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Acidopentaminecobalt(III) Complexes with Polyamine Ligands. III. The Crystal Structure of β-Chloro(ethylenediamine)-(dipropylenetriamine)cobalt(III) Tetrachlorozincate(II)[1]

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The crystal structure of β-chloro(ethylenediamine) (dipropylenetriamine)cobalt(III) tetrachlorozincate(II), β–[Co(en)(dpt)Cl]ZnCl$_4$, has been determined by three-dimensional X-ray diffraction techniques from 799 reflections collected at ambient temperature by multiple film methods. The structure has been solved by the symbolic addition procedure and refined by full-matrix least-squares techniques to a conventional R *factor of 8.0%. The salt crystallises in space group P2$_1$/c of the monoclinic system with 4 formula units in a cell of dimensions* a = *7.875(3),* b = *15.824(11),* c = *14.748(8)Å, β = 94.69(5)°. The observed and calculated densities are 1.65 and 1.63 g/cm^3 respectively. The cobalt atom is surrounded by one chlorine and five nitrogen atoms in an approximately octahedral configuration. The three nitrogen atoms of the dipropylenetriamine ligand ($NH_2(CH_2)_3NH(CH_2)_3NH_2$) are in a plane with one nitrogen atom of the ethylenediamine while the second nitrogen atom is* trans *to the chlorine atom. The orientation about the coordinated secondary amine nitrogen of the dipropylenetriamine is such that the NH proton is remote from the chlorine atom. The tetrachlorozincate(II) anion has a slightly distorted tetrahedral configuration, with an average Zn–Cl bond distance of 2.26(2) Å.*

Introduction

Part I of this series[2] describes the preparation, properties and reactions of three geometric isomers, α, β and γ, of [Co(en)(dpt)Cl]ZnCl$_4$ [3] and tentative assignments for the geometric configurations were made. In this paper we report the crystal structure of the β isomer. The results confirm the assignment of Gainsford and House for this isomer, and provide the first reported crystallographic structure determination of the dipropylenetriamine ligand in an octahedral cobalt(III) complex, and of the ZnCl$_4^{2-}$ anion associated with a transition metal complex cation.

Experimental Section

Crystals of β–[Co(en)(dpt)Cl]ZnCl$_4$ suitable for X-ray analysis were prepared by the method of Gainsford and House.[2]

Crystal Data. Precession and Weissenberg photographs showed the compound possessed monoclinic symmetry, with systematic absences h0l for l odd, and 0k0 for k odd, unambiguously indicating the space group P2$_1$/c. The unit cell constants were determined from Polaroid precession photographs of the hk0 and h0l zones, taken with CoKα radiation (λ = 1.7902) at room temperature. Distances between 22 Friedel pairs were measured, and these together with the reflection indices were used as input to a least squares program[4] which calculated the best cell constants. These were $a = 7.875(3)$, $b = 15.824(11)$, $c = 14.748(8)$ Å; $\beta = 94.69(5)°$. Throughout this paper, numbers in parentheses are estimated standard deviations in the least significant digits usually derived from the inverse matrix in non-linear least-squares calculations. With a formula weight of 440.0, and for $Z = 4$ formula units per unit cell, the calculated density is 1.63 g/cm^3, within the experimental range of 1.65 ± 0.02 g/cm^3 observed for crystals in a calibrated density gradient tube.[5] With four general positions in the space group P2$_1$/c, no crystallographic symmetry conditions are imposed on the anion or cation.

Collection of the Intensity Data. A violet, cylindrical shaped crystal approximately 0.36 mm long and with a radius of 0.05 mm was used for data collection. The linear absorption coefficient for this material is 147.0 cm^{-1} for the CoKα radiation used The reciprocal lattice layers 0kl-4kl were recorded at room temperature using a Nonius integrating Weissenberg camera and an iron filter. The plateaus (0.3×0.3 mm^2) of the integrated spots and adjacent background areas were measured using a single beam photometer and a galvanometer calibrated to read intensities directly. The Weissenberg data totalled 1303 independent reflections of which 504 were too

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[1] Part II, A. R. Gainsford and D. A. House, *Inorg. Chim. Acta*, 3, 367 (1969).

