A stereoscopic view of the packing of the complexes is shown in Figure 4. The complexes are arranged in layers perpendicular to *b* with all the peroxy groups on one side and the pyridine rings on the other. The distances between O(8) and O(1″) of the neighboring complex (2.74 ± 0.01 Å), between O(8) and the uncoordinated water molecule O(9) (2.71 ± 0.01 Å), and between O(2) and O(9) (2.71 ± 0.01 Å) are in the range to suggest hydrogen bonding, and the angles around O(1), O(2), O(8), and O(9) support this evidence. The hydrogen-bonded layers are stacked in such a way that alternatively either their peroxy sides or their pyridine sides face each other. The potassium ions are in the holes between layers the peroxy sides of which point at each other. K(1), the ion sitting on the twofold axis, is in a cavity with six nearest oxygen neighbors at 2.81–2.88 Å and five more oxygen neighbors at 3.12–3.30 Å. However, the disordered ion K(2) occupying a general eightfold position with half occupancy is rather irregularly surrounded by eight oxygens, the K(2)–O distances ranging uniformly from 2.81 to 3.64 Å. The large temperature factors for this ion and the residual electron density found on its fringes in the final difference-Fourier map suggest that the ion is sitting in a hole too large for its size and may be disordered in the hole.

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The Crystal and Molecular Structure of Tris(ethylenediamine)cobalt Pentacyanonitrosylchromate Dihydrate, $[Co(C_2H_8N_2)_3][Cr(CN)_5(NO)]\cdot 2H_2O$

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The structure of tris(ethylenediamine)cobalt pentacyanonitrosylchromate dihydrate $[Co(C_2H_8N_2)_3][Cr(CN)_5(NO)]\cdot 2H_2O$ has been determined from three-dimensional X-ray diffraction data collected by counter methods. The material crystallizes in the space group C_{2h}^5-$P2_1/c$ with four molecules in a cell of dimensions $a = 13.47$ (2), $b = 11.59$ (1), $c = 13.39$ (2) Å, and $\beta = 100.5$ (1)°. Both the observed and calculated densities are 1.58 g cm^{-3}. Least-squares refinement of the structure has led to a final value of the conventional R factor of 0.053 for the 1106 observed data having $F^2 \geq 3\sigma(F^2)$. The structure consists of discrete $Co(C_2H_8N_2)_3^{3+}$ cations and $Cr(CN)_5(NO)^{3-}$ anions. A network of hydrogen bonds connects the cations, anions, and water molecules. The $Cr(CN)_5(NO)^{3-}$ anion is ordered, and the NO ligand is unambiguously distinguished from the CN ligands. The symmetry of the anion is nearly $4mm$-C_{4v}. The Cr–N distance is 1.71 (1) Å and the N–O distance is 1.21 (1) Å. The Cr–N–O angle is 176 (1)°. The average equatorial Cr–C distance is 2.033 (7) Å, and the axial Cr–C distance is 2.075 (14) Å; the average C–N distance is 1.158 (7) Å. The Co atom of the cation has the expected trigonally distorted octahedral coordination environment. For a Λ configuration of the cation the conformation of the complex is $\Delta\partial\lambda\lambda$.

Introduction

In recent years there has been considerable interest in the molecular and electronic structure of transition metal pentacyanonitrosyls of the general formula $M(CN)_5(NO)^{n-}$. An X-ray structure determination[2] showed that the nitroprusside anion, $Fe(CN)_5(NO)^{2-}$, has approximate $4mm$-C_{4v} symmetry. The electronic and electron spin resonance (esr) spectra of several other pentacyanonitrosyl anions were subsequently interpreted[3] on the basis of C_{4v} symmetry, and a general molecular orbital bonding scheme was proposed for the anions. Of particular interest to us was the $Cr(CN)_5(NO)^{3-}$ anion. Although the anion was assumed to have C_{4v} symmetry for the molecular orbital calculations, the esr spectrum of the anion shows an anisotropic ^{14}N hyperfine splitting. McGarvey and Pearlman[4] have interpreted this as indicative of a nonlinear Cr–N–O moiety. Other workers have also postulated a bent Cr–N–O linkage[5] but subsequently reinterpreted[6] their data as favoring linear attachment of the NO group. An X-ray structure determination[7] has been reported for $K_3Cr(CN)_5(NO)$. Unfortunately the crystal structure is disordered so that the CN and NO ligands are statistically distributed about the six coordination positions. Although the Cr–N–O group appeared linear, such might not be the case. Moreover, the disorder precluded obtaining accurate Cr–N and N–O distances.

In order to establish conclusively the coordination geometry of the $Cr(CN)_5(NO)^{3-}$ anion in an ordered

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crystal and to obtain accurate distances and angles, we have determined the crystal structure of tris(ethylenediamine)cobalt pentacyanonitrosylchromate dihydrate.[8] The structure of this compound is of further interest in view of recent proposals[9] relating the conformation of ethylenediamine (en) rings to hydrogen bonding.

