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The Structure of Racemic μ-Amido-μ-hydroxo-bis[bis(ethylenediamine)cobalt(III)] Tetranitrate Hydrate

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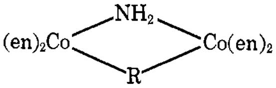
The crystal structure analysis of racemic μ-amido-μ-hydroxo-bis[bis(ethylenediamine)cobalt(III)] tetranitrate hydrate, DL-[(en)$_2$Co-μ-(NH$_2$,OH)-Co(en)$_2$](NO$_3$)$_4 \cdot$H$_2$O, has been carried out using three-dimensional diffractometer data. The salt crystallizes in the monoclinic space group $P2_1/n$ with cell dimensions $a = 8.309$ (3), $b = 23.933$ (7), $c = 12.399$ (3) Å, $\beta = 90.71$ (3)°, and $Z = 4$. The observed density is 1.76 (1) g cm^{-3}, and that calculated for four formula units in the cell is 1.771 g cm^{-3}. The structure was solved using Patterson and Fourier methods and refined by least-squares calculations based on 1794 reflections of nonzero weight. The final R index is 0.055. The configurations and conformations of the cation antipodes in the crystal are described by the absolute symbols ${}^{\partial}_{\partial}\Delta\Delta^{\partial}_{\partial}$ and ${}^{\lambda}_{\lambda}\Delta\Delta^{\lambda}_{\lambda}$. Nonbonded interactions between hydrogen atoms of the ethylenediamine groups seem to favor specifically these geometries. The cobalt atoms, 2.98 Å apart, have slightly distorted octahedral coordinations. The ions and the water molecules are connected by hydrogen bonds to form a three-dimensional network.

Introduction

The formations, the reactivities, and the structures of bridged cobalt complex cations with the skeleton



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where R is, for example, O$_2^{2-}$, O$_2^-$, O$_2$H$^-$, OH$^-$, SO$_4^{2-}$, and NO$_2^-$ and en is ethylenediamine, have been the subject of a great deal of investigation since their discovery by Werner around 1910.[2] The field was recently surveyed by Garbett and Gillard.[3] These cations have an added interest because of the many isomers that can be expected to exist if one takes into account the possible configurations of the ethylenediamine rings around the cobalt atoms and the possible conformations of the ethylenediamine rings themselves.

The three configurational isomers (one pair of antipodes and a meso form) of the (en)$_2$Co-μ-(OH, NH$_2$)-Co(en)$_2^{4+}$ cation, together with the respective configurational symbols, are shown in Figure 1. Werner has found that cations of type **1** usually have a $\Delta\Delta$ or $\Lambda\Lambda$ configuration.[4] (The symbols Δ and Λ are used here as in ref 5.) Only one case is known (for R = NO$_2^-$) where rearrangement of the en rings seems to occur, giving cations with $\Delta\Lambda$ configuration(s).[6] The absolute configuration of cations of type **1** has been established by Garbett and Gillard by transforming a resolved dinuclear salt (R = O$_2^-$) *via* several steps into mononuclear complexes of known absolute configurations.[7]

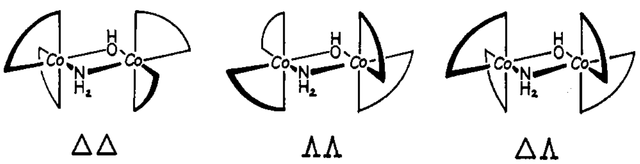

Figure 1.—The three possible isomers of the (en)$_2$Co-μ-(NH$_2$,-OH)-Co(en)$_2^{4+}$ cation, the chirality of the en rings not being considered.

No work, so far, has been concerned with the isomerism caused by the puckering of the en rings. It was therefore of some interest to determine the actual structures of these cations and to look for possible reasons which could determine the conformations of the en rings.

The μ-amido-μ-hydroxo cation is easily formed by reduction of the μ-amido-μ-hydroperoxo cation. Using I$^-$ as the reducing agent, Werner prepared a racemic iodide, a racemic bromide,[2] and one of the optically active iodides.[4] In this paper we report the structure determination of a racemic nitrate.

Experimental Section

In attempting to recrystallize racemic μ-amido-μ-hydroperoxo-bis[bis(ethylenediamine)]cobalt(III) tetranitrate hydrate, DL-[(en)$_2$Co-μ-(NH$_2$,O$_2$H)-Co(en)$_2$](NO$_3$)$_4 \cdot 2$H$_2$O, by slow evaporation of aqueous solutions containing a few drops of nitric acid, we found that over a period of several days the red starting material would decompose, giving a black syrupy residual. This residual turned out to be a mixture of two salts, which could be separated by fractional crystallization. One was the green nitrate of the μ-amido-μ-superoxo cation DL-[(en)$_2$Co-μ-(NH$_2$,O$_2$)-Co(en)$_2$](NO$_3$)$_4 \cdot$H$_2$O. The other salt was the red nitrate of the μ-amido-μ-hydroxo cation DL-[(en)$_2$Co-μ-(NH$_2$,OH)-Co(en)$_2$](NO$_3$)$_4 \cdot$H$_2$O. The first salt was identified by comparison of the rotation and Weissenberg photographs of its crystals with the corresponding photographs of the compound prepared by Werner's method;[2] these photographs were identical. The structure of the second salt was elucidated during the present X-ray investigation. *Anal.* Calcd for C$_8$H$_{37}$N$_{13}$Co$_2$O$_{14}$: C, 14.6; H, 5.7; N 27.7. Found: C, 14.6; H, 5.7; N, 27.5. By chemical analysis it was not possible to determine if the salt contains a μ-hydroxo group or a μ-hydroperoxo group since the content of water of crystallization was not known. Well-formed red crystals of DL-[(en)$_2$Co-μ-(NH$_2$,OH)-Co(en)$_2$](NO$_3$)$_4 \cdot$H$_2$O were grown by slow evaporation of a saturated aqueous solution of the complex. The crystals were monoclinic and elongated along a. The systematic absences ($h0l$ for $h + l = 2n + 1$ and $0k0$ for $k = 2n + 1$) on Weissenberg films taken around a and b uniquely determined the space group $P2_1/n$. The equivalent positions in $P2_1/n$, an alternative setting of $P2_1/c$, are $\pm(x, y, z;\ ^1/_2 + x,\ ^1/_2 - y,\ ^1/_2 + z)$. Cell dimensions were obtained from a least-squares treatment of the 2θ values of several reflections measured on a General Electric diffractometer using Co radiation. The cell dimensions, their standard deviations, and other crystal data are given in Table I. The density at room tem-

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[1] To whom correspondence should be addressed.

