the three ligands in the equatorial plane, because the P–X distance is smallest for the complex which shows the smallest distortion, *i.e.*, $CoH(N_2)(P(C_6H_5)_3)_3$. In cases where it has been postulated that nonbonded repulsions are playing a significant role in determining the final geometry of tertiary phosphine complexes, the X–P distances for all compounds have remained almost constant.[26] Also from considerations of nonbonded repulsions it is difficult to understand why the four-coordinate complexes have X–M–P angles greater than the ideal tetrahedral values although the P–X nonbonded contacts are relatively large (3.4–3.5 Å). We think that the geometries of these complexes may be rationalized by a consideration of the electron-pair repulsions between the M–X and M–P bonds.[27] All the ligands X are capable of forming bonds to the metal with some double-bond character. A consideration of the sum of the covalent radii[28] for the three five-coordinate complexes in Table VI indicates that the ability of X to form multiple bonds with the metal is in the order $NO^+ > CO > N_2$. The electron density in the M–X bond will also follow this order and will be greatest for the nitrosyl complex and least for the nitrogen complex. If electron repulsions are important, the degree of distortion from the ideal will take the following order: $IrH(NO)(P(C_6H_5)_3)_3^+ > RhH(CO)(P(C_6H_5)_3)_3 > CoH(N_2)(P(C_6H_5)_3)_3$, which is the observed order. For five-coordinate complexes the distortions will be limited by the steric requirements of the hydride ligand and would be expected to be less than the distortions in the corresponding four-coordinate complexes, which have approximately the same degree of multiple-bond character as evidenced by the very similar M–C and M–N distances for the carbonyl and nitrosyl complexes. For the four-coordinate complexes the distortions are limited only by the steric requirements of the phenyl rings and this results in X–M–P bond angles greater than the ideal tetrahedral values. Table VI also shows that the degree of distortion is greater for $Ir(NO)(P(C_6H_5)_3)_3$ than for $Pt(CO)(P(C_6H_5)_3)_3$ as one would expect from a consideration of electron-pair repulsions.

We also wish to emphasize the inadequacies of using the ν(NO) stretching frequency to diagnose the mode of coordination of the nitrosyl ligand. Table VII shows ν(NO) for some nitrosyl complexes whose structures have been determined recently. The NO^+ complexes have ν(NO) in the range 1600–1845 cm^{-1} and for the NO^- complexes ν(NO) is in the range 1525–1720 cm^{-1}. The large area of overlap precludes any formulation based solely on ν(NO) in the region 1600–1720 cm^{-1} and frequencies close to these ought also to be treated with caution. Also no direct correlation between ν(NO) and the metal–nitrogen bond length exists.

Acknowledgment.—We wish to thank the National Institutes of Health for support of this work.

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Conformational Effects of Intermolecular Interactions. The Structure of Tris(ethylenediamine)cobalt(III) Monohydrogen Phosphate Nonahydrate

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The crystal and molecular structure of racemic tris(ethylenediamine)cobalt(III) monohydrogen phosphate nonahydrate, $[Co(en)_3]_2[HPO_4]_3 \cdot 9H_2O$, has been determined by three-dimensional X-ray methods. The salt crystallizes in the orthorhombic space group *Pnma* with four formula units in a cell of dimensions $a = 15.616$ (5), $b = 27.514$ (8), and $c = 8.719$ (3) Å. The calculated density of 1.65 g/cm^3 compares well with the observed density of 1.64 g/cm^3. The structure has been refined by full-matrix least-squares methods for 2423 independent reflections to a final agreement factor of 5.0%. The structure is composed of waters of hydration and $Co(en)_3^{3+}$ and HPO_4^{2-} ions linked by hydrogen bonds. One of the HPO_4^{2-} units is on a crystallographic mirror plane and relates an enantiomorphous pair of $Co(en)_3^{3+}$ cations. This biphosphate is positioned approximately on the molecular threefold axes of both cations, forms hydrogen bonds with both cations, and locks them in the $\Lambda\delta\delta\delta$ and $\Delta\lambda\lambda\lambda$ conformations, respectively.

Introduction

The absolute configuration[1] and conformational analysis[2] of the $Co(en)_3^{3+}$ cation have been the subjects of considerable interest and study, and these compounds have been used as a testing ground for models relating optical rotatory strength with structure.[3,4] One of the most curious observations in this area is that the circular dichroism spectrum of aqueous solutions of $Co(en)_3^{3+}$ changes dramatically when an excess of phosphate ion is added.[5] An explanation[5-7] was offered for this phenomenon which hypothesized that an ion pair is formed which strongly affects the charge-transfer and circular dichroism spectra. Hydrogen-bonding effects have previously been found dramatically to alter the conformations of several tris-ethylenediamine complex cat-

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ions.[8-10] The model which was proposed to explain these changes[8] has been used also to explain the conformations found in two additional crystallographic studies of tris-ethylenediamine complex salts.[11,12] In order to explain the peculiar behavior of the circular dichroism spectrum of $Co(en)_3{}^{3+}$ in aqueous solution and to establish its conformation in this environment, we began the structural study reported here. The aquation of $Co(en)_3{}^{3+}$ in extremely basic solution and the poor quality of crystals of the resultant phosphate salt made the latter unsuitable for structure analysis. Good crystals of the biphosphate salt were obtained upon recrystallization, and since it is likely to be the dominant species under most experimental conditions, a full three-dimensional structure analysis was completed.