Experimental Section

A solution of 0.16 g (0.5 mmol) of potassium pentacyanonitrosylchromate[10] in 15 ml of water was added to a solution of 0.25 g (0.5 mmol) of tris(ethylenediamine)cobalt(III) iodide monohydrate[11] in 10 ml of water, and the resulting solution was allowed to stand overnight. Tris(ethylenediamine)cobalt pentacyanonitrosylchromate dihydrate precipitated as thin amber-colored plates, and suitable crystals were collected and used without further purification. The infrared spectrum of the product had an NO stretching frequency (KBr pellet) of 1660 $\mathrm{cm^{-1}}$. This compares with an NO stretching frequency of 1630 $\mathrm{cm^{-1}}$ in $K_3Cr(CN)_5(NO)$.[12]

Preliminary precession and Weissenberg photographs taken with Mo Kα radiation indicated that the crystals are monoclinic. The systematic absences, $h0l$ when $l \neq 2n$ and $0k0$ when $k \neq 2n$, are consistent with the space group C_{2h}^5-$P2_1/c$. At 22 ± 1° the unit cell parameters are a = 13.47 (2), b = 11.59 (1), c = 13.39 (2) Å, and β = 100.5 (1)°. These parameters were determined from least-squares refinement of the setting angles for 12 reflections that had been automatically centered on a Picker FACS-I computer-controlled four-circle diffractometer. In this refinement the wavelength of Mo K$\bar{\alpha}$ radiation was taken as 0.71069 Å. The crystal density, determined as 1.58 (2) g $\mathrm{cm^{-3}}$ by flotation in carbon tetrachloride–bromobenzene mixtures, is in good agreement with that of 1.58 g $\mathrm{cm^{-3}}$ calculated for four formula units per cell. Thus, no crystallographic symmetry conditions need be imposed on the anion or cation.

For data collection a crystal having dimensions 0.03 × 0.18 × 0.35 mm was mounted along the long axis (the crystallographic b axis). The plate faces were {100}. An initial data set of nine levels ($h0l$–$h8l$) was collected on a Supper-Pace automated diffractometer employing Weissenberg geometry, with Zr-filtered Mo Kα radiation and a scintillation detector. Approximately 2000 independent reflections were recorded. The structure was solved from these data, but the precision of the refined parameters was poor, and the nitrosyl group could not be distinguished from the cyanide groups with certainty. Careful inspection of the data set revealed several cases where white radiation streaks from strong reflections had caused errors in the measurement of the intensity of a neighboring weak reflection. In addition there was evidence that the counting circuitry might have malfunctioned intermittently during data collection.

A second data set was collected on the same crystal on a Picker FACS-I computer-controlled four-circle diffractometer. The b axis of the crystal was approximately collinear with the ϕ axis of the diffractometer. An incident beam monochromator equipped with a graphite crystal was used to obtain Mo Kα radiation. The axis of the monochromator was perpendicular to the θ–2θ axis of the diffractometer. The takeoff angle was 3.0°. Data were collected by the θ–2θ scan technique using an asymmetric scan range from $2\theta_{\mathrm{Mo\,K\alpha_1}} - 0.8°$ to $2\theta_{\mathrm{Mo\,K\alpha_2}} + 0.8°$. The scan rate was 2°/min, and stationary-crystal, stationary-counter background counts of 10 sec were taken at both ends of the scan. The pulse height analyzer was set to admit about 90% of the Mo Kα peak, and metal foil attenuators having attenuator factors of 3.2 were inserted in the diffracted beam whenever the counting rate exceeded ~7000 counts/sec. During the data collection the intensities of three standard reflections were monitored every 50 reflections. There were no systematic changes in the intensities of these reflections during the time required to gather the data. The maximum variation of any standard from its mean value was 3.5%. A total of 1767 unique reflections having $2\theta \leq 40°$ were collected. The data were reduced to F^2 and $\sigma(F^2)$ by procedures similar to those previously described.[13,14] The polarization correction used was $P = 0.5(\cos^2 2\theta_m + \cos^2 2\theta)$, where θ_m is the Bragg angle of the monochromator crystal and θ is the Bragg angle of the reflection being observed. A value of 0.04 was assigned to p, the constant in the expression for $\sigma(F^2)$.[13]

Although the linear absorption coefficient of the compound for Mo Kα radiation is only 15.9 $\mathrm{cm^{-1}}$, the morphology of the data crystal makes it necessary to correct for absorption. The crystal was measured with a traveling microscope and the major faces were identified by optical goniometry as {100}, {010}, and {001}. The magnitude of the absorption correction[14] ranged from 1.05 to 1.68. Secondary extinction is not a problem in this crystal (see Table I) and no correction was made.