[2] A. Werner, *Ann. Chem.*, **375**, 1 (1910).

[3] K. Garbett and R. D. Gillard, *J. Chem. Soc. A*, 1725 (1968).

[4] A. Werner, *Ber.*, **47**, 1961 (1914).

[5] *Inorg. Chem.*, **9**, 1 (1970).

[6] A. Werner, *Ber.*, **46**, 3674 (1913).

[7] K. Garbett and R. D. Gillard, *Chem. Commun.*, 99 (1966).

TABLE I
CRYSTAL DATA FOR
DL-$[(en)_2Co\text{-}\mu\text{-}(NH_2,OH)\text{-}Co(en)_2](NO_3)_4 \cdot H_2O$

$Co_2C_8H_{14}N_{13}H_{37}$	Mol wt 657.4
$a = 8.309\ (3)$ Å	$Z = 4$
$b = 23.933\ (7)$ Å	$F(000) = 1368$
$c = 12.399\ (3)$ Å	$\lambda(\text{Co } K\alpha_1)$ 1.78892 Å
$\beta = 90.71\ (3)°$	$\lambda(\text{Co } K\alpha_2)$ 1.79278 Å
Space group $P2_1/n$	$\mu(\text{Co } K\alpha)$ 37.5 cm^{-1}
$d_m = 1.76\ (1)\ \text{g cm}^{-3}$	$d_x = 1.771\ \text{g cm}^{-3}$

perature was measured by the flotation method. It agrees well with the density, D_x, calculated assuming four formula units in the unit cell. Two sets of intensity data were collected. The first was collected visually from multiple-film equiinclination Weissenberg photographs taken about a ($0kl$–$5kl$) and c ($hk0$) with Fe radiation. The crystal fragments used had cross-sectional dimensions of about 0.2 mm. The crystals suffered markedly from X-ray damage during the period of exposure (several hundred hours), which particularly affected the high-angle reflections. Therefore the film data were judged to be of low quality and were used only for the determination of the approximate structure. For the refinement, a second set of data was collected on a Datex-automated General Electric XRD-5 diffractometer that was equipped with a cobalt-target X-ray tube with iron filter, an NaI(Tl) scintillation counter, and a pulse-height analyzer. The crystal fragment used was cut from a larger crystal with a razor blade and had dimensions 0.19 × 0.17 × 0.17 mm^3. It was mounted with b parallel to the φ-axis of the diffractometer. The intensities were measured using a θ–2θ scan. To minimize the effects due to decomposition of the crystal, a scanning speed of 4°/min was used and background was counted for only 9 sec at each end of the scan interval. The measurements were confined to reflections in the range $2\theta \leq 106°$. The scan intervals were adjusted to account for the α_1–α_2 splitting. A reference reflection, (006), was measured periodically during the data collection process. Its intensity dropped continuously to 78% of its original value at the end of the measurements. The measured intensities of all reflections were then rescaled to what their values would have been at the beginning of the measurements on the basis of the time-dependent check-reflection intensity. The individual reflections were assigned intensity values, I_o, and standard deviations of $\sigma(I_o)$ according to the formulas

$$F_o^2 = [S - (B_1 + B_2)T_s/2t]/Lp$$

$$\sigma(F_o^2) = [S + (B_1 + B_2)(T_s/2t)^2 + (0.017S)^2]^{1/2}/Lp$$

with S the total scan count, T_s the scanning time, B_1 and B_2 the background counts, t the time spent counting the background, and Lp the Lorentz–polarization correction factors. The term $(0.017S)^2$ in the second equation was introduced to compensate for errors not due to counting statistics (Busing and Levy[8]). A total of 1846 independent reflections were obtained. The 49 reflections whose intensities became negative were assigned intensities and weights of zero. The 1797 reflections which were measured above zero were treated as observed. An absorption correction was then applied on the assumption that the crystal was a sphere of radius 0.1 mm ($\mu R = 0.37$). Finally the data were brought to an approximate absolute scale by the method of Wilson.[9]

Determination and Refinement of the Structure

The Co coordinates were obtained from a three-dimensional Patterson map and the lighter atoms were located by standard heavy-atom techniques. The R index based on the film data for this trial structure was 0.39 ($R = \Sigma|F_o - |F_c||/\Sigma F_o$). At this stage the diffractometer data became available and refinement of the structure was begun using the new set of data. Atomic form factors for Co^{2+} (corrected for the real part of anomalous dispersion by subtracting 2.2 electrons), O, N, and C were taken from Iber's tabulation.[10] The form factor values for hydrogen were those of Stewart, Davidson, and Simpson.[11] In the least-squares refinement the reflections were assigned individual weights $w = 1/\sigma^2(F_o^2)$, [for $\sigma(F_o^2)$ see the Experimental Section] and the quantity minimized was

$$\sum w(F_o^2 - (1/k^2)F_c^2)^2$$

Two cycles of full-matrix refinement of the scale factor and the positional parameters together with individual isotropic temperature factors for all heavier atoms gave a residual of $R = 0.12$. During these calculations both bridging atoms of the cation, O(1) and N(1), were treated as nitrogen atoms. For one of them this choice resulted in a B value of 2.4 Å^2, a value similar to those of the other atoms within the cation; for the other bridging atom, however, an abnormally low temperature factor of 0.4 Å^2 was obtained. Accordingly, the second atom was identified as an oxygen atom. A three-dimensional difference synthesis was then calculated and inspected for hydrogen atoms. This map clearly indicated some of the hydrogen atoms at stereochemically reasonable positions. However, most H atoms could not be located; among them were the H atoms of the bridging μ-NH_2 and μ-OH groups.

The coordinates for the hydrogen atoms of the ethylenediamine and the μ-NH_2 group were then calculated, assuming N–H and C–H distances of 0.9 Å and H–N–H and H–C–H angles of 109.5°. The hydrogen atoms of the water molecule and the μ-OH group were introduced from consideration of the probable hydrogen-bonding scheme. All hydrogen atoms were assigned isotropic temperature factors equal to those of the heavy atoms to which they are bonded. The hydrogen atoms were included in subsequent structure factor calculations; their parameters were not refined but were readjusted toward the end of the refinement.