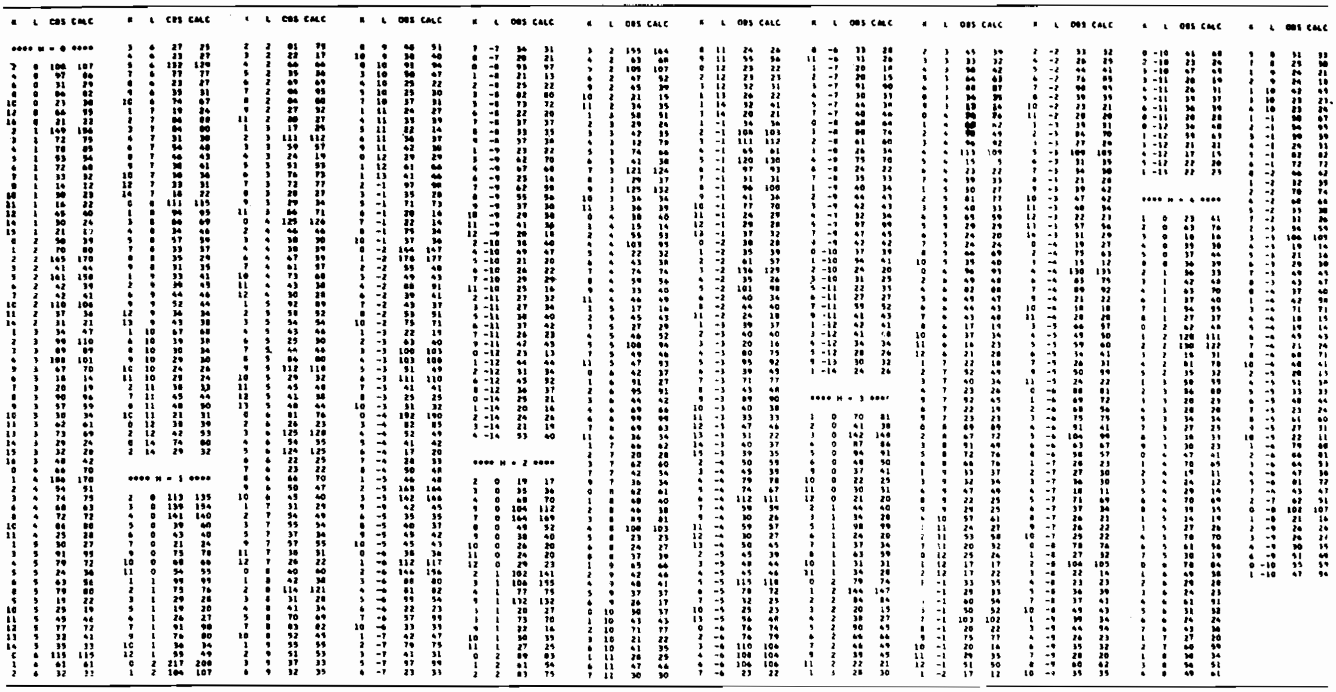
[2] A. R. Gainsford and D. A. House, *Inorg. Chim. Acta*, 3, 33 (1969).

[3] Abbreviations used: en = $NH_2(CH_2)_2NH_2$, dpt = $NH_2(CH_2)_3NH(CH_2)_3NH_2$.

[4] All calculations were performed on an IBM 360/44 computor with 16K words of core storage and twin 2315 disc drives.

[5] « International Tables for X-ray Crystallography » Vol. III, The Kynoch Press, Birmingham, England, 1962, p. 17.

Table I. Observed and Calculated Structure Amplititudes for β—[Co(en)(dpt)Cl]ZnCl$_4$.



weak to be measured accurately and were treated as unobserved. The five layers collected were corrected for Lorentz and polarization effects and scaled according to their exposure times. Integrated reflections on the 3kl and 4kl layers showed considerable differences in spot extension on the top and bottom halves of the films measured. Individual scale factors were therefore applied to each of these sections of data.

Solution and Refinement of the Structure. The data set was converted to a set of normalized structure factors of which the 206 largest were chosen for sign determination by the symbolic addition procedure.[6] A self consistent set of signs was obtained with one symbolic sign inconclusively determined. The two possible electron density maps were plotted[7] with one clearly revealing the $ZnCl_4^{2-}$ anion and the cobalt and chlorine atoms of the cation. Two successive difference Fouriers following intermediate least squares refinements,[8] located all the remaining non-hydrogen atoms. Refinement of the seven scale factors for the data collected, sixty positional parameters and twenty isotropic thermal parameters for the non-hydrogen atoms, converged at a conventional R factor ($R_1 = \Sigma\Delta/\Sigma|F_o|$ where $\Delta = ||F_o|-|F_c||$) of 8.2%. The usual tabulation of atomic scattering factors[9] was used for Zn, Co, Cl, N and C. Corrections for anomolous dispersion for CoKα radiation[10] were included for the Zn, Co and Cl atoms.