Solution and Refinement

The positions of the Cr and Co atoms were readily determined from a three-dimensional Patterson function calculated from the initial data set. Successive difference electron density maps revealed the C, N, and O atoms and verified that the compound is a dihydrate. Attempts to refine the structure using these data and several different weighting schemes were unsuccessful. Several atoms exhibited negative thermal parameters; however, difference electron density maps indicated that the atoms were correctly placed. Eventually it was concluded that there were errors in the data (see Experimental Section).

Successful refinement of the structure was carried out using the data from a Picker automatic diffractometer. Refinement was based on F_o, the quantity minimized being $\Sigma w(|F_o| - |F_c|)^2$, with the weights w taken as $4F_o^2/\sigma^2(F_o^2)$. The atomic scattering factors for C, N, O, Cr, and Co were from the usual tabulation.[15] Hydrogen scattering factors were from the calculation of Stewart, *et al.*[16] The effects of anomalous dispersion were included in F_c;[17] the values of $\Delta f'$ and $\Delta f''$ calculated by Cromer[18] were used for Cr and Co. The initial structure factor calculation with this data set gave $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.137$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2)^{1/2} = 0.154$ for the 1106 reflections with $F_o^2 \geq 3\sigma(F_o^2)$. Two cycles of isotropic refinement assuming six CN groups coordinated to the Cr atom reduced these to $R_1 = 0.073$ and $R_2 = 0.088$. One of the cyanide "carbon" atoms had a temperature factor of 0.8, while the other five were in the range 2.3–2.9. The "nitrogen" atom of this cyanide group had a

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(8) It is reasonable to formulate the cation as a Co(III) species. However, the formal oxidation state of the Cr atom in the anion cannot be meaningfully specified. The limiting formulations are Cr(I) coordinated by NO^+ and five CN^- and Cr(III) coordinated by NO^- and five CN^-. In a tetragonal ligand field both formulations are consistent with one unpaired electron in the anion.[3]

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(14) A local version of PIKOUT, Doedens and Ibers' data processing program, was used for data reduction. Other programs used included modifications of Hamilton's GONO general absorption program, Zalkin's FORDAP Fourier summation program, Iber's NUCLS least-squares refinement program, Busing and Levy's ORFFE bond distance and angle program, Johnson's ORTEP plotting program, and Corfield's RANGER weighting analysis program.

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TABLE I

VALUES OF $10|F_o|$ AND $10|F_c|$ (IN ELECTRONS) FOR $[Co(C_2H_8N_2)_3][Cr(CN)_5(NO)]\cdot 2H_2O$

temperature factor of 2.4, while the other five were in the range 3.4–4.6. A bond distance calculation gave a metal–ligand distance of 1.7 Å for the anomalous cyanide compared to 2.0–2.1 Å for the other five ligands. Therefore the amomalous group was taken to be the NO ligand. At this point the hydrogen atoms of the ethylenediamine rings were included in their calculated positions, assuming tetrahedral angles about the C and N atoms and C–H = 1.10 and N–H = 0.99 Å. After correction for absorption two additional cycles of full-matrix least-squares refinement were carried out in which the metal atoms were presumed to undergo anisotropic thermal motion (123 total variable parameters). Refinement converged to $R_1 = 0.053$ and $R_2 = 0.063$. Complete anisotropic refinement of all 28 nonhydrogen atoms would have exceeded the available computer storage and refinement was terminated at this point. The small isotropic thermal parameters for the light atoms suggest that anisotropic motion is not serious.

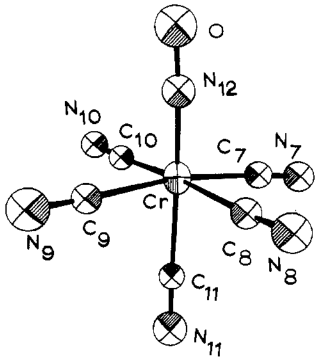

Figure 1.—Perspective view of the $Cr(CN)_5(NO)^{3-}$anion.

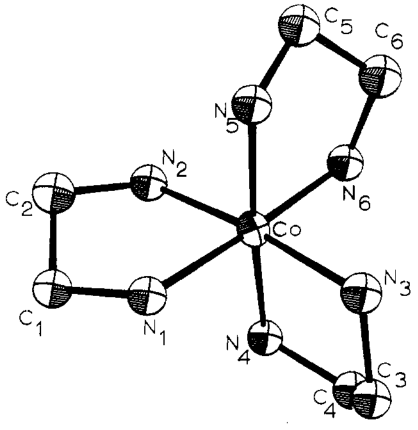

Figure 2.—Perspective view of the $Co(en)_3^{3+}$ cation viewed along the pseudo threefold axis. The ion shown has the conformation Δλ∂∂.[27]

The average standard deviation for an observation of unit weight is 1.95. The normalized weighting parameter[19] ranges from 1.5 to 3.1 as a function of $\lambda^{-1} \sin \theta$ and $|F_o|$, with the intense low-angle data being somewhat overweighted. Perhaps a larger value of p should have been used in assigning errors to the individual intensities. The variation in σ_1' may also be due to the limitations of an isotropic model for describing the motion of the light atoms.