Experimental Section

Preparation of $[Co(en)_3]_2[HPO_4]_3 \cdot 9H_2O$.—A thin paste was made from 15 g of $[Co(en)_3]I_3 \cdot 3H_2O$ (22 mmol) and 21 g of Ag_3PO_4 (50 mmol) mixed in 10 ml of water and was stirred for more than 1 hr. The solution was periodically tested for I^- to indicate completion of the metathesis reaction. After filtration, the addition of a small amount of methanol to the filtrate yielded approximately 1.4 g of the phosphate salt as a powder. This powder was dried and analyzed. Several determinations of the waters of hydration showed it to be variable with an average value of 6.4.

Anal. Calcd for $[Co(NH_2CH_2CH_2NH_2)_3]PO_4$: Co, 17.63; N, 25.15; C, 21.56; P, 9.27; H, 7.24. Found: Co, 17.27; N, 24.95; C, 21.60; P, 9.05; H, 7.39.

Attempts to get larger crystals of the phosphate salt failed. Recrystallization of the powder from a warm, dilute, aqueous solution (0.03 *M* at 50°) gave, upon the slow addition of methanol followed by cooling to 0°, clear orange needles. The crystalline solid is the biphosphate salt with nine waters of hydration.

Anal. Calcd for $[Co(NH_2CH_2CH_2NH_2)_3]_2[HPO_4]_3 \cdot 9H_2O$: Co, 12.73; N, 18.18; C, 15.56; P, 10.02; H, 7.18. Found (average of two analyses): Co, 12.82; N, 17.97; C, 15.47; P, 9.90; H, 7.32.

Data Collection.—Several crystals were sealed within thin-walled glass capillaries to maintain a constant-humidity atmosphere. Precession photographs (Mo $K\alpha$ radiation, Zr filtered) showed *mmm* symmetry and the systematic absences $0kl$, $k + l \neq 2n$, and $hk0$, $h \neq 2n$. The centrosymmetric space group *Pnma* and its noncentric subgroup $Pna2_1$ are both consistent with these observations. Subsequent solution and refinement of the structure shows the correct choice is *Pnma* ($D_{2h}{}^{16}$).

Several crystals were examined and found to be excessively mosaic in the a^* direction. A suitable data crystal (0.19 × 0.22 × 0.25 mm in dimension) was chosen which gave ω scan widths at half-height of 0.10, 0.04, and 0.05° for the 200, 020, and 002 reflections, respectively. Unit cell parameters and the crystal orientation were determined by a least-squares fit to the setting angles of 12 carefully centered reflections whose Bragg 2θ values ranged from 9 to 48°.[13] The cell parameters at 22° (for Mo $K\alpha_1$, λ 0.70926 Å) are a = 15.616 (5), b = 27.514 (8), and c = 8.719 (3) Å.

The density calculated for four formula units of $[Co(en)_3]_2[HPO_4]_3 \cdot 9H_2O$ per cell is 1.65 g/cm³. This agrees well with that observed by flotation in CCl_4–$CHBr_3$ solutions of 1.64 g/cm³. The crystal was purposely mounted slightly off a symmetry axis to minimize multiple diffraction effects.[14]

Intensity data were collected by the θ–2θ scan technique on a Picker diffractometer with PDP8/I computer automation and monochromatic Mo $K\alpha$ radiation. The Bragg 2θ angle for the highly oriented graphite crystal was 12.02°. The X-ray tube takeoff angle was 2.0°. The pulse height analyzer was set to admit 90% of the maximum intensity at full window width and was centered on the energy of Mo $K\alpha$ radiation. The detector was placed 33 cm from the source with a receiving aperture 7 × 7 mm. Scans were from 0.50° below the calculated $K\alpha_1$ peak to 0.50° above the $K\alpha_2$ peak at a rate of 1.0°/min. A fixed 10-sec background count was recorded at the beginning and end of each scan. Attenuators were automatically used to keep the count rate for each reflection below 10,000 cps. Three standards in different regions of the reciprocal lattice were monitored every 60 reflections. One unique form (the octant $hk\bar{l}$ with $h \geq 0$, $k \geq 0$, $l \leq 0$) was collected out to a Bragg 2θ angle of 55°. A second, symmetry-related form ($\bar{h}\bar{k}l$ with $h \leq 0$, $k \leq 0$, $l \geq 0$) was collected out to 2θ = 35°. During the data collection the crystal moved within the capillary several times. Data collected after each movement of the crystal were discarded; the crystal was carefully reoriented and data collection was resumed at the end of the last reflection measured before the movement. A total of 6312 reflections were recorded.

