13)	174[a]
O_2	N_1	H_1	2.991 (13)	177[a]
O_3	N_1	H_1	3.019 (13)	170[a]
O_3	N_2	H_2	3.202 (13)	172[a]

[a] These angles were made close to 180° when assigning the positions of the water H atoms.

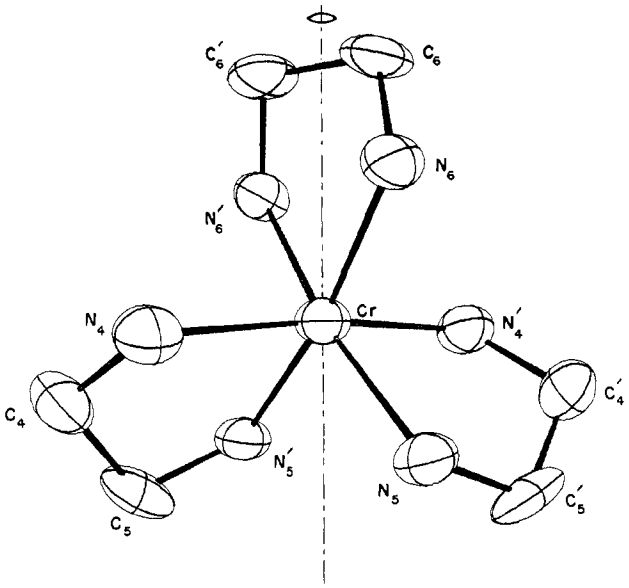


Figure 3.—A perspective drawing of the tris(ethylenediamine)-chromium(III) cation in $[Cr(en)_3][Co(CN)_6]\cdot 6H_2O$. The contours represent 50% probability of thermal motion. The cation is shown in its Λ configuration about the Cr. The conformation is ΛΛΛΛ. The crystallographic 2 axis is shown.

TABLE VI

IMPORTANT BOND DISTANCES AND ANGLES[a]

Atoms	Distance, Å	Atoms	Angle, deg
$Co-C_1$	1.846 (13)	C_1-Co-C_2	90.33 (54)[b]
$Co-C_2$	1.906 (12)	C_1-Co-C_3	90.91 (51)[b]
$Co-C_3$	1.856 (13)	C_2-Co-C_3	89.06 (53)[b]
$Co-N_1$	3.001 (12)	$Co-C_1-N_1$	179.0 (13)
$Co-N_2$	3.060 (12)	$Co-C_2-N_2$	178.5 (12)
$Co-N_3$	3.011 (11)	$Co-C_3-N_3$	177.6 (11)
C_1-N_1	1.155 (13)	$Cr-N_4-C_4$	110.7 (7)
C_2-N_2	1.154 (13)	$Cr-N_5'-C_5$	110.7 (7)
C_3-N_3	1.156 (13)	$Cr-N_6-C_6$	109.4 (6)
$Cr-N_4$	2.081 (8)	$N_4-C_4-C_5$	108.5 (8)
$Cr-N_5$	2.074 (9)	$N_5'-C_5-C_4$	109.8 (9)
$Cr-N_6$	2.088 (9)	$N_6-C_6-C_6'$	108.7 (7)
$Cr-C_4$	2.940 (11)		
$Cr-C_5$	2.922 (11)	N_4-Cr-N_4'	173.2 (5)
$Cr-C_6$	2.952 (11)	N_4-Cr-N_5	93.6 (4)
		N_4-Cr-N_5'	81.7 (3)
N_4-C_4	1.468 (13)	N_4-Cr-N_6	91.4 (4)
N_5-C_5'	1.469 (13)	N_4-Cr-N_6'	93.7 (3)
N_6-C_6	1.506 (13)	N_5-Cr-N_5'	92.9 (5)
C_4-C_5	1.497 (16)	N_5-Cr-N_6	92.9 (3)
C_6-C_6'	1.480 (16)	N_5-Cr-N_6'	171.2 (4)
		N_6-Cr-N_6'	82.1 (5)

[a] The primed atoms are related to those in Table II by the twofold operation. [b] The second angles of this type are supplements of the values given.

are essentially independent of the conformation, as is expected.