A final structure factor calculation on all 1767 reflections gave $R_1 = 0.094$ and $R_2 = 0.068$. All reflections with $F_o^2 < \sigma(F_o^2)$ had $F_c^2 < 3\sigma(F_o^2)$; only three such weak reflections had $F_c^2 < 2\sigma(F_o^2)$.

TABLE II

ATOMIC PARAMETERS[a]

Atom	x[b]	y	z	B, Å²
Cr	0.2233 (2)	0.4635 (1)	0.6364 (1)	*c*
Co	0.7424 (1)	0.4474 (2)	0.7983 (1)	*c*
C_1	0.9167 (9)	0.4234 (10)	0.7067 (8)	2.2 (3)
C_2	0.9524 (10)	0.3934 (11)	0.8169 (9)	2.8 (3)
C_3	0.5787 (9)	0.4735 (10)	0.6330 (8)	2.2 (3)
C_4	0.5807 (9)	0.3472 (10)	0.6605 (8)	2.3 (3)
C_5	0.7697 (9)	0.5508 (11)	0.9951 (8)	2.6 (3)
C_6	0.6678 (10)	0.4935 (11)	0.9787 (9)	3.0 (3)
C_7	0.1510 (10)	0.5677 (11)	0.7244 (8)	2.5 (3)
C_8	0.2137 (10)	0.3322 (11)	0.7340 (8)	2.4 (3)
C_9	0.3133 (9)	0.3622 (11)	0.5678 (8)	2.4 (3)
C_{10}	0.2438 (10)	0.6038 (11)	0.5495 (9)	2.2 (3)
C_{11}	0.3536 (10)	0.5182 (10)	0.7329 (8)	2.1 (3)
N_1	0.8245 (7)	0.4964 (8)	0.6988 (6)	2.1 (2)
N_2	0.8625 (8)	0.3546 (8)	0.8576 (7)	2.3 (2)
N_3	0.6275 (7)	0.5367 (8)	0.7261 (6)	2.4 (2)
N_4	0.6846 (8)	0.3178 (8)	0.7103 (6)	2.2 (2)
N_5	0.7900 (8)	0.5746 (8)	0.8912 (6)	2.2 (2)
N_6	0.6663 (8)	0.4032 (8)	0.9039 (7)	2.3 (2)
N_7	0.1154 (8)	0.6292 (9)	0.7766 (8)	3.4 (3)
N_8	0.2046 (8)	0.2524 (10)	0.7846 (8)	3.6 (3)
N_9	0.3617 (10)	0.3033 (10)	0.5265 (8)	4.4 (3)
N_{10}	0.2504 (8)	0.6817 (9)	0.4978 (7)	2.7 (2)
N_{11}	0.4262 (9)	0.5498 (10)	0.7884 (7)	3.8 (3)
N_{12}	0.1185 (8)	0.4174 (9)	0.5539 (8)	3.1 (2)
O	0.0486 (8)	0.3799 (9)	0.4927 (7)	4.6 (2)
$H_2O(1)$	−0.0089 (7)	0.3422 (7)	0.0647 (6)	3.2 (2)
$H_2O(2)$	0.4592 (7)	0.2078 (8)	0.3738 (7)	4.4 (2)

Atom	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Cr	44 (2)	37 (2)	42 (2)	−1 (2)	15 (1)	−1 (1)
Co	26 (1)	36 (2)	28 (1)	0 (1)	7 (1)	0 (1)

[a] Standard deviation of least significant figure is given in parentheses. [b] x, y, and z are fractional monoclinic coordinates. [c] Anisotropic thermal parameters are in the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

TABLE III

CALCULATED POSITIONS FOR HYDROGEN ATOMS[a]

Atom	x	y	z
N_1H_1	0.785	0.492	0.629
N_1H_2	0.847	0.579	0.713
N_2H_1	0.874	0.361	0.933
N_2H_2	0.848	0.271	0.839
N_3H_1	0.577	0.550	0.772
N_3H_2	0.651	0.616	0.708
N_4H_1	0.727	0.303	0.657
N_4H_2	0.685	0.245	0.751
N_5H_1	0.865	0.589	0.894
N_5H_2	0.755	0.650	0.865
N_6H_1	0.594	0.384	0.870
N_6H_2	0.695	0.331	0.938

[a] Only positions for the hydrogen atoms attached to nitrogen are listed.

A final difference electron density map was calculated based upon the 1106 data used in refinement. The maximum residual density was 0.5 e⁻ Å⁻³. On the same scale a C atom had a height of ∼5 e⁻ Å⁻³. The hydrogen atoms on the water molecules could not be located in this difference map.