The data were processed by our local program UCFACS.[15] This reads data directly from the teletype paper tape output and carries out an extensive search for errors. A character by character search is made first for format errors. Several other checks are than made such as (1) all angles are required to be in the region 0–360°, (2) the total scan count cannot be less than half the sum of the background counts, and (3) the 2θ angle calculated from the Miller indices must not differ substantially from that read. Any failure in these tests causes the reflection to be rejected and a notation regarding the error is recorded. The accepted values are than converted to values of F^2 after correcting for Lorentz and polarization effects. We assume the monochromator crystal to be perfect and, since its axis ($2\theta_m$) is perpendicular to the diffractometer axis (2θ), apply the correction

$$\frac{1}{Lp} = \frac{2 \sin 2\theta}{(\cos^2 2\theta_m + \cos^2 2\theta)}$$

Standard deviations were assigned according to the formula

$$\sigma(I) = [CT + 9 + {}^1/_4(t_c/t_b)^2(B_1 + B_2 + 18) + (pI)^2]^{1/2}$$

where CT is the total integrated peak count obtained in a time t_c, B_1 and B_2 are the background counts each obtained in the time t_b, and $I = CT + 4.5 - 0.5(t_c/t_b)(B_1 + B_2 + 9)$. The appearance of the constants 4.5, 9, and 18 is due to the statistical effect of integer truncation. In the output of counts from the scaler, the last digit is dropped. Our data processing program multiplies all counts by 10 to bring them back to their true magnitude, but the truncation results in a systematically lower count if a correction is not applied. The average value of the error introduced by truncation is

$$\frac{1}{10}\sum_{i=0}^{9} i = 4.5$$

and this value is then added to each count after scaling up by the factor 10. There is also a contribution to the standard deviations of the counts. If we estimate this error as the average variance, the contribution to σ^2 for the count is

$$\frac{1}{10}\sum_{i=0}^{9} (i - 4.5)^2 \approx 9$$

The parameter p is introduced to avoid overweighting strong reflections. It represents the standard deviation as a percentage error when counting statistics are negligible and was assigned a value of 0.04 for this data set.

Our data processing program also summarizes the information provided by the standards for the crystal stability. Any loss in counts is ascribed to crystal decay since the stability of the electronics is periodically checked. After processing, the intensities for each standard reflection are plotted on the standard

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TABLE I

POSITIONAL AND THERMAL PARAMETERS AND STANDARD DEVIATIONS[a]

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	22,000 (3)	10,140 (2)	10,330 (7)	136 (25)	56 (8)	381 (80)	−5 (1)	−11 (4)	9 (2)
P_1	10,200 (7)	4,240 (5)	59,840 (15)	177 (25)	68 (8)	525 (82)	−15 (2)	−14 (8)	12 (5)
P_m	9,640 (12)	$^1/_4$	12,650 (23)	269 (26)	79 (8)	820 (86)	0	6 (13)	0
N_1	11,180 (22)	11,340 (15)	−260 (45)	168 (30)	81 (10)	583 (95)	13 (8)	−43 (25)	−9 (16)
N_2	17,480 (22)	13,110 (14)	29,230 (43)	187 (29)	65 (10)	510 (100)	3 (8)	45 (24)	−7 (15)
N_3	26,680 (21)	16,340 (14)	2,800 (46)	179 (29)	71 (10)	561 (100)	−7 (8)	10 (25)	31 (15)
N_4	17,210 (22)	3,810 (14)	15,780 (45)	174 (30)	56 (10)	627 (96)	−22 (8)	6 (25)	16 (15)
N_5	32,370 (22)	8,760 (14)	22,330 (47)	138 (29)	78 (10)	663 (104)	16 (8)	−52 (25)	8 (15)
N_6	27,190 (22)	7,250 (14)	−8,090 (42)	194 (30)	76 (10)	560 (99)	−10 (8)	68 (26)	−18 (16)
C_1	4,950 (27)	7,540 (19)	4,320 (58)	136 (30)	101 (12)	785 (110)	−36 (10)	−4 (30)	3 (21)
C_2	24,750 (29)	13,850 (20)	40,140 (59)	273 (32)	98 (12)	622 (105)	−57 (10)	−75 (35)	−43 (22)
C_3	29,620 (30)	15,680 (20)	−13,290 (56)	291 (33)	95 (12)	593 (110)	−17 (11)	120 (32)	92 (20)
C_4	9,790 (29)	2,840 (18)	5,560 (58)	244 (33)	86 (11)	681 (108)	−71 (11)	−45 (32)	−15 (19)
C_5	30,510 (30)	9,500 (19)	38,870 (59)	250 (32)	109 (12)	589 (104)	−23 (11)	−119 (34)	64 (22)
C_6	33,480 (31)	10,710 (20)	14,630 (58)	239 (32)	102 (12)	796 (109)	−45 (11)	211 (32)	−35 (21)
O_{1P}	17,530 (26)	930 (17)	−38,560 (77)	387 (34)	136 (11)	5390 (204)	92 (11)	−249 (52)	166 (34)
O_{2P}	12,180 (22)	8,920 (14)	−32,020 (46)	411 (31)	122 (10)	1039 (102)	−48 (8)	68 (27)	−100 (16)
O_{3P}	7,390 (26)	5,030 (16)	43,600 (43)	611 (34)	237 (12)	534 (97)	−234 (12)	−114 (29)	35 (17)
O_{4P}	2,380 (24)	1,910 (17)	−31,310 (44)	510 (32)	269 (13)	509 (96)	−243 (11)	149 (28)	−47 (19)
O_{1m}	4,550 (22)	20,460 (12)	12,140 (38)	372 (30)	79 (10)	956 (99)	−54 (8)	108 (25)	−36 (14)
O_{2m}	15,190 (38)	$^1/_4$	28,200 (75)	481 (42)	241 (15)	1379 (142)	0	−330 (49)	0
O_{3m}	16,220 (30)	$^1/_4$	60 (65)	290 (34)	106 (12)	1322 (128)	0	229 (40)	0
				Oxygens of Waters of Crystallization					
O_{1w}	3,510 (24)	17,140 (14)	−36,590 (47)	425 (32)	123 (10)	1254 (107)	−17 (9)	−11 (29)	−45 (18)
O_{2w}	44,650 (23)	16,760 (19)	14,560 (45)	289 (30)	325 (14)	1063 (103)	−143 (11)	16 (27)	−78 (21)
O_{3w}	43,600 (21)	17,730 (14)	−40,440 (45)	293 (11)	149 (11)	1390 (106)	13 (9)	108 (28)	60 (19)
O_{4w}	31,500 (33)	$^1/_4$	−42,110 (66)	364 (35)	137 (13)	1335 (133)	0	124 (41)	0
O_{5w}	14,760 (33)	$^1/_4$	−31,000 (70)	361 (37)	140 (13)	1415 (129)	0	39 (42)	0
O_{6w}	32,680 (47)	$^1/_4$	26,330 (83)	766 (50)	213 (15)	1821 (151)	0	−287 (59)	0