In the next two least-squares cycles the bridging N(1) and O(1) atoms were refined isotropically and the remaining nonhydrogen atoms were refined anisotropically. R dropped to 0.083 and the temperature factors of both bridging atoms then had reasonable values, $B[O(1)] = 2.1$ and $B[N(1)] = 2.0$ Å^2. During these and the following least-squares calculations the parameters were included in five matrices of about equal size, the positional and thermal parameters of a given atom being in one matrix. Three reflections ($\bar{2}11$, $\bar{1}31$, 063) with relatively large residuals were given zero weight. After six more cycles the anisotropic refinement was terminated. The final R index for the 1794 reflections of nonzero weight is 0.055 and the goodness of fit, $[\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$, is 1.8. A total of 334 parameters were adjusted: three positional and six anisotropic temperature parameters for each of the 37 heavy atoms and one scale factor. During the last four cycles the scale factor was kept constant. In the final cycle some of the parameters of the nitrate oxygen atom, O(11), still showed shifts of the same order of magnitude as the corresponding standard deviations. All other parameters had converged; the largest shift:deviation ratio for them was 0.7 [for β_{22} of N(9) which belongs to the same nitrate group as O(11) and for z of the water oxygen atom O(14)]. The refinement was stopped at this point, since the high values of the thermal parameters of

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(8) W. R. Busing and H. A. Levy, *J. Chem. Phys.*, **26**, 563 (1957).

(9) A. J. C. Wilson, *Nature (London)*, **150**, 151 (1942).

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

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

TABLE II

POSITIONAL AND THERMAL PARAMETERS OF THE NONHYDROGEN ATOMS AND THEIR STANDARD DEVIATIONS[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co(1)	37,408 (12)	8,054 (4)	24,356 (8)	650 (19)	78 (2)	293 (9)	−13 (11)	−99 (20)	10 (8)
Co(1′)	36,838 (12)	16,797 (4)	7,281 (8)	640 (19)	80 (2)	327 (9)	−33 (11)	−50 (20)	43 (8)
O(1)	3,745 (4)	874 (2)	888 (3)	80 (8)	12 (1)	42 (4)	5 (5)	28 (9)	5 (3)
O(2)	7,624 (7)	2,230 (2)	3,175 (4)	209 (13)	20 (1)	68 (5)	70 (7)	72 (13)	−3 (4)
O(3)	8,819 (5)	1,590 (2)	2,257 (4)	96 (9)	13 (1)	36 (4)	0 (5)	−0 (9)	−11 (4)
O(4)	10,150 (7)	2,061 (2)	3,452 (4)	214 (13)	19 (1)	67 (5)	−32 (7)	−137 (13)	1 (4)
O(5)	6,581 (6)	441 (2)	5,377 (4)	170 (11)	16 (1)	60 (5)	−20 (7)	−32 (11)	22 (4)
O(6)	8,311 (7)	927 (2)	6,286 (5)	228 (13)	28 (2)	63 (5)	−23 (7)	−53 (14)	1 (5)
O(7)	7,657 (6)	1,170 (2)	4,669 (5)	232 (13)	16 (1)	59 (5)	−10 (6)	51 (12)	29 (4)
O(8)	10,510 (7)	2,861 (2)	1,644 (5)	203 (12)	18 (1)	87 (6)	34 (7)	67 (13)	23 (4)
O(9)	9,084 (7)	3,597 (2)	1,367 (5)	267 (14)	14 (1)	98 (6)	52 (7)	20 (14)	−13 (5)
O(10)	9,712 (7)	3,077 (2)	31 (5)	236 (13)	19 (1)	65 (5)	−8 (6)	50 (14)	−3 (5)
O(11)	6,903 (10)	359 (3)	−109 (5)	466 (20)	92 (3)	77 (7)	−304 (13)	145 (19)	−76 (7)
O(12)	9,107 (7)	401 (2)	−957 (5)	205 (13)	27 (1)	58 (5)	−25 (7)	50 (14)	−6 (5)
O(13)	8,869 (7)	758 (2)	644 (5)	291 (15)	23 (1)	61 (5)	−65 (7)	−82 (14)	−13 (5)
O(14)	7,035 (6)	1,483 (2)	−1,688 (4)	142 (10)	41 (2)	84 (5)	29 (7)	−13 (11)	−36 (5)
N(1)	3,666 (5)	1,615 (2)	2,294 (4)	67 (10)	8 (1)	30 (4)	0 (5)	−20 (10)	1 (4)
N(2)	3,627 (6)	818 (2)	4,010 (4)	124 (11)	11 (1)	39 (5)	−1 (6)	−33 (11)	−3 (4)
N(2′)	3,639 (6)	2,498 (2)	701 (4)	100 (10)	12 (1)	36 (5)	1 (6)	2 (11)	1 (4)
N(3)	3,845 (6)	−15 (2)	2,376 (4)	93 (10)	12 (1)	23 (4)	−11 (6)	−15 (10)	3 (4)
N(3′)	3,697 (6)	1,628 (2)	−859 (4)	62 (10)	9 (1)	43 (5)	4 (5)	6 (11)	3 (4)
N(4)	6,108 (6)	751 (2)	2,509 (4)	91 (10)	11 (1)	48 (5)	−5 (6)	−26 (11)	9 (4)
N(4′)	1,341 (6)	1,667 (2)	548 (4)	109 (10)	10 (1)	28 (4)	6 (6)	19 (10)	7 (4)
N(5)	1,401 (6)	745 (2)	2,482 (4)	109 (10)	8 (1)	24 (4)	−3 (6)	−14 (10)	4 (4)
N(5′)	6,018 (6)	1,766 (2)	754 (4)	89 (10)	11 (1)	52 (5)	−8 (6)	−24 (11)	9 (4)
N(6)	8,860 (8)	1,967 (3)	2,973 (5)	134 (15)	9 (2)	31 (6)	−6 (8)	−11 (16)	10 (5)
N(7)	7,521 (8)	852 (3)	5,440 (6)	111 (14)	14 (2)	45 (7)	17 (8)	46 (16)	5 (6)
N(8)	9,760 (8)	3,184 (3)	1,005 (6)	114 (14)	14 (2)	70 (8)	−28 (8)	14 (17)	8 (7)
N(9)	8,351 (10)	487 (3)	−126 (7)	189 (18)	32 (2)	57 (8)	−97 (10)	−41 (20)	20 (7)
C(2)	1,945 (8)	850 (3)	4,370 (5)	121 (14)	18 (2)	36 (6)	24 (8)	19 (16)	4 (6)
C(2′)	5,230 (9)	2,709 (3)	1,068 (6)	163 (16)	11 (2)	57 (7)	−7 (9)	−63 (16)	9 (6)
C(3)	5,493 (8)	−207 (3)	2,163 (5)	118 (14)	10 (2)	49 (6)	25 (8)	54 (16)	4 (5)
C(3′)	2,083 (8)	1,449 (3)	−1,246 (5)	136 (14)	14 (2)	27 (6)	−2 (8)	−8 (15)	1 (5)
C(4′)	6,605 (8)	176 (3)	2,738 (5)	81 (14)	18 (2)	55 (7)	7 (8)	−10 (15)	0 (6)
C(4′)	884 (7)	1,765 (3)	−584 (5)	70 (13)	18 (2)	44 (6)	−11 (7)	−34 (14)	12 (5)
C(5)	912 (8)	556 (3)	3,568 (5)	88 (13)	17 (2)	50 (7)	22 (8)	21 (15)	8 (5)
C(5′)	6,649 (8)	2,359 (3)	560 (6)	88 (14)	17 (2)	78 (7)	−22 (8)	−61 (16)	29 (6)

