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Structural Studies on Metal Complexes of Chiral Cyclen. III.
The Structure of Chloro[(2R,5S,8R,11S)-1,4,7,10-tetrabenzyl-2,5,8,11-tetraethyl-1,4,7,10-tetraazacyclododecane]copper(II) Chloride Chloroform Solvate

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Abstract

[Cu($C_{44}H_{60}N_4$)Cl]Cl.$2CHCl_3$ is triclinic, $P\bar{1}$, with $a = 14.297$ (13), $b = 14.542$ (18), $c = 12.960$ (9) Å, $\alpha = 99.81$ (8), $\beta = 108.33$ (7), $\gamma = 85.67$ (10)°, $U = 2520$ (4) Å^3, $Z = 2$, $D_m = 1.324$, $D_c = 1.342$ Mg m^{-3}. The structure was refined to a final R of 6.4% for 4646 independent reflections. The 12-membered tetramine ring is coordinated to Cu^{II} as a quadridentate ligand, and takes a rectangular form. The Cu^{II} atom forms an approximate trigonal bipyramid with five coordination. The observed Cu–Cl distance, 2.354 (3)Å, is shorter than those found in the cyclen complexes of Cu with a square-pyramidal conformation.

Introduction

This paper is part of a series of investigations on the metal complexes of chiral cyclens.* The cyclens can be divided into four geometrical isomers, viz C_4, C_i, C_1 and S_4, and all the molecular structures have been determined (Sakurai, Kobayashi, Tsuboyama &

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* Abbreviations: cyclen: 1,4,7,10-tetraazacyclododecane; tbte-(RRRR)-cyclen: (2R,5R,8R,11R)-1,4,7,10-tetrabenzyl-2,5,8,11-tetraethyl-cyclen; C_4 isomer: tbte-(RRRR)-cyclen; C_1 isomer: tbte-(RRRS)-cyclen; S_4 isomer: tbte-(RSRS)-cyclen; C_i isomer: tbte-(RRSS)-cyclen.

Tsuboyama, 1978a,b; Hiramatsu, Sakurai, Tsuboyama & Tsuboyama, 1979; Sakurai, Hiramatsu, Tsuboyama & Tsuboyama, 1980; Sakurai, Watanabe, Tsuboyama & Tsuboyama, 1981). These molecules form metal complexes, and the C_4 isomer has square-pyramidal coordination (Sakurai, Kobayashi, Hasegawa, Tsuboyama & Tsuboyama, 1982). Electronic absorption, circular dichroism and ESR spectra reveal that the form of the complex with the S_4 isomer is considerably different from the other three (Tsuboyama et al., 1981). This paper reports the structure of the complex with the S_4 isomer.

Experimental

The Cu^{II} complex was prepared by heating a mixture of $CuCl_2.2H_2O$ (1 mmol) in absolute ethanol (25 ml) and tbte-(RSRS)-cyclen (1 mmol). The heating was continued until the solvent had evaporated. By repeated recrystallization from chloroform–ethyl acetate yellow-green plate crystals were obtained.

A crystal, $0.4 \times 0.4 \times 0.2$ mm, sealed in a glass capillary with the solvent, was used for the X-ray study. Intensity data were measured on a Rigaku automated four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. Within the range $2\theta \leq 50°$, 4646 independent reflections with $F > 3\sigma(F)$

Table 1. Atomic parameters

Positional parameters are multiplied by 10^4.

$$B_{eq} = \tfrac{4}{3} \Sigma_i \Sigma_j \beta_{ij} (\mathbf{a}_i \cdot \mathbf{a}_j).$$