[a] Positional parameters, thermal parameters, and deviations are multiplied by 10^5.

line printer as a function of the sequence number of the reflection (in effect time is then the abscissa). There are as many plots as different standards and inspection of these graphs gives an immediate check not only on the general crystal stability but also on the relative crystal decomposition in various directions. Correction for these losses is very important since with diffractometer data it is more the rule than the exception that a significant change in the crystal scattering is observed with time. In the present study a rapid loss in intensity of approximately 10% was observed during the first few hours of data collection. These reflections were discarded since the subsequent data showed a total loss of intensity during the remainder of the experiment of less than 1%.

An absorption correction was not applied since, for an absorption coefficient μ of 11.4 cm^{-1}, μt ranged from a minimum of 0.18 to a maximum of 0.28 to give a maximum error in the integrated transmission coefficient of much less than 6%. Refinements were carried out using all 2566 reflections for which $F^2 > 3\sigma(F^2)$. The final structure factor calculation was carried out for the 2081 independent reflections that were obtained by averaging equivalent forms for which $F^2 > 3\sigma(F^2)$.

Solution and Refinement of the Structure.—A three-dimensional Patterson function[15] could be interpreted in *Pnma* and gave trial positions for the heavy atoms. Full-matrix least-squares and difference Fourier techniques gave the remaining atom positions. The function minimized in the least-squares refinements was $\Sigma w(|F_o| - |F_c|)^2$ where F_o and F_c are the observed and calculated structure factors, respectively. The weights, w, were taken as $1/\sigma^2(F) = 4F_o^2/\sigma^2(F_o^2)$. The atomic scattering factors for neutral Co, P, O, N, and C were calculated from the values tabulated by Cromer and Mann.[16] Those for neutral hydrogen were of Stewart, *et al.*[17] Both f' and f'' for Co and P[18] were used in the correction for anomalous scattering. The contributions of the hydrogen atoms to the structure factors were included by calculating the position for the ethylenediamine hydrogens assuming a tetrahedral geometry for C and N with a C–H and N–H bond length of 1.0 Å. The temperature factors for all hydrogen atoms were assumed to be the same, and this one value was refined. Although a search was made for the other hydrogen atoms in the difference Fourier maps, no well-defined positions could be found. The final agreement factors using values of F and full nonhydrogen anisotropic refinement gave $R_1 = 5.6$ and $R_2 = 5.0\%$ where

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} \qquad R_2 = \left(\frac{\sum w(|F_o| - |F_c|)^2}{\sum w F_o^2}\right)^{1/2}$$

The final error in an observation of unit weight defined as

$$\left(\frac{\sum w(|F_o| - |F_c|)^2}{N_0 - N_v}\right)^{1/2}$$

is 0.96 and shows no systematic change for various classes of reflections based on F^2. A final difference Fourier showed no peak greater than 15% of the height for a carbon atom in the structure.[19] The final values of positional and thermal parameters are given in Tables I and II. Table III gives the rms amplitudes of vibration along the principal axes of the thermal ellipsoids for the nonhydrogen atoms.

Description of the Structure

The structure consists of $Co(en)_3^{3+}$ cations, HPO_4^{2-} anions, and waters of crystallization, all linked by hydrogen bonds. There is only one crystallographically independent $Co(en)_3^{3+}$ cation, and it occupies the general position 8(d). There are two different HPO_4^{2-} anions. The first (Figure 1), which we will call "free," occupies the general position 8(d) and can be considered a simple ion, although it does engage in the extensive hydrogen-bond network. The second biphosphate anion, which we will call "bridging," lies on the mirror plane at position 4(c). It links an enantiomorphous pair of $Co(en)_3^{3+}$ cations to form an ion trimer which has mirror symmetry. The structure can be considered

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[19] 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 St., 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.