[a] Values for the cobalt atoms have been multiplied by 10^5; those for other atoms by 10^4. The standard deviations are given in parentheses and refer to the last digits of the respective values.

O(14) and of the atoms of the nitrate group N(9) [particularly O(11)] imply disorder at these sites and since *R* did not change significantly during the last cycles.

That some kind of disorder is associated with O(11) is supported by the finding that in difference Fourier syntheses, calculated at various stages of the refinement, the highest electron density peak always was found in the neighborhood of that atom. In a final difference Fourier map this peak was 0.76 $e^-/Å^3$, whereas all other excursions were below 0.43 $e^-/Å^3$. The final structure factors are available as indicated in ref 12. Table II gives the heavy-atom parameters and their standard deviations, calculated in the usual way from the least-squares residuals. The average esd's (Å) in the final positional coordinates are as follows: Co, 0.001; O(cation), 0.004; O(NO_3^- and water), 0.006; N(cation), 0.005; N(NO_3^-), 0.007; C, 0.007. These errors correspond to the following average esd's in bond lengths (Å): Co–N, 0.005; Co–O, 0.004; C–N, 0.009; N–O(NO_3^-), 0.010. The esd's in bond angles are about 0.2° at Co, 0.4° at C and N(cation), and 0.6° at N(NO_3^-). The assumed hydrogen atom parameters are given in Table III.

All computations were carried out on an IBM 7094 computer. For the preparation of Figure 2 the ORTEP

TABLE III

POSITIONAL PARAMETERS ASSIGNED TO HYDROGEN ATOMS[a]

	Atom	x	y	z		Atom	x	y	z
O(1)	H(1)	468	73	61	C(2)	H(20)	186	68	501
N(1)	H(2)	453	179	261		H(21)	164	121	441
	H(3)	276	177	259	C(3)	H(22)	568	−21	146
N(2)	H(4)	409	50	427		H(23)	562	−56	243
	H(5)	417	112	425	C(4)	H(24)	762	12	249
N(3)	H(6)	318	−13	184		H(25)	658	11	345
	H(7)	351	−15	301	C(5)	H(26)	107	18	362
N(4)	H(8)	652	86	187		H(27)	−12	64	367
	H(9)	648	97	304	C(2′)	H(28)	531	268	178
N(5)	H(10)	105	50	198		H(29)	535	306	85
	H(11)	95	108	235	C(3′)	H(30)	195	153	−195
N(2′)	H(12)	288	262	115		H(31)	196	107	−115
	H(13)	344	262	2	C(4′)	H(32)	93	213	−74
N(3′)	H(14)	392	196	−114		H(33)	−11	163	−72
	H(15)	444	138	−106	C(5′)	H(34)	742	243	86
N(4′)	H(16)	92	194	96		H(35)	647	242	−15
	H(17)	97	133	76	O(14)	H(36)	646	173	−210
N(5′)	H(18)	641	167	141		H(37)	753	127	−219
	H(19)	645	156	24					

[a] All values have been multiplied by 10^3.

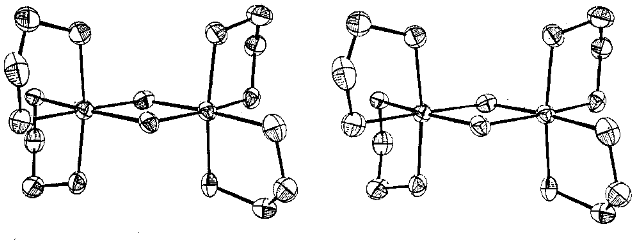

Figure 2.—Stereoscopic drawing of one of the optically isomeric cations in DL-[$(en)_2Co$-μ-(NH_2,OH)-$Co(en)_2$]$(NO_3)_4 \cdot H_2O$.

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

program of Johnson[13a] was used. All other calculations were performed with programs of the CRYRM system.[13b]

Discussion

The Cation.—As the X-ray analysis shows, the salt under investigation is a racemate containing cations with ΔΔ and ΛΛ configurations. This could be expected since according to Werner's investigations the chirality of cations of type **1** usually is retained during replacement of bridging groups at the position R^4 and since the starting complex was a racemate of ΔΔ and ΛΛ cations. A stereodrawing of the ΔΔ isomer of the cation is shown in Figure 2 from which it can be seen that both cobalt atoms have a slightly distorted octahedral coordination. The numbering scheme of the atoms is given in Figure 3.

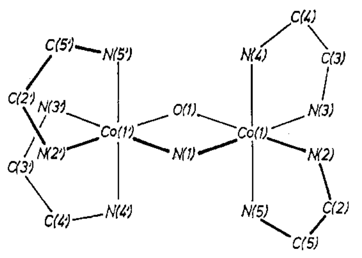
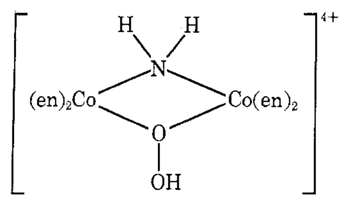


Figure 3.—Identification and numbering of the atoms in the cation.