	x	y	z	B_{eq} (Å²)
Cu	3559 (1)	1882 (1)	2 (1)	3·24 (2)
Cl(1)	4699 (1)	1340 (1)	−950 (1)	4·1 (1)
Cl(2)	1342 (2)	3224 (2)	2019 (2)	5·9 (1)
N(1)	4478 (4)	1766 (4)	1612 (4)	3·2 (2)
N(4)	3562 (4)	3311 (4)	502 (4)	3·4 (2)
N(7)	2340 (4)	2130 (4)	−1398 (4)	3·5 (2)
N(10)	2624 (4)	990 (4)	254 (4)	3·2 (2)
C(2)	4567 (5)	2747 (5)	2264 (6)	3·6 (2)
C(3)	3755 (5)	3394 (5)	1717 (5)	3·7 (2)
C(5)	2500 (5)	3595 (5)	−36 (6)	4·0 (2)
C(6)	2229 (5)	3168 (5)	−1246 (6)	4·4 (3)
C(8)	1469 (5)	1602 (5)	−1380 (5)	3·6 (2)
C(9)	1619 (5)	1370 (5)	−241 (5)	3·5 (2)
C(11)	2867 (5)	1143 (5)	1489 (5)	3·2 (2)
C(12)	3980 (5)	1070 (5)	1977 (5)	3·4 (2)
C(1)1	5501 (5)	1383 (5)	1628 (6)	3·7 (2)
C(1)2	6249 (5)	1323 (5)	2747 (6)	4·1 (2)
C(1)3	6278 (6)	550 (5)	3267 (6)	4·3 (2)
C(1)4	6978 (7)	484 (7)	4274 (7)	5·9 (3)
C(1)5	7643 (7)	1168 (7)	4765 (7)	6·9 (4)
C(1)6	7639 (7)	1928 (7)	4266 (8)	7·4 (4)
C(1)7	6934 (6)	1993 (6)	3251 (8)	5·9 (3)
C(2)1	4627 (6)	2822 (5)	3482 (6)	4·5 (3)
C(2)2	5006 (9)	3764 (7)	4128 (7)	7·7 (4)
C(4)1	4250 (6)	3826 (6)	127 (6)	4·6 (3)
C(4)2	5237 (5)	4089 (5)	933 (6)	4·0 (2)
C(4)3	6089 (6)	3581 (6)	837 (7)	5·0 (3)
C(4)4	7003 (7)	3824 (7)	1545 (8)	6·5 (4)
C(4)5	7078 (7)	4580 (8)	2369 (8)	7·4 (4)
C(4)6	6265 (8)	5096 (7)	2460 (8)	7·3 (4)
C(4)7	5351 (6)	4859 (6)	1738 (7)	5·3 (3)
C(5)1	2251 (7)	4641 (6)	145 (8)	5·8 (3)
C(5)2	1165 (8)	4853 (7)	−138 (9)	7·7 (4)
C(7)1	2554 (5)	1783 (6)	−2482 (6)	4·3 (3)
C(7)2	1752 (5)	1930 (6)	−3537 (6)	4·3 (3)
C(7)3	1673 (7)	2744 (7)	−3993 (7)	5·9 (3)
C(7)4	972 (8)	2825 (8)	−4995 (8)	7·8 (4)
C(7)5	353 (8)	2117 (9)	−5530 (7)	8·0 (4)
C(7)6	417 (7)	1312 (8)	−5107 (7)	7·5 (4)
C(7)7	1130 (6)	1220 (6)	−4111 (6)	5·3 (3)
C(8)1	451 (5)	2065 (6)	−1805 (6)	4·4 (3)
C(8)2	−382 (6)	1370 (7)	−2130 (7)	6·1 (3)
C(10)1	2808 (5)	28 (5)	−302 (6)	3·7 (2)
C(10)2	2169 (5)	−764 (5)	−357 (6)	3·8 (2)
C(10)3	1239 (6)	−883 (5)	−1118 (7)	4·8 (3)
C(10)4	663 (6)	−1627 (6)	−1179 (7)	5·5 (3)
C(10)5	1000 (7)	−2269 (6)	−484 (8)	5·7 (3)
C(10)6	1931 (7)	−2189 (6)	247 (7)	5·6 (3)
C(10)7	2508 (6)	−1445 (5)	315 (7)	4·5 (3)
C(11)1	2341 (6)	525 (5)	1973 (6)	4·1 (2)
C(11)2	2327 (7)	943 (6)	3118 (7)	5·6 (3)
Cl(13)1	8255 (7)	3861 (4)	7139 (5)	25·1 (5)
Cl(13)2	7657 (6)	4811 (4)	5372 (5)	25·4 (4)
Cl(13)3	9504 (7)	4325 (6)	6209 (8)	27·7 (6)
Cl(14)1	4100 (3)	2259 (3)	5904 (3)	11·4 (2)
Cl(14)2	5716 (5)	1035 (4)	6207 (5)	19·7 (4)
Cl(14)3	5969 (4)	2867 (4)	7230 (5)	19·2 (3)
C(13)	8489 (12)	4693 (8)	6550 (10)	10·7 (6)
C(14)	5212 (9)	1951 (9)	6798 (9)	8·4 (5)

were obtained. The intensities were corrected for Lorentz–polarization effects and for deterioration, but no absorption correction was applied.

