Crystal and Molecular Structure of a Linear-Chain Solid with Two Different Metal Chains: Tris[bis(1,2-diaminoethane)platinum(II)dichloro-bis(1,2-diaminoethane)platinum(IV)] Tetrakis[tetrachlorocuprate(I)]

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Abstract

$[Pt_3(C_2H_8N_2)_6][Pt_3(C_2H_8N_2)_6Cl_6](CuCl_4)_4$, $C_{24}H_{96}$-$Cl_6N_{24}Pt_6^{12+}.4Cl_4Cu^{3-}$, hexagonal, $P6_3/m$, $a = 15.657$ (2), $c = 10.522$ (7) Å, $Z = 1$, $V = 2234$ Å^3, $d_c = 2.2$ Mg m^{-3}. The structure was refined to $R = 0.070$ for 990 counter data. The 'platinum' part of the structure can best be described as a Wolffram's salt analogue with alternating Pt^{IV}–Cl [2.328 (9) Å] and Pt^{II}···Cl [2.937 (9) Å] interactions along the linear Pt^{II}···Cl–Pt^{IV} chains. Parallel to the Pt–Cl···Pt system there are linear Cl–Cu(2)–Cl···Cu(1)···Cl chains. The shorter Cu(2)–Cl bond is 2.16 (1) Å, the longer Cu(1)···Cl distance is 3.10 (1) Å. Cu(1) is further trigonally coordinated by three chlorides at 2.291 (9) Å and Cu(2) has three equivalent Cl neighbors at 3.48 (1) Å.

Introduction

The formal oxidation state of Pt ions in the linear-chain mixed-valence Wolffram's salt analogues depends on the Pt–X···Pt distances along the linear chains (Endres, Keller, Martin, Nam Gung & Traeger, 1979). Equidistant Pt–X–Pt arrangements give equivalent Pt ions with a formal oxidation number of three. Only a few linear-chain compounds of this type have been found so far (Endres, Keller, Van de Sand & Dong, 1978; Endres, Keller, Martin & Traeger, 1979; Endres, Keller, Martin, Nam Gung & Traeger, 1979). In an attempt to find new materials of this kind we investigated the structure of the title compound, which was prepared by oxidizing an aqueous solution of Pt(en)$_2$Cl$_2$ with an aqueous solution of CuCl$_2$ (Kurnakov, 1898). Rotating-crystal and Weissenberg photographs (Cu $K\alpha$ radiation) showed the crystal to be hexagonal and yielded approximate lattice constants. Exact lattice constants (see *Abstract*) were determined by least squares (Berdesinski & Nuber, 1966) from the θ values of 39 reflections, centered on a single-crystal diffractometer.

For the intensity measurements (Siemens diffractometer, Mo $K\alpha$ radiation, θ–2θ scans, five-value method, $2\theta \le 70°$) the crystal was treated as being monoclinic. The observed intensities $[I > 2.58\sigma(I)]$ were corrected for Lorentz and polarization factors. Due to the small crystal size (0.04 × 0.08 × 0.02 mm), no absorption correction was applied ($\mu = 11.6$ mm^{-1}). The observations were reindexed to hexagonal symmetry and equivalent reflections were averaged to a set of 990 independent intensities. Unit weights were assigned. Calculations were performed with programs of the XRAY system (Stewart, Kundell & Baldwin, 1970). Scattering factors were derived from *International Tables for X-ray Crystallography* (1974).

Structure determination and refinement

Systematic extinctions were 00l with $l = 2n + 1$. Space group $P6_3/m$ (C_{6h}^2) was chosen, because the multiplicity and the point symmetry of the special positions fitted best with the composition of the compound and the expected surroundings of the heavy atoms. The positions of Pt and the Cl atoms within the Pt–Cl–Pt chain were taken from a Patterson synthesis. A Fourier synthesis yielded several possibilities for the positions of the other heavy atoms. Reasonable positions were selected by R-factor calculations. For the heavy-atom positions and anisotropic temperature factors, R was 0.109. A difference Fourier map revealed the positions of the ligand atoms around Pt. They were refined with isotropic temperature factors, yielding $R = 0.073$. Refinement with anisotropic temperature factors resulted in $R = 0.069$ and a non-positive temperature factor for one N atom. When the refinement was attempted in the noncentrosymmetric space group $P6_3$, where the Pt^{II} and Pt^{IV} sites would be crystallographically non-equivalent, refinement failed; one ligand atom was shifted far away from a reasonable position, and the temperature factor for one Cl atom became negative. For all further refinements $P6_3/m$ was used. In the final cycles with anisotropic temperature factors for the