The $Co(CN)_6^{3-}$ ion is displayed in Figure 4. The ion has its expected octahedral geometry, as can be discerned from Figure 4 and the data of Table VI. Table VII lists the best weighted least-squares planes through the various atoms of the $Co(CN)_6^{3-}$ anion. None of the atoms listed differs significantly from the planes. The three independent Co–C distances appear to differ slightly. Correction of these distances for either the riding or the independent model[17] does not reduce the discrepancy between $Co-C_2$ and the other Co–C distances. Their average value is 1.869 Å. This value may be compared with that of 1.89 Å from a neutron

(17) W. R. Busing and H. A. Levy, *Acta Cryst.*, **17**, 142 (1964).

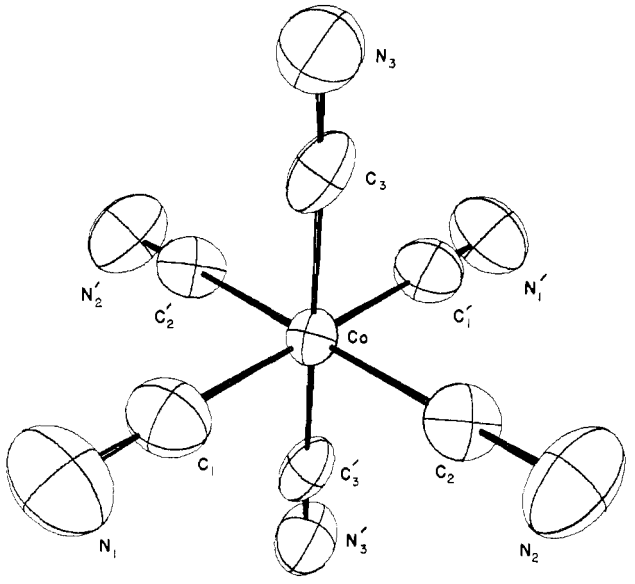


Figure 4.—A perspective drawing of the hexacyanocobaltate(III) anion in $[Cr(en)_3][Co(CN)_6] \cdot 6H_2O$ down one of the molecular $\bar{3}$ axes.

diffraction study of $K_3Co(CN)_6$.[18] It is difficult to gauge the accuracy of this determination, for atomic parameters were determined from positions that overlapped in projection. Nevertheless, a Co–C bond length of 1.89 Å seems much more reasonable in view of the results reported here than does the value of 2.07 Å reported for another form of the potassium salt.[19] The average C–N distance in the present structure is 1.155 (8) Å; this is in excellent agreement with the value of 1.156 (4) Å obtained from the average of the ten independent C–N distances in the $Ni(CN)_5^{3-}$ salt.[5] One can see from Figure 4 that the outer atoms are vibrating with greater amplitude than the atoms directly attached to Co. This, of course, is physically reasonable in view of the expected librational and torsional modes in the solid. If one assumes that the linkage is Co–N–C, rather than Co–C–N, then this trend is reversed and the atoms directly attached to Co show the greatest thermal amplitudes. Such a result is physically unreasonable. Thus there is strong evidence that the linkage is Co–C–N. In $K_3Co(CN)_6$[18] the linkage is known to be Co–C–N from the neutron diffraction study.

(18) J. A. Kohn and W. D. Townes, *Acta Cryst.*, **14**, 617 (1961).
(19) Y. Okaya and R. Pepinsky, Abstracts, American Crystallographic Association, French Lick, Ind., 1956, paper I-6.

TABLE VII

Best Weighted Least-Squares Planes through the $Co(CN)_6^{3-}$ Anion with the Equation of Planes of the Form $AX + BY + CZ = D$ (Monoclinic Coordinates)

Atoms	Plane no.	A	B	C	D[a]
N_1, N_2, C_1, C_2	1	14.01	−4.09	4.06	−0.002
N_2, N_3, C_2, C_3	2	7.32	0.90	−13.49	−0.002
N_1, N_3, C_1, C_3	3	4.90	9.78	2.81	0.0004

Distance of Atoms from Planes (Å)

Atom	Plane no. 1	Plane no. 2	Plane no. 3
N_1	−0.003 (11)		0.007 (12)
N_2	0.003 (12)	−0.011 (12)	
N_3		0.009 (11)	−0.004 (11)
C_1	0.004 (12)		−0.009 (13)
C_2	−0.004 (11)	0.014 (11)	
C_3		−0.014 (11)	0.007 (12)

[a] The value of D is the distance in ångströms of Co from these planes.

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