Structure determination

The structure was solved by the heavy-atom method, and refined by the block-diagonal least-squares method. Unit weight was given to all reflections. All the H positions were located from difference Fourier syntheses, and were included in the refinement with isotropic temperature factors. The final R value was 6·4%. The atomic parameters of the non-hydrogen atoms are shown in Table 1.*

Discussion

Fig. 1 is a stereoscopic drawing of the molecule (Johnson, 1965). In the five-coordination Cu complexes of cyclen so far studied (Clay, Murray-Rust & Murray-Rust, 1979; DeSimone, Blinn & Mucker, 1980; Sakurai, Kobayashi et al., 1982), the 12-membered ring forms a [3333]† square conformation. The free molecule of tbte-(RSRS)-cyclen also forms another square conformation (Sakurai, Watanabe et al., 1981); however, it is not possible for the ligand to form a metal complex in this orientation because the N atoms are located at sides that are above and below the mean plane through the 12-membered ring. On formation of the metal complex, the ring changes to a rectangular [2424] form, similar to that for the Co^{III} complex (Sakurai, Tsuboyama & Tsuboyama, 1980), so that all N atoms occupy the same side of the ring.

The coordination to the Cu atom is a distorted trigonal bipyramid; the trigonal plane consists of atoms Cl(1), N(4), N(10) and the apical atoms are N(1) and

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* Lists of structure factors, hydrogen atomic parameters and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36505 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† The conformation type is expressed by a series of numbers within brackets, each giving the number of bonds in one side (Dale, 1973).
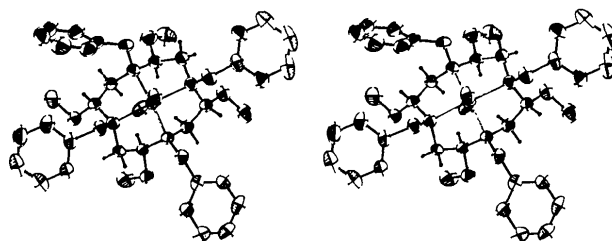

Fig. 1. A stereoscopic drawing of the molecule.

Table 2. Bond angles about the Cu atom (°)

Cl(1)–Cu–N(1)	98·3 (2)	N(1)–Cu–N(4)	87·1 (2)
Cl(1)–Cu–N(4)	114·0 (2)	N(1)–Cu–N(7)	164·4 (2)
Cl(1)–Cu–N(7)	97·4 (2)	N(1)–Cu–N(10)	86·8 (2)
Cl(1)–Cu–N(10)	121·8 (2)	N(4)–Cu–N(7)	86·7 (2)
Cl(1)–Cu···Cl(2)	175·5 (1)	N(4)–Cu–N(10)	124·2 (3)
		N(7)–Cu–N(10)	84·8 (2)
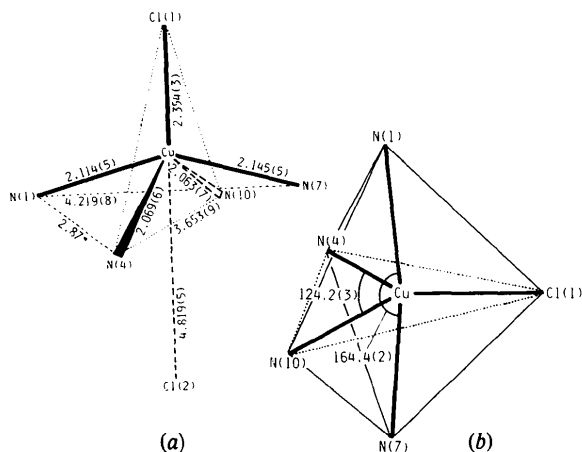
Fig. 2. Bond parameters about the Cu atom (Å and deg). The trigonal-plane atoms are Cl(1), N(4) and N(10). The apical atoms are N(1) and N(7). (a) Bond lengths (Å). The starred value is the average N–N value. (b) The trigonal-bipyramidal view.