Bond lengths and bond angles are presented in Table IV.



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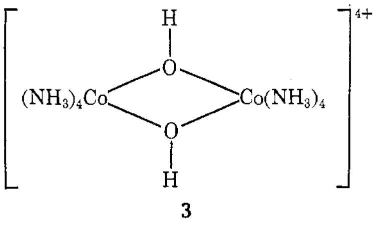

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TABLE IV

BOND DISTANCES AND BOND ANGLES IN THE CATION[a]

Atoms	Distance, Å	Atoms	Distance, Å
Co(1)–Co(1')	2.977 (2)		
O(1)	1.926 (4)	Co(1')–O(1)	1.940 (4)
N(1)	1.947 (5)	N(1)	1.948 (5)
N(2)	1.956 (5)	N(2')	1.960 (5)
N(3)	1.966 (5)	N(3')	1.972 (5)
N(4)	1.972 (5)	N(4')	1.957 (5)
N(5)	1.951 (5)	N(5')	1.950 (5)
N(2)–C(2)	1.474 (8)	N(2')–C(2')	1.481 (9)
N(3)–C(3)	1.472 (8)	N(3')–C(3')	1.482 (8)
N(4)–C(4)	1.464 (9)	N(4')–C(4')	1.468 (8)
N(5)–C(5)	1.482 (8)	N(5')–C(5')	1.489 (9)
C(2)–C(5)	1.484 (9)	C(2')–C(5')	1.474 (10)
C(3)–C(4)	1.479 (9)	C(3')–C(4')	1.503 (9)
Atoms	**Angle, deg**	**Atoms**	**Angle, deg**
Co(1)–O(1)–Co(1')	100.7 (2)	Co(1)–N(1)–Co(1')	99.7 (2)
O(1)–Co(1)–N(1)	80.0 (2)	O(1)–Co(1')–N(1)	79.6 (2)
N(2)	173.7 (2)	N(2')	175.1 (2)
N(3)	92.7 (2)	N(3')	92.3 (2)
N(4)	92.1 (2)	N(4')	91.2 (2)
N(5)	92.8 (2)	N(5')	94.5 (2)
N(1)–Co(1)–N(2)	94.2 (2)	N(1)–Co(1')–N(2')	95.5 (2)
N(3)	172.6 (2)	N(3')	171.9 (2)
N(4)	95.7 (2)	N(4')	95.3 (2)
N(5)	92.7 (2)	N(5')	90.7 (2)
N(2)–Co(1)–N(3)	93.2 (2)	N(2')–Co(1')–N(3')	92.6 .2)
N(4)	90.9 (2)	N(4')	89.7 (2)
N(5)	84.9 (2)	N(5')	85.0 (2)
N(3)–Co(1)–N(4)	83.8 (2)	N(3')–Co(1')–N(4')	84.4 (2)
N(5)	88.3 (2)	N(5')	90.3 (2)
N(4)–Co(1)–N(5)	170.9 (2)	N(4')–Co(1')–N(5')	172.4 (2)
Co(1)–N(2)–C(2)	111.1 (4)	Co(1')–N(2')–C(2')	108.5 (4)
N(2)–C(2)–C(5)	108.4 (5)	N(2')–C(2')–C(5')	107.5 (5)
C(2)–C(5)–N(5)	107.5 (5)	C(2')–C(5')–N(5')	107.1 (5)
C(5)–N(5)–Co(1)	109.5 (3)	C(5')–N(5')–Co(1')	110.5 (4)
Co(1)–N(3)–C(3)	111.2 (3)	Co(1')–N(3')–C(3')	108.9 (3)
N(3)–C(3)–C(4)	107.2 (5)	N(3')–C(3')–C(4')	106.3 (5)
C(3)–C(4)–N(4)	108.5 (5)	C(3')–C(4')–N(4')	106.0 (5)
C(4)–N(4)–Co(1)	110.5 (3)	C(4')–N(4')–Co(1')	110.6 (3)

[a] These values contain no corrections for thermal motion.

The bridging atoms O(1) and N(1), both Co atoms, and the atoms trans to O(1) and N(1) are approximately coplanar. The equation of the weighted least-squares plane passing through these eight atoms is given by $8.300x + 0.834y + 0.211z = 3.215$ Å, where x, y, and z are fractional coordinates referred to the monoclinic unit cell. The deviations of the atoms from this plane are as follows (Å): N(1), 0.011; O(1), −0.015; Co(1), 0.008; Co(1'), −0.002; N(2), −0.052; N(2'), 0.029; N(3), 0.025; N(3'), −0.029. The corresponding atoms in the related μ-amido-μ-hydroperoxo cation **2** are also approximately coplanar.[14] Within the four-membered central ring of the cation all four angles are about 10° smaller than one would expect for undistorted octahedral and tetrahedral angles, respectively [80.0 ± 0.2° at Co(1), 79.6 ± 0.2° at Co(1'), 100.7 ± 0.2° at O(1), and 99.7 ± 0.2° at N(1)]. These angles are essentially the same as those in the μ-amido-μ-hydroperoxo cation **2** (79° at both Co atoms, 100° at the N atom, and 102° at the O atom) and those in the di-μ-hydroxo cation **3** (79.9 ± 0.3° at Co and 100.1 ± 0.5° at O).[15] The Co–μ-OH distances in the latter cation (1.911 ± 0.005 and 1.913 ± 0.005 Å) are similar to the Co–μ-OH distances in the present cation (1.926 ± 0.004 and 1.940 ± 0.004 Å). The Co–μ-NH_2 distances (1.947 ± 0.005 and 1.948 ± 0.005 Å) agree well with those observed in **2** (1.94 and 1.95 Å) and with those of the μ-amido-μ-superoxo cation $(en)_2Co\text{-}\mu\text{-}(NH_2,O_2)\text{-}Co(en)_2^{4+}$ (1.95 and 1.92 Å).[14] Similar Co–μ-NH_2 distances have also been found in the cations $(NH_3)_4Co\text{-}\mu\text{-}(NH_2,O_2)\text{-}Co(NH_3)_4^{4+}$ (1.916 ± 0.004 and 1.928 ± 0.004 Å)[16] and $(NH_3)_4Co\text{-}\mu\text{-}(NH_2,NO_2)\text{-}Co(NH_3)_4^{4+}$ (1.929 ± 0.007 and 1.923 ± 0.007 Å).[17] There are no surprises in the dimensions of the Co–en rings. The six Co–N(en) bond lengths range from 1.950 to 1.972 Å, the average being 1.960 Å. This value is essentially the same as the average Co–N(ammonia) distance found in recent determinations of crystal structures on salts containing bridged cobalt ammines (see, for example, ref 18). The standard deviation of the Co–N(en) bond lengths as calculated from the spread of the individual values is $\sigma = 0.009$ Å. The C–N bond lengths range from 1.464