Values of $10|F_o|$ and $10|F_c|$ (in electrons) for all 1767 reflections appear in Table I. The 661 reflections not used in refinement generally have $10|F_o| < 170$. On the same scale $10F_{000} = 10{,}120$. Low-angle reflections which were obscured by the beam stop are denoted by an asterisk. Table II contains the final structural

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(19) It is desirable to investigate the weighting scheme as a function of $|F_o|$, $\lambda^{-1} \sin \theta$, and hkl. For this purpose we define the normalized weighting parameter $\sigma_1' = (n\Sigma w(|F_o| - |F_o|)^2/m(n - p))^{1/2}$, where n is the total number of observations, p is the number of variable parameters, m is the number of observations in a subset, and w is the weight of an individual observation. If the relative weights are correct then σ_1' should be the same for any subset. If the absolute weights are correct, then $\sigma_1' \approx 1$ for all subsets. When $m = n$, then σ_1' becomes σ_1, the standard deviation of an observation of a unit weight.

TABLE IV

BOND DISTANCES (Å)

Atoms	Distance	Av[a]	Atoms	Distance	Av[a]
Co–N$_1$	1.961 (9)	1.964 (4)	Cr–C$_7$	2.047 (13)	2.033 (7)
Co–N$_2$	1.979 (10)		Cr–C$_8$	2.021 (13)	
Co–N$_3$	1.958 (10)		Cr–C$_9$	2.022 (14)	
Co–N$_4$	1.974 (10)		Cr–C$_{10}$	2.043 (13)	
Co–N$_5$	1.955 (10)		Cr–C$_{11}$	2.075 (14)	
Co–N$_6$	1.956 (10)		Cr–N$_{12}$	1.708 (11)	
N$_1$–C$_1$	1.487 (15)	1.477 (7)	C$_7$–N$_7$	1.160 (13)	1.158 (7)
N$_2$–C$_2$	1.483 (15)		C$_8$–N$_8$	1.163 (14)	
N$_3$–C$_3$	1.488 (14)		C$_9$–N$_9$	1.150 (14)	
N$_4$–C$_4$	1.472 (15)		C$_{10}$–N$_{10}$	1.148 (14)	
N$_5$–C$_5$	1.489 (14)		C$_{11}$–N$_{11}$	1.171 (14)	
N$_6$–C$_6$	1.443 (15)		N$_{12}$–O	1.207 (12)	
C$_1$–C$_2$	1.505 (16)	1.503 (10)			
C$_3$–C$_4$	1.505 (17)				
C$_5$–C$_6$	1.500 (17)				

[a] The average is the unbiased estimate of the mean. The number in parentheses is the estimated standard deviation of the mean,[b] $\hat{\sigma} = (\Sigma_i(x_i - \bar{x})^2/n(n - 1))^{1/2}$, where x_i is an individual observation, $\bar{x}$ is the unbiased estimate of the mean, and n is the number of observations. If $\hat{\sigma}$ is less than $\sigma_i/n^{1/2}$, then the latter value appears in parentheses. [b] W. C. Hamilton, "Statistics in Physical Science," Ronald Press, New York, N. Y., 1964, p 43.

TABLE V

BOND ANGLES (DEG)

Atoms	Angle	Av[a]	Atoms	Angle	Av[a]
Co–N$_1$–C$_1$	110.7 (7)	110.5 (3)	Cr–C$_7$–N$_7$	176.1 (12)	176.6 (6)
Co–N$_2$–C$_2$	110.4 (7)		Cr–C$_8$–N$_8$	175.3 (11)	
Co–N$_3$–C$_3$	109.9 (7)		Cr–C$_9$–N$_9$	177.6 (12)	
Co–N$_4$–C$_4$	109.3 (7)		Cr–C$_{10}$–N$_{10}$	176.4 (12)	
Co–N$_5$–C$_5$	111.0 (7)		Cr–C$_{11}$–N$_{11}$	178.9 (11)	
Co–N$_6$–C$_6$	111.6 (8)		Cr–N$_{12}$–O	175.6 (10)	
N$_1$–C$_1$–C$_2$	108.2 (9)	107.6 (5)	C$_7$–Cr–C$_8$	88.8 (5)	89.8 (6)
N$_2$–C$_2$–C$_1$	107.0 (10)		C$_7$–Cr–C$_{10}$	89.3 (5)	
N$_3$–C$_3$–C$_4$	106.6 (9)		C$_8$–Cr–C$_9$	88.4 (5)	
N$_4$–C$_4$–C$_3$	107.9 (10)		C$_9$–Cr–C$_{10}$	92.7 (5)	
N$_5$–C$_5$–C$_6$	105.3 (9)				
N$_6$–C$_6$–C$_5$	108.5 (10)		C$_7$–Cr–C$_{11}$	84.2 (5)	86.4 (9)
			C$_8$–Cr–C$_{11}$	88.5 (5)	
N$_1$–Co–N$_2$	84.4 (4)	84.5 (6)	C$_9$–Cr–C$_{11}$	87.2 (5)	
N$_3$–Co–N$_4$	85.3 (4)		C$_{10}$–Cr–C$_{11}$	85.7 (5)	
N$_5$–Co–N$_6$	83.8 (4)				
N$_1$–Co–N$_3$	90.2 (4)	91.8 (4)	C$_7$–Cr–N$_{12}$	97.6 (5)	93.7 (15)
N$_1$–Co–N$_4$	91.3 (4)		C$_8$–Cr–N$_{12}$	92.3 (5)	
N$_1$–Co–N$_5$	93.1 (4)		C$_9$–Cr–N$_{12}$	91.0 (5)	
N$_2$–Co–N$_4$	91.7 (4)		C$_{10}$–Cr–N$_{12}$	93.5 (5)	
N$_2$–Co–N$_5$	90.3 (4)				
N$_2$–Co–N$_6$	93.7 (4)		C$_7$–Cr–C$_9$	171.0 (5)	172.5 (15)
N$_3$–Co–N$_5$	93.1 (4)		C$_8$–Cr–C$_{10}$	174.0 (5)	
N$_3$–Co–N$_6$	91.4 (4)		C$_{11}$–Cr–N$_{12}$	178.0 (5)	
N$_4$–Co–N$_6$	91.8 (4)				
N$_1$–Co–N$_6$	176.6 (4)	175.3 (7)			
N$_2$–Co–N$_3$	174.1 (4)				
N$_4$–Co–N$_5$	175.3 (4)				