An examination of the low angle, high intensity sured dimensions of the crystal. Transmission factors varied between 0.31 and 0.37, so the absorption correction was small and had a negligible effect on the residuals.

An examination of the low angle, high intensity reflections revealed the need for a correction for secondary extinction effects. An approximate correction of the form given by Zachariasen,[11] F_{corr} =

Table II. Final Positional and Thermal Parameters for β—[Co(en)(dpt)Cl]ZnCl$_4$

Atom	x	y	z	B [a]
Co	0.1239(6) [b]	0.8946(2)	0.2546(3)	3.0(1)
Cl	—0.060(1)	0.0023(4)	0.2706(4)	4.3(2)
N(1)	0.148(3)	0.944(1)	0.130(1)	4.0(5)
N(2)	0.079(3)	0.845(1)	0.375(1)	2.9(5)
N(4)	0.327(3)	0.957(1)	0.312(1)	3.8(5)
N(5)	—0.071(3)	0.826(1)	0.205(1)	3.4(5)
N(6)	0.270(3)	0.798(1)	0.230(1)	2.7(4)
C(1)	0.319(5)	0.948(2)	0.094(2)	5.7(8)
C(2)	0.471(4)	0.968(2)	0.165(2)	5.2(7)
C(3)	0.407(4)	0.018(2)	0.248(2)	5.3(7)
C(5)	0.306(4)	0.005(2)	0.397(2)	5.0(7)
C(6)	0.269(4)	0.942(2)	0.474(2)	5.1(7)
C(7)	0.092(4)	0.904(2)	0.458(2)	4.4(7)
C(8)	—0.017(4)	0.734(2)	0.203(2)	4.8(7)
C(9)	0.160(4)	0.730(2)	0.174(2)	4.0(6)
Zn	0.3834(5)	0.2317(2)	0.0347(2)	3.5(1)
Cl(2)	0.144(1)	0.1529(5)	0.0321(5)	5.0(2)
Cl(3)	0.336(1)	0.3469(5)	0.1227(5)	4.6(2)
Cl(4)	0.372(1)	0.6751(5)	0.4012(5)	4.9(2)
Cl(5)	0.429(1)	0.2687(5)	—0.1088(5)	4.5(2)

[a] The B values are the parameters in the isotropic temperature factor expression exp[$-B(\sin\theta)^2/\lambda^2$]. [b] Numbers in parentheses here and in succeeding tables are standard deviations in the least significant digits.

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(6) Symbolic addition as carried out using SAP, a program derived from NRC-4 (S. R. Hall and F. R. Ahmed).

(7) All Fourier summations were carried out using an adapted version of A. Zalkin's FORDAP.

(8) Full matrix least squares refinements were carried out using CUCILS, a composite program containing elements of ORFLS (W. R. Busing, K. O. Martin and H. A. Levy), NULSA (J. A. Ibers) and UCILS (R. J. Doedens).

(9) Ref. 5, p. 202.

(10) D. T. Cromer, *Acta Cryst.*, *18*, 71 (1965).

(11) W. H. Zachriasen, *Acta Cryst.*, *16*, 1139 (1963).

$F_{obs}(1+CJ)$, where J is the raw intensity and C is the extinction parameter, was included in the least squares refinement. The final value of the variable C was 3.7×10^{-3}.

A weighting scheme of the form $w=(A+BF_o+CF_o^2+DF_o^3)^{-1}$ was calculated so that the $\Sigma w\Delta^2$ would be approximately independent of $|F_o|$ and $\sin\theta/\lambda$. The values of the constants A, B, C and D in the weighting expression for the final cycle of refinement were 49.7, −1.55, 0.027 and −0.0001, respectively. The final conventional *R* factor was 8.0% while the weighted *R* factor $R_2=(\Sigma w\Delta^2/\Sigma wF_o^2)^{1/2}$ was 10.1%. Isotropic temperature factors were all uniform, giving no indication that assigning anisotropic thermal parameters would improve the model.

A final three dimensional difference Fourier showed no significant features, with the highest peak having a density of 0.7 e/Å^3 or about 0.3 of the height of the last carbon atom located by this technique. The final structure factor listing is given in Table I and the atom position and thermal parameters are given in Table II.

Discussion

The crystal structure consists of monomeric Co(en)(dpt)Cl^{2+} cations packed with well separated $ZnCl_4^{2-}$ anions. The shortest interionic distance is 3.23(2) Å as shown in Figure 1. All intramolecular bond lengths and angles are given in Table III.