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to 1.489 Å, the mean value of 1.476 Å (σ = 0.009 Å) agreeing well with that of the paraffin–quaternary amine bond length of 1.479 Å (σ = 0.005 Å) given in Sutton's tabulation.[19] The four C–C distances ranging from 1.474 to 1.503 Å with a mean value of 1.485 Å (σ = 0.013 Å) are considerably shorter than the usual paraffinic C–C bond distance of 1.54 Å. The Co–N–C and N–C–C valence angles inside the chelate rings all come close to the expected tetrahedral angle of 109.5°; the maximum deviation [at C(4′)] is −3.5°. The average N–C–C bond angle (107.3°; σ = 0.9°) is smaller than the average Co–N–C angle (110.1°; σ = 1.0°). The N–Co–N angles of the chelate rings with a mean value of 84.5° and σ = 0.6° all are smaller by *ca.* 5° than the 90° angle that one would expect for an undistorted octahedral coordination about the cobalt atoms. On the other hand, most angles between Co–N bonds of adjacent chelate rings are larger than 90°. The same effect has been described for the $Ni(en)_3^{2+}$ cation by Swink and Atoji[20] and is usually observed in metal–ethylenediamine compounds. The four Co–en rings are all in the unstrained gauche form which is commonly observed in metal–ethylenediamine complexes. The extent to which the rings are puckered is specified in Table V. There, the deviations of the carbon atoms of each ring from their respective N–Co–N planes and the dihedral angles α and β are listed. (α and β are as used in ref 21: α is the angle between the N–metal–N plane and the C–metal–C plane; β is the torsion angle between the nitrogen atoms across the C–C bond.) The mean values are 26.3° for α and 48.9° for β with standard deviations of 1.4 and 2.8°, respectively. The average distance of a carbon atom from its N–Co–N plane calculates as 0.33 Å (σ = 0.09 Å). The two deviations from the N(2)–Co(1)–N(5) ring (0.17 Å for C(2) and −0.45 Å for C(5)), particularly, are quite different from this mean and from each other, which indicates a considerable departure from the theoretical C_2 symmetry of this en ring. The four ethylenediamine rings all have identical conformations. The complete designation of the cation shown in Figures 2 and 3 is ${}^{\lambda}_{\lambda}\Delta\Delta^{\lambda}_{\lambda}$ (and that of its enantiomer ${}^{\partial}_{\partial}\Lambda\Lambda^{\partial}_{\partial}$). In these notations the symbols Δ and Λ, representing configurations of the metal atoms, and ∂ and λ, representing ring conformations, are arranged in an obvious way to represent the cation isomers. It is interesting to note that theoretically there exist 36 isomers of the cation (16 pairs of antipodes and 4 inactive forms), if one takes into account the two possible configurations about each metal atom and the two possible conformations of each ethylenediamine ring. Whereas the two enantiomers observed in the present investigation exhibit approximate C_2 symmetry (with the twofold axis in the O(1)–N(1) direction), most of the other possible isomers do not have any element of symmetry except the identity.

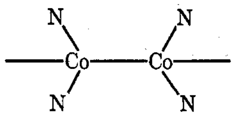
TABLE V

PUCKERING OF THE ETHYLENEDIAMINE CHELATE RINGS

Plane defined by atoms	Atom	Dev from plane, Å	α, deg	β, deg
Co(1), N(2), N(5)	C(2)	0.17	24.9	46.3
	C(5)	−0.45		
Co(1), N(3), N(4)	C(3)	0.31	25.2	47.3
	C(4)	−0.32		
Co(1′), N(2′), N(5′)	C(2′)	0.44	26.9	49.7
	C(5′)	−0.22		
Co(1′), N(3′), N(4′)	C(3′)	0.39	28.3	52.4
	C(4′)	−0.32		

Recently Raymond, Corfield, and Ibers[21] explained the stabilization of the different conformers of $M(en)_3$ type cations (M = metal) in terms of two forces (in the following discussion only Δ isomers will be regarded; the discussion of Raymond, *et al.*, actually was based on Λ isomers). (1) Hydrogen bonding between the amine groups of the en rings and adjacent hydrogen bond acceptors favors a ∂ conformation of the en rings. For this conformation the steric conditions allowing the axial hydrogen atoms to take part in the hydrogen bonding are more favorable than for the λ conformation. (2) H–H repulsion between the en rings favors a λ conformation. This is supported by calculations of Corey and Bailar,[22] who showed that if no hydrogen bonds are present, the $\Delta\lambda\lambda\lambda$ conformer of $Co(en)_3^{3+}$ is more stable than the $\Delta\partial\partial\partial$ conformer by *ca.* 1.8 kcal/mol. These considerations are probably less important for the present dinuclear cations, where only two en groups are around each Co atom, than they are for $M(en)_3$ cations.

Most likely the reason for the stabilization of the ${}^{\lambda}_{\lambda}\Delta\Delta^{\lambda}_{\lambda}$ isomer lies in the fact that there are fewer nonbonded interactions between amine hydrogen atoms of en rings belonging to different cobalt atoms than in all other conformers. In Figure 4 the three possible arrangements of en groups are shown. From the drawing it is evident that in I (both en rings in the ∂ conformation) there is the most severe overlap and that in III (both rings in the λ conformation) there is the least overlap, whereas II (one ring in the ∂ conformation, the other ring in the λ conformation) represents an intermediate situation. With the more realistic van der Waals radius for hydrogen of *ca.* 1.2 Å (Pauling[23]) than the 0.84 Å used in Figure 4, even in III a considerable amount of interaction would occur and the bent arrangement



of the "out-of-central-plane" Co–N bonds [N(4)–Co(1)–N(5) = 170.9 ± 0.2°; N(4′)–Co(1′)–N(5′) = 172.4 ± 0.2°] is most probably caused by these nonbonded H···H interactions (see also Figure 2). The H···H repulsion concept seems also to apply to other cations of type **1**. For example, in salts of the μ-amido-μ-hydroperoxo cations and of the μ-amido-μ-superoxo cations the ${}^{\lambda}_{\lambda}\Delta\Delta^{\lambda}_{\lambda}$ (and ${}^{\partial}_{\partial}\Lambda\Lambda^{\partial}_{\partial}$) isomers have been found (see Figures 1 and 2 in ref 14).