[a] See footnote *a*, Table IV.

parameters, and the calculated positions for the H atoms of the ethylenediamine rings appear in Table III.

Description and Discussion

The numbering schemes and perspective views of the anion and cation are shown in Figures 1 and 2, respectively. Interatomic distances and angles computed from the final parameters of Table II appear in Tables IV and V. The estimated standard deviations of the distances and angles were derived from the inverse least-square matrix from the final refinement.

The effective coordination symmetry about the Cr atom is $4mm$-C_{4v}, and the Cr–N–O and Cr–C–N groups are nearly linear. These results are in agreement with the conclusions drawn by Vannerberg[7] from his structural investigation of the disordered crystal $K_3Cr(CN)_5(NO)$. In the present study, however, the $Cr(CN)_5(NO)^{3-}$ anion is ordered, and the NO group has been unambiguously distinguished from the CN groups on the basis of isotropic thermal parameters and metal–ligand distances (see above). The Cr–N distance of 1.71 (1) Å is considerably longer than the Fe–N distance of 1.63 (2) Å in $Fe(CN)_5(NO)^{2-}$,[2] probably reflecting the larger size of the Cr atom. The M–N distances for the known pentacyanonitrosyls of the first-row transition metals (Table VI) show the expected trend of decreasing M–N distance with increasing atomic number. The Cr–N distance is similar to the values of 1.70 (1) and 1.72 (1) Å found[20] in π-$(C_5H_5)CrCl(NO)_2$. The N–O distance of 1.21 (1) Å is quite long. Most N–O distances in metal–nitrosyl compounds are in the range 1.13–1.18 Å.[21a] However, an N–O distance of 1.21 (1) Å has also been found[21b] in the $Ir(NO)_2(P(C_6H_5)_3)_2^+$ cation. The N–O distance in $Fe(CN)_5(NO)^{2-}$ is 1.13 (2) Å.[2] A longer N–O bond distance in $Cr(CN)_5(NO)^{3-}$ compared to $Fe(CN)_5(NO)^{2-}$ is consistent with the NO stretching frequencies, which are 1660 and 1935 cm^{-1}, respectively.

TABLE VI

COMPARISON OF METAL PENTACYANONITROSYLS

Anion	M–CN distance, Å	M–NO distance, Å	M–N–O angle, deg
$V(CN)_5(NO)^{3-}$ [a]	2.18 (2)	1.79[b]	176[b]
$Cr(CN)_5(NO)^{3-}$ [c]	2.033 (7)[d] 2.075 (14)[e]	1.71 (1)	176 (1)
$Mn(CN)_5(NO)^{3-}$ [f]	1.95–1.99[g]	1.65[g]	173[g]
$Fe(CN)_5(NO)^{2-}$ [h]	1.91 (2)	1.63 (2)	178 (1)

[a] S. Jagner and N. G. Vannerberg, *Acta Chem. Scand.*, **22**, 3330 (1968). [b] Average of an NO group and a CN group statistically disordered. [c] This work. [d] Average equatorial distance. [e] Axial distance. [f] A. Tullberg and N. G. Vannerberg, *Acta Chem. Scand.*, **20**, 1180 (1966). [g] Preliminary communication, errors not given. [h] Reference 2.