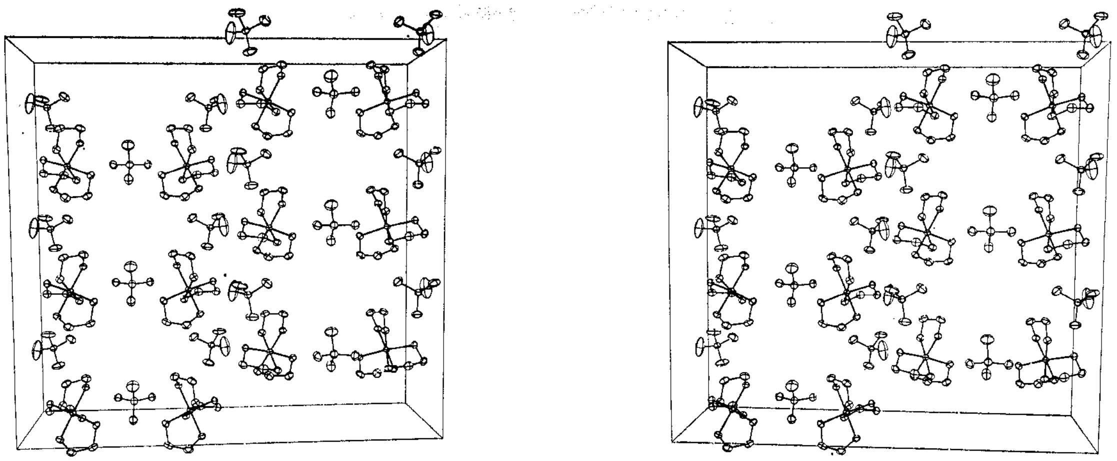

Figure 1.—A stereopacking diagram of $[Co(en)_3]_2[HPO_4]_3 \cdot 9H_2O$. The horizontal axis is b and the vertical axis is c. The depth of the cell is $^1/_2a$ and the length is $3c$. Note that the waters of crystallization have been omitted.

TABLE II

CALCULATED AMINE AND METHYLENE HYDROGEN POSITIONAL PARAMETERS[a]

		x	y	z
N_1	H_1	1191	1127	−1188
	H_2	876	1470	225
N_2	H_1	1276	1099	3389
	H_2	1478	1638	2708
N_3	H_1	3160	540	2073
	H_2	2215	1887	290
N_4	H_1	2203	134	1394
	H_2	1583	384	2672
N_5	H_1	3731	1111	1962
	H_2	3467	1735	918
N_6	H_1	2213	670	−1568
	H_2	2954	409	−545
C_1	H_1	−38	712	−435
	H_2	176	848	1537
C_2	H_1	2209	1377	5233
	H_2	2807	1705	3818
C_3	H_1	3456	1849	−1591
	H_2	2428	1615	−2126
C_4	H_1	594	1	1083
	H_2	1201	171	−576
C_5	H_1	3639	1010	4546
	H_2	2739	613	4318
C_6	H_1	3464	982	−2718
	H_2	3964	1042	−879

[a] Positional parameters are multiplied by 10^4. Final isotropic thermal parameter 3.54 $Å^2$.

TABLE III

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION OF NONHYDROGEN ATOMS ALONG PRINCIPAL AXES ($Å \times 10^3$)

Atom	Axis 1	Axis 2	Axis 3	Av
Co	125 (12)	134 (12)	153 (10)	134 (12)
P_1	145 (11)	147 (11)	172 (9)	155 (10)
P_m	178 (9)	181 (9)	186 (9)	182 (9)
N_1	140 (13)	158 (12)	183 (11)	160 (12)
N_2	138 (14)	162 (11)	162 (12)	154 (12)
N_3	143 (14)	154 (12)	175 (11)	157 (12)
N_4	133 (14)	159 (12)	168 (11)	153 (12)
N_5	128 (14)	167 (12)	179 (11)	158 (12)
N_6	139 (14)	163 (12)	181 (11)	161 (12)
C_1	135 (15)	178 (11)	222 (11)	178 (12)
C_2	127 (15)	169 (12)	220 (10)	172 (12)
C_3	125 (15)	178 (12)	207 (11)	170 (13)
C_4	132 (15)	179 (12)	222 (10)	178 (12)
C_5	120 (17)	202 (11)	210 (11)	177 (13)
C_6	127 (15)	183 (12)	232 (10)	181 (13)
Biphosphate 1 Oxygens				
O_1	165 (12)	267 (9)	461 (9)	298 (10)
O_2	178 (11)	209 (9)	257 (8)	215 (9)
O_3	144 (13)	192 (10)	373 (7)	233 (10)
O_4	132 (14)	174 (11)	377 (7)	233 (11)
Bridging Biphosphate Oxygens				
O_{1m}	159 (12)	185 (10)	239 (8)	194 (10)
O_{3m}	165 (13)	205 (11)	249 (10)	206 (11)
O_{2m}	186 (13)	284 (10)	306 (10)	259 (11)
Oxygens of the Waters of Crystallization				
O_{1w}	206 (10)	230 (9)	238 (9)	225 (9)
O_{2w}	164 (11)	204 (10)	370 (7)	246 (9)
O_{3w}	186 (10)	224 (9)	257 (9)	222 (9)
O_{4w}	201 (11)	232 (11)	242 (10)	225 (11)
O_{5w}	213 (11)	235 (11)	238 (10)	229 (11)
O_{6w}	246 (11)	288 (10)	327 (10)	281 (10)

as a salt of this cationic trimer and the remaining biphosphate anion.