The ellipsoids of thermal vibrations for the atoms of the cation are shown in Figure 2. The thermal motions are in general agreement with those that would be expected on the basis of the cation geometry. The vibrations of the cobalt atoms are almost isotropic with an average rms amplitude of 0.15 Å. The largest rms

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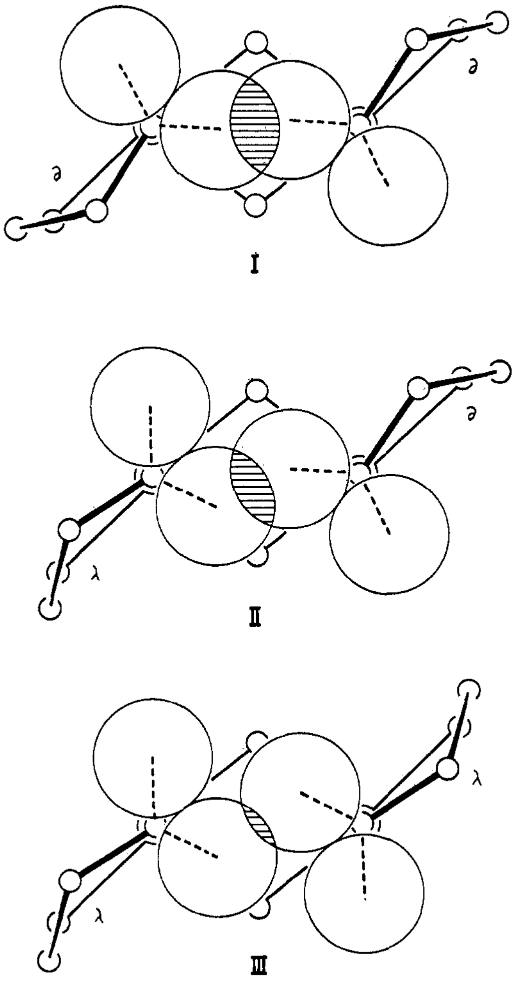


Figure 4.—Possible conformations of the en rings in the $\Delta\Delta$ isomer of $(en)_2Co\text{-}\mu\text{-}(NH_2,OH)\text{-}Co(en)_2{}^{4+}$ showing different degrees of nonbonded H···H interaction. For this drawing tetrahedral coordination of the N atoms and an N–H distance of 1.03 Å are assumed. Only the en rings above the central plane of the cation need to be considered, since the en rings below it show the same kind of nonbonded interaction. The hydrogen atoms are drawn with a 0.84 Å radius, so that the spheres representing the H atoms for the two amine hydrogen atoms bonded to the same nitrogen atom just touch. For simplicity the amine N atoms are shown exactly above the Co atoms. Actually they are slightly displaced, as can be seen from Figure 2.

amplitudes (up to 0.29 Å) are shown by the carbon atoms.

The Nitrate Groups.—There are four independent nitrate groups. The N–O bond distances and O–N–O bond angles are shown in Figure 5. The bond lengths vary between 1.225 and 1.266 Å. The rms deviation of these values from the average value (1.241 Å) is 0.014 Å. Except for the N(9) nitrate group all O–N–O bond angles are close to the expected value of 120°. These values are in good agreement with those observed in other nitrate salts. As was pointed out earlier, nitrate group N(9) presumably is disordered, so that not much significance should be attributed to its geometry. The three NO_3^- ions N(6), N(7), and N(8) are planar within experimental error; the distances of the N atoms from the planes formed by their oxygen ligands are as follows (Å): N(6), 0.000; N(7), 0.003; N(8), 0.003. Again, the disorder of the nitrate group N(9) might be used to explain the relatively large N–(O-plane) distance of 0.06 Å. As is usually observed in complex salts of the present type, where relatively large cations and relatively small anions are present, the atoms of the anionic groups show a considerably higher thermal movement than the atoms of the cation, which is evident from the data in Table II.

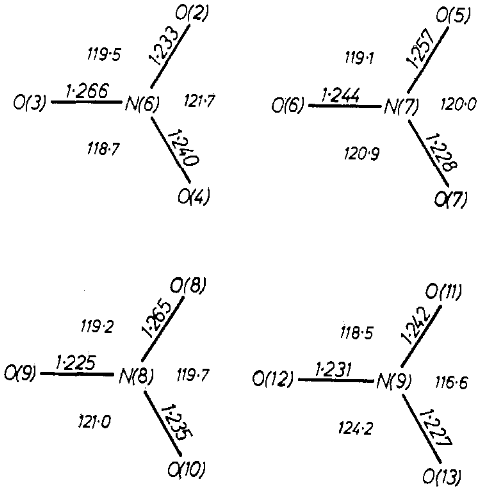


Figure 5.—Bond distances (Å) and bond angles (deg) in the nitrate groups. Error assignments are described in the text. No corrections for thermal motion were applied.