Table 3. Conformations of the five-membered rings

		Pseudorotation angle P [in units of (2π/20) radian]
Ring	Conformation*	Present complex
N(4)--------Cu---C(2)–N(1) \\C(3)/ –0·59 (1) Å	$_3E$	11
N(7)–C(6)---Cu--------N(4) \\C(5)/ –0·68 (1) Å	$_2E$	19
N(10)--------Cu---C(8)–N(7) \\C(9)/ –0·61 (1) Å	$_3E$	11
N(1)–C(12)---Cu--------N(10) \\C(11)/ –0·66 (1) Å	$_2E$	19

* The notations are those given by Altona & Sundaralingam (1972).

N(7). The bond parameters about the Cu atom are shown in Table 2 and Fig. 2. The Cu atom lies 0·012 (3) Å out of the trigonal plane towards N(1). The dihedral angle between the N(1), N(4), N(10) and N(4), N(7), N(10) planes [35·6 (3)°] is displaced ~30% from the trigonal-bipyramidal conformation towards the square-pyramidal conformation along the Berry coordinate (Holmes & Deiters, 1977). However, the equatorial N(4)–Cu–N(10) angle, 124·2 (3)°, is almost the same as the value for a regular trigonal bipyramid, while the axial N(1)–Cu–N(7) angle, 164·4 (2)°, is close to the value observed in the square-pyramidal case. These irregularities are probably due to the constrained effect on the ligand in forming the 12-membered ring.

The mean Cu–axial-N distance, 2·130 (15) Å, is significantly longer than the mean equatorial Cu–N distance, 2·066 (7) Å. The Cu–Cl(1) distance, 2·354 (3) Å, is shorter than those found in the cyclen complexes of Cu with a square-pyramidal conformation (DeSimone et al., 1980; Sakurai, Kobayashi et al., 1982). The chiralities of the four N atoms are R. All five-membered chelate rings, as shown in Table 3, have the envelope form. The line connecting the Cl ligand, Cu and Cl⁻ counter ion is nearly straight, deviating only 4·5 (1)° from linearity.

The bond parameters of the tbte-cyclen part are shown in Fig. 3. The 12-membered ring has an approximate mm symmetry with respect to the two planes passing through Cu, N(1), N(7) and Cu, N(4), N(10). The te-cyclen part has twofold symmetry, but the overall conformation of the molecule has no symmetry. The torsion angles of the benzyl group are different for N(4) than for the other N atoms, as shown in Table 4. The conformation energy was calculated with respect to the rotation about the two single bonds in the benzyl groups attached to the long side of the rectangle. The energy map (Fig. 4) shows two broad low-energy regions, and the observed values for N(4) and N(10) correspond to the regions circled.

When the ring takes a rectangular form, there are two different possible directions for the ethyl group at the corner (as shown in Fig. 5), one towards the long side of the rectangle [RRRR configuration, Fig. 5(a)], and the other towards the short side [RSRS configuration, Fig. 5(b)]. The Co^{III}te-(RRRR)-cyclen complex (Sakurai, Tsuboyama & Tsuboyama, 1980) takes the form shown in Fig. 5(a). However, when a

Table 4. Torsion angles for the benzyl groups (°)