The Cr–N–O angle of 176 (1)° is not significantly different from 180° and agrees well with the angle of 178 (1)° found[2] in $Fe(CN)_5(NO)^{2-}$. A Cr–N–O bond angle as small as 135° has been postulated.[5] The anisotropy of the ^{14}N hyperfine tensor in the esr spectrum of $Cr(CN)_5(NO)^{3-}$ is well known.[3–6,22] It is not readily apparent whether this anisotropy arises from the small distortions of the ion from C_{4v} symmetry or from other factors. However, our structural results reemphasize the danger of predicting molecular structure from indirect measurements.[23]

The average equatorial Cr–C distance is 2.033 (7) Å, and the axial Cr–C distance is 2.075 (14) Å. The respective Fe–C distances in $Fe(CN)_5(NO)^{2-}$ are 1.92 (2) and 1.90 (2) Å.[2] The differences between the Fe–C and Cr–C distances are similar to the differences between the Fe–N and Cr–N distances and again probably reflect the difference in the sizes of Fe and Cr. The average C–N distance of 1.158 (7) Å is in good agreement with recent values of 1.155 (8)[24] and 1.156 (4) Å[25] for coordinated cyanide groups.

The Co atom has the expected trigonally distorted octahedral coordination environment. The average intraligand N–Co–N angle is 84.5 (6)°, whereas the average interligand N–Co–N angle is 91.8 (4)°. The average Co–N distance of 1.964 (4) Å is similar to earlier values of 1.99[26a] and 2.00 Å[26b,c] reported for other structures containing the $Co(en)_3^{3+}$ ion. Figure 2 shows the $Co(en)_3^{3+}$ cation viewed down the pseudo threefold axis of the ion. Relative to this axis the ligands have a Δ configuration about the Co.[27] Figure 2 also shows that the ethylenediamine chelate rings do not have identical conformations. The ion shown has the conformation $\Delta\lambda\partial\partial$. Corey and Bailar[28] calculated that for a Λ configuration about the metal, the most stable conformation of the rings for a free ion should be $\partial\partial\partial$. Recently, however, the conformers $\Lambda\partial\partial\lambda$,[25] $\Lambda\partial\lambda\lambda$,[25] and $\Lambda\lambda\lambda\lambda$[24] have been reported for $Cr(en)_3^{3+}$ salts of penta- and hexacyanometalates. Raymond, *et al.*,[9] have proposed that the higher energy conformers are stabilized by hydrogen bonding. They found the $\Lambda\partial\partial\lambda$ conformer involved in three strong hydrogen bonds (N···N or N···O less than 3.1 Å), the $\Lambda\partial\lambda\lambda$ conformer in seven, and the $\Lambda\lambda\lambda\lambda$ conformer in ten hydrogen bonds. Table VII summarizes the hydrogen-bonding interactions in $[Co(en)_3][Cr(CN)_5(NO)]\cdot 2H_2O$. The ethylenediamine rings are involved in eight hydrogen bonds with N···N (or N···O) $\leq$ 3.1 Å. However, one of these has a calculated N–H···N angle of only 122° and may be rather weak. Thus, the number of strong hydrogen bonds stabilizing the $\Lambda\partial\lambda\lambda$ (or $\Delta\lambda\partial\partial$) conformation in this structure is consistent with the hypothesis of Raymond, *et al.*[9]

TABLE VII

POSSIBLE A–H···B HYDROGEN BONDS[a]

Ring conformation[b]	A	H	B	A···B, Å	Angle around H, deg
λ	N_1	H_2	N_8	3.0	144
	N_2	H_2	N_7	3.2	141
	N_2	H_1	$H_2O(1)$	3.0	141
∂	N_3	H_1	N_{11}	3.0	148
	N_4	H_1	N_{10}	3.0	150
λ	N_5	H_2	N_8	3.1	122
	N_5	H_1	$H_2O(1)$	3.1	160
	N_6	H_2	N_{10}	3.0	177
	N_6	H_1	$H_2O(2)$	3.0	148
	$H_2O(1)$	···	N_7	2.8	
	$H_2O(1)$	···	O	2.8	
	$H_2O(2)$	···	N_9	2.8	
	$H_2O(2)$	···	N_{11}	3.2	

[a] All possible hydrogen bonds with A···B $\leq$ 3.2 Å and A–H···B angles greater than 120° are listed. [b] For a Λ configuration about the metal.

The crystal structure consists of a three-dimensional

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(20) O. L. Carter, A. T. McPhail, and G. A. Sim, *J. Chem. Soc. A*, 1095 (1966).

(21) (a) D. J. Hodgson, *Inorg. Chem.*, **7**, 2345 (1968); (b) D. M. P. Mingos and J. A. Ibers, *ibid.*, **9**, 1105 (1970).

(22) H. A. Kuska and M. T. Rogers, *J. Chem. Phys.*, **42**, 3034 (1965).

(23) A recent neutron diffraction study has shown the Mn–H distance in HMn(CO) is 1.60 (2) Å, although earlier interpretations of broad-line nmr data gave Mn–H = 1.28 (2) Å. See S. J. LaPlaca, W. C. Hamilton, J. A. Ibers, and A. Davison, *Inorg. Chem.*, **8**, 1928 (1969), and references therein.

(24) K. N. Raymond and J. A. Ibers, *ibid.*, **7**, 2333 (1968).