The Overall Structure.—The structure viewed down the *a* axis is shown in Figure 6. The arrangement of the cations is such that their central planes are almost parallel to each other (and to the *yz* plane); these central planes lie approximately at $x = {}^{1}/_{8}, {}^{3}/_{8}, {}^{5}/_{8}$, and ${}^{7}/_{8}$. The cations are surrounded by nitrate groups and water molecules. Electrostatic forces and hydrogen bonds hold the different groups together. In Table VI the close contacts between the cation and its surrounding groups are listed. For those contacts, D···A (A = acceptor), where a hydrogen atom is not too far from the D···A line, the D–H···A angle is also given. These angles surely are not very accurate, since the H positions were calculated on the basis of C–H and N–H distances of 0.9 Å (which is a value typical for X-ray diffraction investigations, although not representing the true separation of the atomic nuclei), assuming an idealized angular arrangement. All hydrogen atoms except

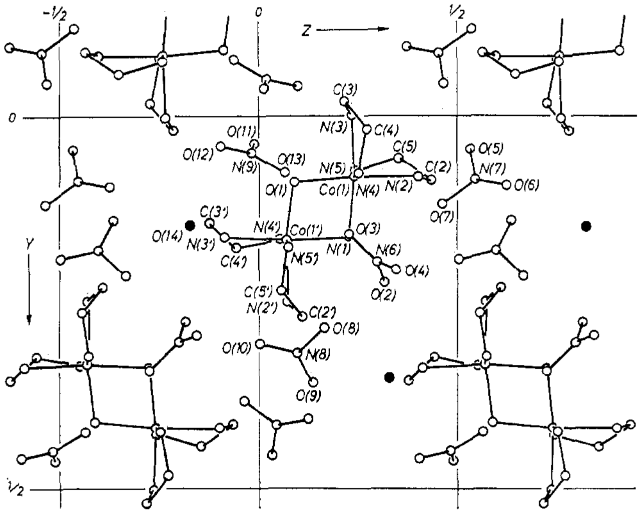


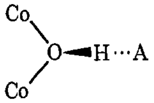
Figure 6.—The crystal structure viewed along the *a* axis.

TABLE VI
SHORT CONTACTS, D···A, BETWEEN THE NONHYDROGEN ATOMS OF THE CATION AND ATOMS OF SURROUNDING GROUPS[a]

D	A	H	D···A, Å	D–H···A, deg
O(1)	O(11, b)		3.15	
	O(11)	H(1)	3.16	178
N(2)	O(5)	H(4)	3.10	127
	O(5, a)	H(4)	3.11	140
	O(10, d)	H(5)	3.06	161
N(3)	O(11, b)	H(6)	2.99	143
	O(12, b)	H(6)	3.14	160
	O(5, a)	H(7)	2.99	164
N(4)	O(13)	H(8)	3.28	144
	O(7)	H(9)	3.12	155
N(5)	O(13, c)	H(10)	3.08	121
	O(3, c)	H(11)	2.96	148
N(2′)	O(8, c)	H(12)	2.99	157
	O(4, e)	H(13)	3.25	135
	O(2, e)	H(13)	3.30	169
N(3′)	O(2, e)	H(14)	3.11	141
	O(14)		2.99	
N(4′)	O(3, c)	H(16)	3.00	113
	O(13, c)	H(17)	3.00	143
N(5′)	O(3)	H(18)	2.99	138
	O(14)	H(19)	3.23	145
C(5′)	O(4, e)	H(35)	3.14	143

[a] Hydrogen atoms not too far from the D···A line and angles D–H···A are also given. Symmetry code: no letter, coordinates are given in Tables II and III; (a) $1 - x, -y, 1 - z$; (b) $1 - x, -y, -z$; (c), $-1 + x, y, z$; (d) $-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (e) $-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$; (f) $x, y, z - 1$.

H(15) of the amine groups in the en ligands seem to participate in hydrogen bonds. The N–H···A distances for some of these bonds are rather long, however, and the angles at some of the H atoms are considerably less than 180°, suggesting only weak interactions. There are two amine hydrogen atoms [H(4) and H(6)] which appear to be shared by two acceptor oxygen atoms each. The water molecule oxygen, O(14), forms four close contacts, three of which can be considered as hydrogen bonds: O(14)–H(37)···O(6, f) = 3.04 Å; O(14)–H(36)···O(8, e) = 2.88 Å; N(5′)–H(19)···O(14) = 3.23 Å (for symmetry code, see Table VI). The fourth contact, of 2.99 Å to N(3′), does not involve a hydrogen atom. The two hydrogen atoms of the bridging μ-NH_2 group are not engaged in hydrogen bonding, as there are no suitable hydrogen-bond acceptors. The μ-OH group oxygen, O(1), has a suitable hydrogen-bond acceptor: the nitrate oxygen, O(11), 3.16 Å away. The hydrogen atom H(1) [whose coordinates were calculated on the basis of a tetrahedral sp^3 configuration around O(1) and which was put arbitrarily on that side of the central ring where it can form a hydrogen bond to O(11)] deviates only slightly from the O(1)···O(11) line, the O–H···O angle being about 178°. A similar geometry of a



arrangement has been observed for cation **3** in its tetrachloride tetrahydrate salt.[15] The shortest nonbonded contact (3.14 Å) between a nitrate group and a carbon atom of the en ring is between O(4, e) and C(5′). This contact, with a C–H···O angle of 143° at H(35), may be regarded as an accidental result of the molecular packing rather than hydrogen bonding. All other C···O contacts in this structure exceed 3.2 Å. The closest contact between oxygen atoms of different nitrate groups, 2.82 Å, is between O(3) and O(13).

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CONTRIBUTION FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY,
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The Crystal and Molecular Structure of *cis*-Dichlorobis(dimethylphenylphosphine)palladium(II)[1]

BY LESLIE L. MARTIN AND ROBERT A. JACOBSON*

Received May 21, 1970

The crystal and molecular structure of *cis*-dichlorobis(dimethylphenylphosphine)palladium(II) has been determined from 1722 independent, nonzero reflections using conventional, three-dimensional, single-crystal techniques. The compound crystallizes in the space group $P4_2/n$ with four molecules in a unit cell of dimensions $a = b = 9.324 \pm 0.004$ Å and $c = 21.485 \pm 0.004$ Å ($\rho_{calcd} = 1.612 \pm 0.003$ g/cm^3 and $\rho_{obsd} = 1.61 \pm 0.01$ g/cm^3). The structure is approximately cis square planar with a slight tetragonal distortion of 4.3°. A strong "trans effect" is evident. The Pd–P distance of 2.260 ± 0.002 Å is 0.12 Å shorter while the Pd–Cl distance of 2.362 ± 0.003 Å is 0.08 Å longer than the respective, expected values. The shortest Pd–Pd distance is 6.6 Å.

Introduction

It has been observed that square-planar complexes of the type PdX_2Y_2, where X is a halide, very often adopt the trans configuration.[2] In fact, only recently have any cis complexes of this type been characterized. The cis chloro complexes usually form pale yellow or colorless crystals while crystals of the trans complexes are decidedly more yellow.[3] However, a recent far-infrared study by Keiter[4] of $PdCl_2(P(CH_3)_2C_6H_5)_2$, which forms

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[1] Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 2708.

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