The biphosphate anions have the expected distortion from tetrahedral symmetry. In both anions the bond which we assign as P–OH is approximately 0.1 Å longer than the P–O bonds. This is a general property of biphosphate salts.[20] The hydrogen bonding in this structure is summarized in Table IV. The biphosphate bond lengths and angles are in Table V. They agree well with values from other biphosphate structures.[20–22]

There are six crystallographically independent water molecules. Three are in the general positions 8(d) and the remaining three lie on the mirror plane in positions 4(c). The water molecules on the mirror plane form hydrogen bonds among themselves and with the bridging biphosphate ions to form the planar network shown in Figure 2. This network forms only two types of hydrogen bonds to the rest of the structure: those between the three water molecules on the mirror plane to the three water molecules off the mirror plane and those formed between the bridging biphosphate oxygens and the axial amine protons of the $Co(en)_3^{3+}$ cation. The water molecules off the mirror plane also form hydrogen bonds to the $Co(en)_3^{3+}$ amine protons and to the free biphosphate.

The most important feature of this structure is the conformation of the cation and its interaction with the biphosphate anion. The bridging biphosphate is positioned approximately on the molecular threefold axis of the $Co(en)_3^{3+}$ cation such that the symmetry axes for

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(20) D. J. Sutor, *Acta Crystallogr.*, **23**, 418 (1967).

(21) C. Li and C. N. Caughlan, *ibid.*, **19**, 637 (1965).

(22) R. C. L. Mooney-Slater, *ibid.*, **20**, 526 (1966).

TABLE IV

POSSIBLE A–H···B BONDS WITH A···B DISTANCES LESS THAN 3.3 Å

General phosphate oxygen			Oxygens of bridging biphosphate			Water		
Bond	Distance	Amine hydrogen type	Bond	Distance	Amine hydrogen type	Bond	Distance	Amine hydrogen type
O_1–N_4	2.743 (5)	a	O_{1m}–N_1	2.956 (5)	a	O_{1w}–O_{2w}	2.806 (5)	
O_1–N_5	2.831 (6)	a	O_{1m}–N_2	3.184 (5)	a	O_{1w}–O_{3w}	2.824 (5)	
O_1–N_6	2.941 (7)	a	O_{1m}–O_{2w}	2.684 (5)		O_{1w}–O_{5w}	2.829 (5)	
O_2–N_1	2.852 (6)	e	O_{1m}–O_{3w}	2.721 (5)		O_{2w}–N_3	2.991 (5)	e
O_2–N_6	3.171 (5)	e	O_{2m}–N_2	3.293 (4)	a	O_{2w}–N_5	2.997 (6)	e
O_2–O_{1w}	2.664 (6)		O_{2m}–O_{6w}	2.729 (10)		O_{2w}–O_{6w}	3.117 (7)	
O_3–N_2	2.997 (5)	e	O_{3m}–N_3	2.900 (5)	a	O_{3w}–O_{4w}	2.756 (5)	
O_3–N_4	2.890 (6)	e	O_{3m}–O_{5w}	2.718 (8)		O_{4w}–O_{5w}	2.788 (7)	
						O_{4w}–O_{6w}	2.758 (10)	
						O_{6w}–N_3	3.280 (6)	e

Average A–H···B Distance to Each Ring

Ring	Distance
N_1–C_1–C_4–N_4	2.860 (6)
N_2–C_2–C_5–N_5	3.060 (5)
N_3–C_3–C_6–N_6	3.056 (6)

TABLE V

BOND LENGTHS, ANGLES, AND ERRORS FOR THE BIOPHOSPHATE ANIONS

Bond	Length, Å	Group	Angle, deg
	Biphosphate 1		
O_1–P_1	1.466 (4)	O_1–P_1–O_2	109.24 (4)
O_2–P_1	1.502 (4)	O_1–P_1–O_3	114.16 (17)
O_3–P_1	1.499 (4)	O_1–P_1–O_4	107.68 (4)
O_4–P_1[a]	1.583 (4)	O_2–P_1–O_3	112.45 (16)
		O_2–P_1–O_4	105.95 (4)
		O_3–P_1–O_4	106.90 (19)
	Biphosphate on the Mirror Plane		
O_1–P_m[b]	1.482 (3)	O_1–P_m–O_1[c]	115.02 (29)
		O_1–P_m–O_2	105.36 (20)
O_2–P_m[a]	1.609 (6)	O_1–P_m–O_3	112.79 (18)
O_3–P_m	1.503 (5)	O_2–P_m–O_3	104.29 (32)

[a] Assigned as the P–OH bond. [b] There is another P_m–O_1 distance since O_1 is displaced from the mirror plane. [c] Angle between two mirror-related O_1 atoms.

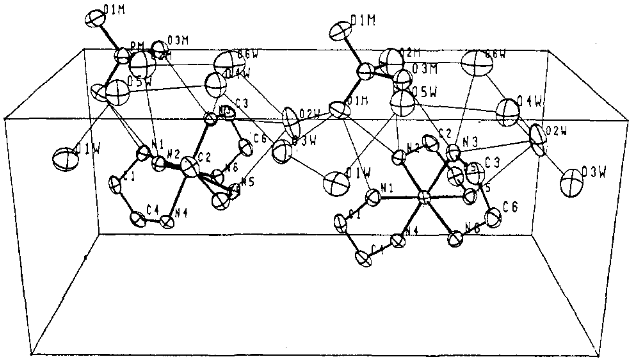

Figure 2.—The hydrogen-bonding network of the bridging biphosphates, waters of crystallization, and $Co(en)_3{}^{3+}$. The view is normal to the *ab* plane with the horizontal axis corresponding to 1 unit along *a* and the vertical axis corresponding to $^1/_4 b$.