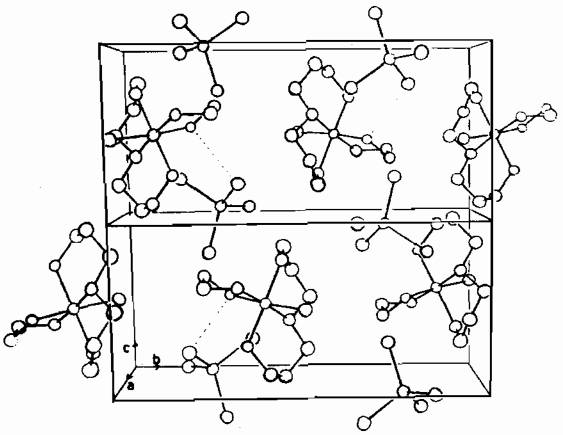

Figure 1. The packing of the ions in β—[Co(en)(dpt)Cl]-ZnCl$_4$, as viewed down the *a* axis.

The atom numbering system for the cation is defined in Figure 2. The stereochemical arrangement of the chlorine and five nitrogen atoms about the cobalt atom is approximately octahedral with a mean Co–N distance of 1.99(3) Å which is normal for this type of cobalt(III) complex cation. The chlorine atom is 2.26(1) Å from the cobalt atom and distorted away from the nitrogen atoms N(2) and N(4) of the dipropylenetriamine ligand.

Table III. Interatomic Distances (Å) and Angles (Degrees)

Intramolecular	Distance	Angle	
Co—Cl	2.259(9)	Cl—Co—N(1)	85.0(7)
—N(1)	2.02(2)	—N(2)	92.6(6)
—N(2)	2.00(2)	—N(4)	94.5(6)
—N(4)	2.00(2)	—N(5)	88.3(7)
—N(5)	1.97(2)	—N(6)	174.3(6)
—N(6)	1.97(2)	N(1)—Co—N(2)	175.1(9)
N(1)—C(1)	1.49(4)	—N(4)	93.3(9)
C(1)—C(2)	1.56(4)	—N(5)	90.1(9)
C(2)—C(3)	1.57(4)	—N(6)	91.8(9)
C(3)—N(4)	1.52(3)	N(2)—Co—N(4)	91.1(8)
N(4)—C(5)	1.49(3)	—N(5)	85.6(8)
C(5)—C(6)	1.56(4)	—N(6)	90.3(8)
C(6)—C(7)	1.53(4)	N(4)—Co—N(5)	175.9(9)
C(7)—N(2)	1.53(3)	—N(6)	90.4(9)
N(5)—C(8)	1.52(3)	N(5)—Co—N(6)	87.1(9)
C(8)—C(9)	1.50(4)	Co—N(1)—C(1)	120(2)
C(9)—N(6)	1.57(3)	N(1)—C(1)—C(2)	116(2)
		C(1)—C(2)—C(3)	110(2)
Zn—Cl(2)	2.255(9)	C(2)—C(3)—N(4)	110(2)
—Cl(3)	2.286(8)	C(3)—N(4)—Co	114(2)
—Cl(4)	2.259(9)	C(5)—N(4)—Co	118(2)
—Cl(5)	2.254(8)	C(3)—N(4)—C(5)	106(2)
		N(4)—C(5)—C(6)	109(2)
		C(5)—C(6)—C(7)	111(2)
		C(6)—C(7)—N(2)	112(2)
		C(7)—N(2)—Co	117(2)
		Co—N(5)—C(8)	109(2)
		N(5)—C(8)—C(9)	108(2)
		C(8)—C(9)—N(6)	108(2)
		C(9)—N(6)—Co	109(2)
		Cl(2)—Zn—Cl(3)	106.0(3)
		Cl(2)—Zn—Cl(4)	118.0(3)
		Cl(2)—Zn—Cl(5)	109.0(3)
		Cl(3)—Zn—Cl(4)	104.5(3)
		Cl(3)—Zn—Cl(5)	111.8(3)
		Cl(4)—Zn—Cl(5)	107.4(3)

Figure 3 shows a perspective view of the cation and illustrates the puckering of the chelate ring systems. The angles about the nitrogen and carbon atoms in the ethylenediamine ring are all within their standard deviation of the tetrahedral angle (109°) with these leading to a dihedral angle of 47°. This is similar to the dihedral angles (35-50°) found in related complexes with C$_2$ bridges between adjacent nitrogen atoms.[12]