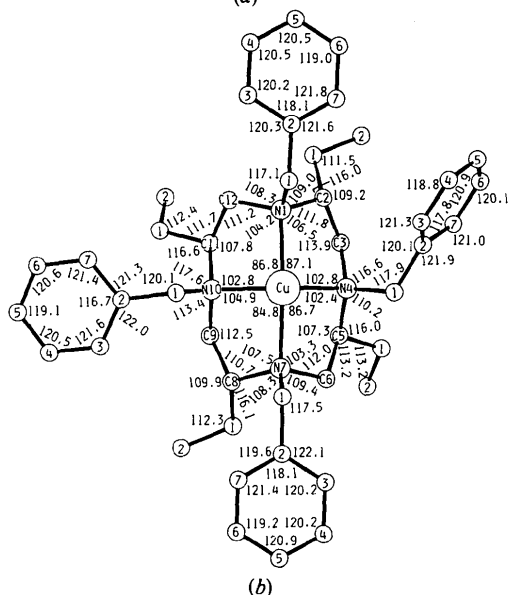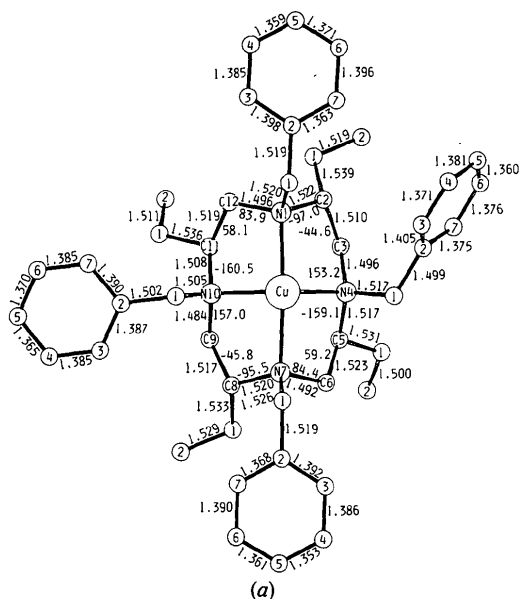| Bond	n = 1	n = 4	n = 7	n = 10
Cu–N(n)–C(n)1–C(n)2	176·4 (5)	–99·3 (7)	–179·2 (5)	–174·2 (5)
C(n + 2)–C(n + 1)–N(n)–C(n)1	140·0 (6)	71·3 (7)	141·1 (6)	68·3 (7)
C(n – 2)–C(n – 1)–N(n)–C(n)1	–152·8 (6)	–80·9 (8)	–152·8 (6)	–69·6 (7)
C(n + 1)–N(n)–C(n)1–C(n)2	58·6 (8)	146·1 (7)	62·2 (8)	70·6 (8)
C(n – 1)–N(n)–C(n)1–C(n)2	–69·2 (7)	20·6 (9)	–65·1 (8)	–58·8 (8)
N(n)–C(n)1–C(n)2–C(n)3	84·6 (9)	104·2 (9)	88·2 (9)	79·0 (9)
N(n)–C(n)1–C(n)2–C(n)7	–98·3 (9)	–80·1 (1·0)	–97·0 (9)	–104·8 (8)

(a)

(b)

Fig. 3. Bond parameters in tbte-cyclen. (a) Bond lengths (Å) and torsion angles (°). The torsion angles are given within the ring. (b) Bond angles (°). The standard deviations are: bond lengths: N—C 0·009, C—C(ring) 0·010, C—C(ring—ethyl) 0·011, C—C(ethyl) 0·012, N—C(benzyl) 0·010, C—C(benzyl) 0·011, C—C(in the benzyl group) 0·013 Å; torsion angles: 0·7°; bond angles: in the ring 0·6, in the ring—ethyl group 0·6, in the ethyl group 0·7, in the ring—benzyl group 0·6, in the benzyl group 0·8°.

benzyl group is present, substantial repulsion between the benzyl and the ethyl groups occurs in this form and the tbte-($RRRR$) complex cannot be rectangular.

The packing of the complex in the crystal is shown in Fig. 6. There are no particularly short intermolecular distances. The crystal contains two molecules of chloroform solvent. $C[CHCl_3(1)]\cdots Cl(1)$ and $C[CHCl_3(2)]\cdots Cl(2)$ distances are respectively 3·49 (1) and 3·25 (1)Å.
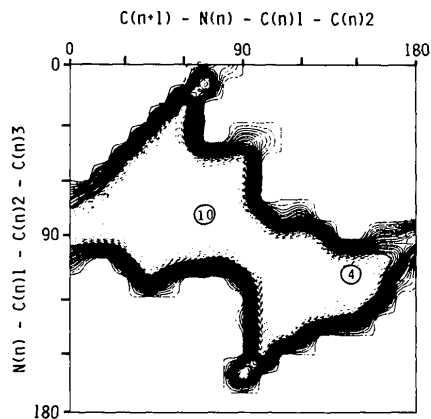
C(n+1) - N(n) - C(n)1 - C(n)2

Fig. 4. The conformational-energy map. The contour lines are drawn at intervals of 2·5 kcal mol^{-1} (1 kcal mol^{-1} = 4·2 kJ mol^{-1}). The observed values are marked by a circle.