TABLE VI

BOND LENGTHS, ANGLES, AND ERRORS FOR THE $Co(en)_3{}^{3+}$ CATION

Bond	Length, Å	Group	Angle, deg
Co–N_1	1.954 (4)	N_1–Co–N_2	90.9 (2)
Co–N_2	1.970 (4)	N_1–Co–N_3	91.0 (2)
Co–N_3	1.967 (4)	N_1–Co–N_4	86.2 (2)
Co–N_4	1.955 (4)	N_1–Co–N_5	175.6 (2)
Co–N_5	1.965 (4)	N_1–Co–N_6	92.1 (2)
Co–N_6	1.968 (4)	N_2–Co–N_3	93.1 (2)
N_1–C_1	1.483 (6)	N_2–Co–N_4	91.7 (2)
N_2–C_2	1.496 (6)	N_2–Co–N_5	86.0 (2)
N_3–C_3	1.488 (6)	N_2–Co–N_6	176.7 (2)
N_4–C_4	1.486 (6)	N_3–Co–N_4	174.6 (2)
N_5–C_5	1.485 (6)	N_3–Co–N_5	92.2 (2)
N_6–C_6	1.483 (7)	N_3–Co–N_6	85.7 (2)
C_1–C_4	1.501 (7)	N_4–Co–N_5	90.8 (2)
C_2–C_5	1.502 (7)	N_4–Co–N_6	89.7 (2)
C_3–C_6	1.500 (7)	N_5–Co–N_6	91.0 (2)
		Co–N_1–C_1	108.8 (3)
		N_1–C_1–C_4	107.2 (4)
		C_1–C_4–N_4	106.4 (4)
		C_4–N_4–Co	108.2 (2)
		Co–N_2–C_2	108.5 (3)
		N_2–C_2–C_5	107.3 (4)
		C_2–C_5–N_5	107.4 (4)
		C_5–N_5–Co	109.2 (3)
		Co–N_3–C_3	109.0 (3)
		N_3–C_3–C_6	107.9 (4)
		C_3–C_6–N_6	106.9 (4)
		C_6–N_6–Co	109.0 (3)

Dihedral Angles for Chelate Rings. Crossing Angle of C–C Bond with N–N Axis

Planes	Angle, deg
C_1–Co–C_4 N_1–Co–N_4	28.0 (3)
C_2–Co–C_5 N_2–Co–N_5	27.0 (3)
C_3–Co–C_6 N_3–Co–N_6	26.9 (3)

Angle between Ring Nitrogens As Viewed down the C–C Axis

Ring	Angle, deg
N_1–C_1–C_4–N_4	52.4 (5)
N_2–C_2–C_5–N_5	50.7 (5)
N_3–C_3–C_6–N_6	50.5 (5)

Average N–Co–N Angles

Type	Angle, deg
Intra-ring nitrogens	86.0 (1)
Trans	175.6 (1)

Average Bond Lengths

Type	Length, Å
Co–N	1.963 (2)
N–C	1.487 (3)
C–C	1.501 (4)

Average Ring Angles

Type	Angle, deg
Co–N–C	108.8 (3)
N–C–C	107.2 (2)

both ions are nearly coincident (Figures 3 and 4). The cations of the trimer are in the low-energy enantiomorphous conformations Λδδδ and Δλλλ.[23] Each chelate ring participates in at least four hydrogen bonds with biphosphate anions and water molecules (Table VI). Seven of these involve the free biphosphate with A–H···B distances ranging from 2.83 to 3.17 Å. The bridging biphosphate forms one strong hydrogen bond to the axial protons of the cation (between N_3 and O_{3m}). As shown in Figures 3 and 4, the oxygen is directly above the axial proton and forms a nearly linear A–H···B bond. The motion required to bring the biphosphate and $Co(en)_3{}^{3+}$ axes into coincidence can be viewed as a rotation of the biphosphate. The hydrogen bond formed by O_{3m} is the pivotal axis for this rotation. Bond lengths and angles for the $Co(en)_3{}^{3+}$ cation are given in

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[23] The nomenclature used here is the IUPAC convention, *Inorg Chem.*, **9**, 1 (1970). The conformations Λδδδ and Δλλλ are enantiomorphous and so identical in energy. A Λ configuration about the metal ion is assumed when not specified.

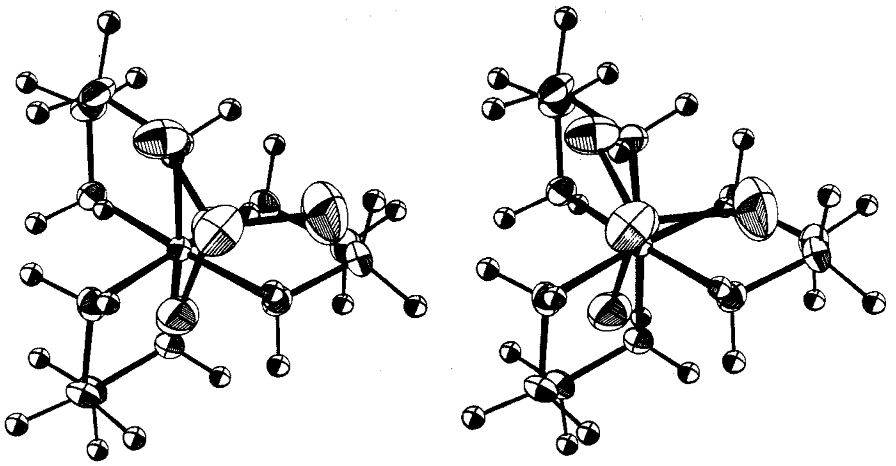

Figure 3.—A stereopair showing the bridging biphosphate and Co(en)$_3^{3+}$ as viewed down the molecular threefold axis of the cation.