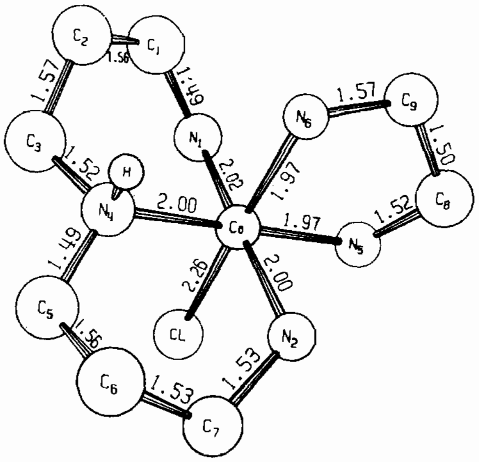

Figure 2. A general view of the β—Co(en)(dpt)Cl^{2+} cation showing the atom numbering scheme. Bond lengths are in Å.

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(12) M. R. Snow, D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *Chem. Commun.*, 891 (1969).

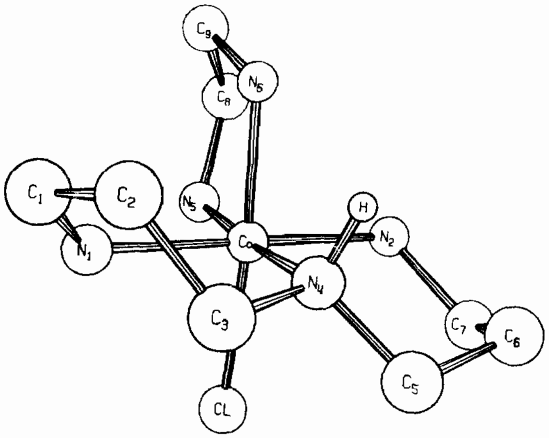

Figure 3. A perspective view of the β—Co(en)(dpt)Cl^{2+} cation.

In the dipropylenetriamine ligand, one 6-membered ring adopts the favored « chair » conformation[13] while the other is constrained into a distorted « boat » form by the approximately tetrahedrally coordinated N(4) nitrogen atom. The mean Co–N–C angle of 117(2)° in the 6-membered « chair » ring is similar to that found in [Co(tmd)$_3$]Br$_3$ [14] (tmd = NH$_2$(CH$_2$)$_3$-NH$_2$) of 117.4, with analogous ring systems. In the boat ring, however, the Co–N–C angles of 114(2) and 120(2)° are significantly different from each other. The structure of a recently reported square planar nickel complex[15] with a dipropylenetriamine moiety also shows similar ring puckering.

Structural data have also been reported for [Ni(dpt)$_2$](ClO$_4$)$_2$.[15a] In this complex, the donor atoms coordinate in an equatorial plane of an octahedron but all four of the six-membered rings have the chair conformation.

Although the data were not sufficiently accurate to enable hydrogen atom positions to be located and refined, the bond angles about the N(4) nitrogen atom in the dipropylenetriamine ligand unambiguously indicate that the NH proton is remote from the chlorine atom as shown in Figures 2 and 3. All carbon-carbon and carbon-nitrogen distances in the cation are normal within their standard deviations with mean values of 1.55(5) and 1.52(5) Å, respectively.

The tetrachlorozincate(II) anion has a slightly distorted tetrahedral arrangement of chlorine atoms about the central zinc atom. The average Zn–Cl bond length is 2.264(17) Å, similar to the values of 2.26 and 2.287(15)Å found in the compounds Na$_2$ZnCl$_4$. 3H$_2$O[16] and [N(CH$_3$)$_4$]$_2$[ZnCl$_4$],[17] respectively.

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(13) Y. Saito, *Pure and Applied Chemistry, 17,* 21 (1968).
(14) T. Nomura, F. Marumo, and Y. Saito, *Bull. Chem. Soc. Japan, 42,* 1016 (1969).
(15) R. Dewar and E. Fleischer, *Nature. 222,* 372 (1969).
(15a) P. Paoletti, S. Biagini, and M. Cannas, *Chem. Commun.,* 513 (1969). We thank one of the referees for drawing our attention to this work.
(16) B. Brehler, *Z. Krist., 114,* 66 (1960).
(17) J. R. Wierner, R. C. Srivastava, C. H. L. Kennard, M. DiVaira, and E. C. Lingafelter, *Acta Cryst., 23,* 565 (1967).