(a)   (b)

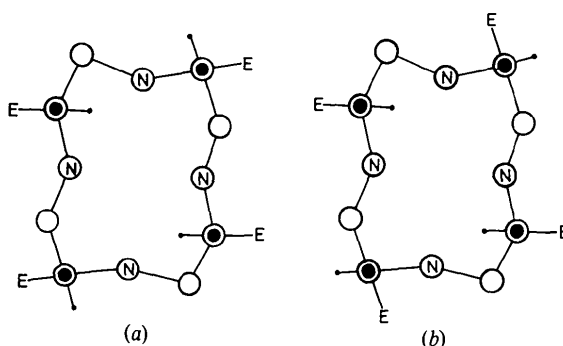Fig. 5. The two directions of an ethyl group at the corner; the asymmetric carbon is represented by ⬤. (a) Co^{III}te-($RRRR$)-cyclen. (b) Cu^{II}tbte-($RSRS$)-cyclen.
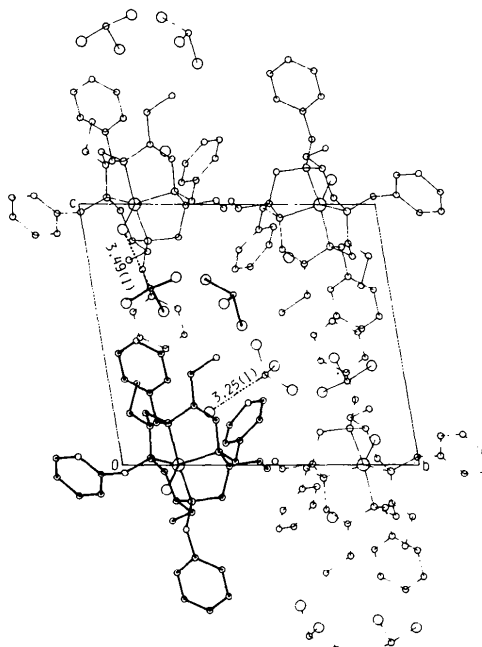

Fig. 6. The crystal structure projected along the a axis. Distances shown are in Å.

Calculations were performed on a FACOM 230-75 computer at this Institute using the UNICS III program system (Sakurai & Kobayashi, 1979) for the crystallographic calculations, and MMB80 (Sakurai, 1978) for the conformational-energy calculation.

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Structure of Bis(ethylenediamine)palladium(II) Dichlorobis(ethylenediamine)palladium(IV) Tetraperchlorate* and Remarks Concerning the Structures of Analogous Mixed-Valence Platinum Compounds

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Abstract

$[Pd(C_2H_8N_2)_2][Pd(C_2H_8N_2)_2Cl_2](ClO_4)_4$, $C_8H_{32}Cl_2N_8Pd_2^{4+}.4ClO_4^-$, is orthorhombic, space group $Ibam$, $a = 9.665$ (2), $b = 13.636$ (3), $c = 10.715$ (7) Å, $Z = 2[Pd(en)_2][PdCl_2(en)_2](ClO_4)_4$ units per cell (en = ethylenediamine, $NH_2CH_2CH_2NH_2$). The structure was solved in space group $Ibam$ and refined to a conventional R factor of 0.033 for 573 nonzero reflections. The crystal contains infinite stacks of roughly planar $Pd(en)_2$ units perpendicular to the chain axis and bridged by the halogens. Bridging is clearly unsymmetrical [Pd—Cl = 2.324 (3) and 3.033 (3) Å], leading to four-coordinate Pd^{II} species alternating with trans octahedral Pd^{IV} groups along the chain. The chains are separated by sheets of ClO_4^- ions parallel to the ac plane at $y \sim 1/4$ and $\sim 3/4$. Each ClO_4^- anion is

bridging successive $Pd(en)_2$ units by using two of its oxygen atoms to form H bonds with coordinated ethylenediamine. The anion is found in two disordered orientations differing by their interactions with the rest of the structure. The presence of diffuse background under the normal Bragg diffraction spots for the odd layer lines in the oscillation diagram of the crystal mounted along the c axis indicates that the bridging halogens are disordered over two sites along the chain axis, as is usually found for similar halide-bridged $Pt^{II}–Pt^{IV}$ mixed-valence complexes.

Introduction

Mixed-valence metal compounds have been known for a long time (Smith & Sterns, 1976). In many cases, the color, spectra, electrical and magnetic properties, and not very common semiconductive and temperature

* Alternative name: catena-μ-chloro-bis(ethylenediamine)palladium(II, IV) tetraperchlorate.