(25) K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *ibid.*, **7**, 1362 (1968).

(26) (a) K. Nakatsu, M. Shiro, Y. Saito, and H. Kuroya, *Bull. Chem. Soc. Jap.*, **30**, 158 (1957); (b) K. Nakatsu, Y. Saito, and H. Kuroya, *ibid.*, **29**, 428 (1956); (c) K. Nakatsu, *ibid.*, **35**, 832 (1962).

(27) The nomenclature is that of ref 9. Since the space group is centrosymmetric, the crystal is a racemic mixture of $\Delta\lambda\partial\partial$ and $\Delta\partial\lambda\lambda$ conformers. These two conformers are mirror images of each other and hence have identical stabilities.

(28) E. J. Corey and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, **81**, 2620 (1959).

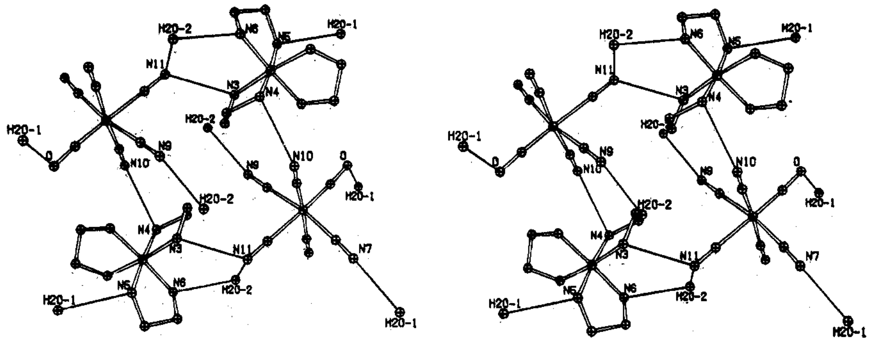

Figure 3.—Stereoscopic pair showing the hydrogen bonding and ionic packing in $[Co(en)_3][Cr(CN)_5(NO)]\cdot 2H_2O$ as viewed along the *b* axis. The horizontal axis is *a;* the vertical axis is *c*. For visual clarity only one layer of ions is shown. A second layer of ions can be generated by the twofold screw axes parallel to *b*. The hydrogen bonding between layers of ions can be inferred from Table VII. The identities of the unlabeled atoms can be determined by comparison to Figures 1 and 2.

array of alternating cations and anions. Layers of water molecules occur at $x \approx 0$ and $x \approx 0.5$ and probably account for the fact that the crystals grow as thin plates with the faces $\{100\}$ as the plate faces. The NO group, both H_2O molecules, all five CN ligands, and at least one H atom from each of the N atoms of the ethylenediamines are all involved in the network of hydrogen bonds (Table VII). The network of strong hydrogen bonds may also account for the slight deviations of the Cr–C–N and Cr–N–O groups from linearity. A stereoscopic view of the hydrogen-bonding scheme and ionic packing appears in Figure 3. For visual clarity only a portion of the unit cell is shown.

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The Structure of Hydridotetrakis(trifluorophosphine)cobalt(I), $CoH(PF_3)_4$

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The crystal structure of hydridotetrakis(trifluorophosphine)cobalt(I), $CoH(PF_3)_4$, has been determined from three-dimensional X-ray data collected by photographic methods at −125°. The material, as grown from the liquid phase, crystallizes in the monoclinic system, space group C_{2h}^6-$C2/c$, with four molecules in a cell of dimensions $a = 13.02$ (1), $b = 7.63$ (1), $c = 13.08$ (1) Å, and $\beta = 122.4$ (1)°. The calculated density is 2.49 g/cm³. The structure has been solved by standard methods and refined by full-matrix least-squares methods to a final R factor on F of 0.11, based on 664 visually estimated intensities. The $CoH(PF_3)_4$ molecule is required crystallographically to possess C_2 symmetry. There is a distorted tetrahedron of PF_3 groups about the Co atom, the P–Co–P angles being 101.8 (3), 108.2 (2), 109.7 (2), and 118.0 (2)°. Various positions for the H atom, which was not located, are considered in terms of the distorted geometry of the molecule. A model is favored in which the H atom occupies an apical position of a distorted trigonal bipyramid. The Co–P distances average 2.052 (5) Å, indicative of considerably more multiple bonding than in metal–PR_3 bonds, where R is alkyl or aryl.

Introduction

The structure of $CoH(CO)_4$, and indeed of other simple carbonyl hydrides, has been the subject of study and contention for many years. A brief history of the subject has been given previously.[1] Ewens and Lister[2] deduced from electron diffraction studies of the gas that the CO groups are arranged approximately tetrahedrally about the central Co atom in $CoH(CO)_4$. (At that time it was assumed that the H atom was attached to one of the O atoms.) Eventually, spectroscopic studies[3] provided evidence that the H atom is bonded to the Co atom. The characteristic band initially identified as a Co–H stretching band[4,5] was later shown[6]

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