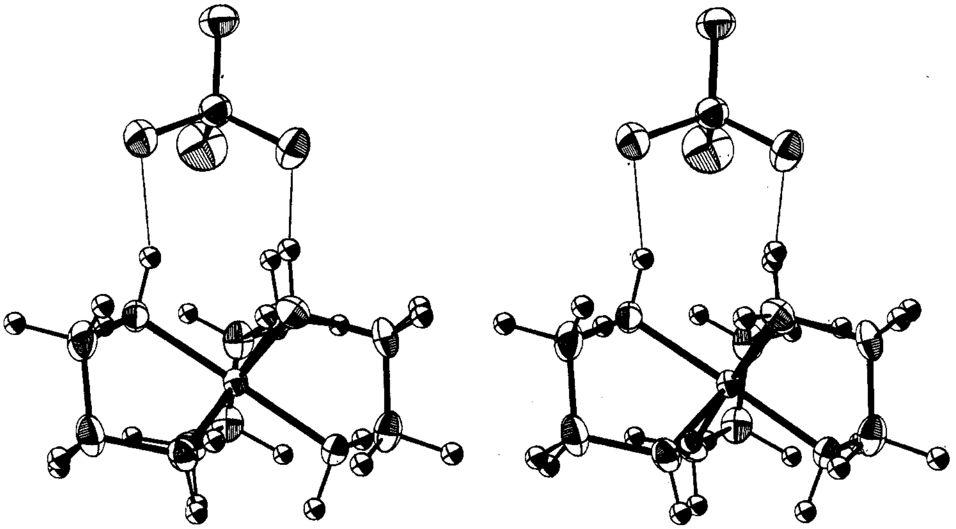

Figure 4.—A stereopair showing bridging biphosphate and Co(en)$_3^{3+}$ as viewed normal to the molecular threefold axis of the cation.

Table VI. These agree well with those of previously reported structures.[8,11,12,24]

Discussion

The structure proposed for the ion pair formed in aqueous media between Co(en)$_3^{3+}$ and PO$_4^{3-}$, based on CD and nmr spectra,[5-7] has one essential feature: the phosphate must be positioned on the cation's molecular threefold axis and form multiple hydrogen bonds to the axial amine protons. This feature is confirmed by this solid-state structure determination, which then substantially verifies the structure for the ion pair in aqueous solution. Linking of two cations to an ion trimer, as found for this biphosphate salt, is a process which is strongly favored in the solid state relative to solutions. In aqueous solutions containing excess phosphate, an ion trimer of this type is unlikely since the relative basicity of an ion-pair phosphate must certainly be less than free phosphate. The phosphate and Co(en)$_3^{3+}$ threefold symmetry axes are not exactly coincident in this structure. We ascribe this asymmetry to two factors. The first is the distortion caused by the bridging of two cations to form the ion trimer. The second is that the phosphate is slightly too large to match exactly the configuration of axial protons formed when the cation is in the $\Lambda\delta\delta\delta$ conformation.

The first conformational analysis of tris-ethylenediamine complexes determined the relative energies to be $\Lambda\delta\delta\delta < \Lambda\delta\delta\lambda < \Lambda\delta\lambda\lambda < \Lambda\lambda\lambda\lambda$.[2] A recent calculation[25] indicates that the $\delta\delta\lambda$ and $\delta\delta\delta$ conformers may be very close in stability. In fact, entropy considerations have led to the suggestion[11] that when the conformational energy difference is small, as in Ni(en)$_3^{2+}$,[24] the order for the lower two conformations may be reversed. However it is clear that, in general, a greater number of λ ring conformations (for Λ metal configuration) implies greater ring–ring interaction and a higher energy for the complex. The expected $\Lambda\delta\delta\delta$ conformations were observed in the earliest M(en)$_3$ structure determinations[26-30] and two recent reports.[24,31] However, the other recent structure determinations[9-12] have found the higher energy conformers in each case. All four conformations have been observed in various recent

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(24) Mazhar-Ul-Haque, C. N. Caughlan, and K. Emerson, *Inorg. Chem.*, **9**, 2421 (1970). A report on the isostructural copper salt appeared earlier: D. L. Cullen and E. C. Lingafelter, *ibid.*, **9**, 1858 (1970).

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(27) K. Nakatsu, Y. Saito, and H. Kuroya, *ibid.*, **30**, 795 (1957).

(28) K. Nakatsu, *ibid.*, **35**, 832 (1962).

(29) L. N. Swink and M. Atoji, *Acta Crystallogr.*, **13**, 639 (1960).

(30) T. Watanabe and M. Atoji, *Kagaku* (*Tokyo*), **21**, 301 (1951).

(31) D. L. Cullen and E. C. Lingafelter, *Inorg. Chem.*, **9**, 1858 (1970).

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 $\Lambda\delta\delta\delta$ conformation effectively blocks the remaining two protons and so the maximum number of hydrogen bonds can only be formed in the $\Lambda\lambda\lambda\lambda$ 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 $\Lambda\delta\delta\delta$ 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 $2\theta = 10°$ to 2.6° at $2\theta = 100°$. 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).