Table 1. *Atomic positional parameters* ($\times 10^3$)

	x	y	z
Pt	0	500	500
Cl(1)	505 (1)	498 (1)	221 (1)
Cl(2)	667	333	45 (1)
Cl(3)	248 (1)	498 (1)	250
Cl(4)	795 (1)	590 (1)	250
Cu(1)	333	667	250
Cu(2)	667	333	250
N(1)	353 (1)	455 (1)	−16 (2)
N(2)	455 (2)	349 (2)	−10 (3)
C(1)	45 (3)	342 (3)	44 (4)
C(2)	52 (2)	706 (2)	36 (3)

heavy atoms and isotropic for the light atoms all atoms were refined together. Refinement converged with $R = 0.070$. Atomic coordinates are listed in Table 1.* A final difference map showed no peaks larger than 20% of an N atom.

Discussion

The numbering scheme, bond distances and angles of the platinum complex units are indicated in Fig. 1. These species are stacked parallel to the c axis and linearly bridged by Cl ions with alternating $Pt^{II}\cdots Cl$–Pt^{IV} distances of 2·937 (9) and 2·328 (9) Å. The chain is not linear by symmetry, but the departure from linearity is within experimental error and therefore not significant.

This 'splitting' of the Cl positions is shown in Fig. 2. The Pt^{II}–Pt^{IV} distance of 5·261 Å is one of the shortest observed so far in Wolffram's salt analogues with linear Cl bridges. This may explain the pronounced optical absorption and reflection parallel to the $Pt^{II}\cdots Cl$–Pt^{IV} chains in single crystals. Additionally the difference between the $Pt^{II}\cdots Cl$ and the Pt^{IV}–Cl bond lengths

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34635 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
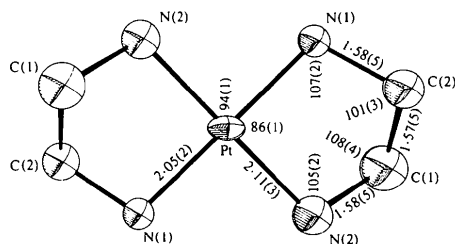
[0·60 (1) Å] is comparatively small. In 'Wolffram's Red' (0·87 Å) or in [PtenCl$_2$][PtenCl$_4$] (1·23 Å) the alternations along the Pt^{IV}–Cl$\cdots Pt^{II}$ chain are much more pronounced.

Since there are no diffuse lines superimposed on the layer lines with l odd, there is no one-dimensional ordering of the Cl(1) distribution over the two half-occupied sites. The weak layer lines with l odd and hence the doubling of the c axis to become equal to two Pt—Pt separations originate from the three-dimensionally-ordered ligand molecules and the ordered Cu—Cl chains: The 'copper' part of the structure consists of linearly chloride-bridged Cu^I chains which run parallel to the Pt^{IV}–Cl$\cdots Pt^{II}$ system. Each Cu is surrounded additionally by three Cl ions, leading principally to a trigonal–bipyramidal coordination around the Cu ions (Fig. 3). This part of the structure could be described as an alternating linear array of two
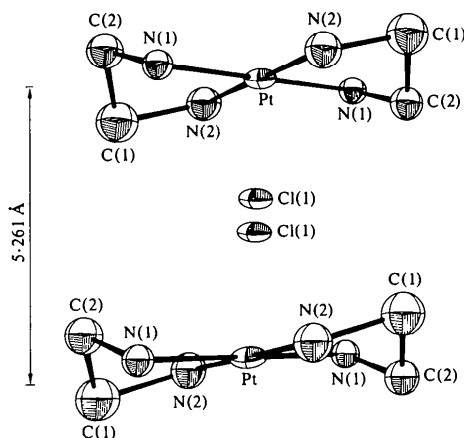

Fig. 2. View of the $Pt^{IV}en_2$–Cl–$Pt^{II}en_2$ chain. The two half-occupied Cl⁻ positions between two platinum atoms of the Pt^{IV}–$X\cdots Pt^{II}$ chain are indicated by two positions for Cl(1). Only half of the repeat distance along c is drawn.

Fig. 1. Projection of the $(Pten_2)^{2+}$ cation on to the ab plane with numbering scheme, bond lengths (Å) and angles (°). As Pt^{II} and Pt^{IV} occupy equivalent sites, the figure is an average of the two species.
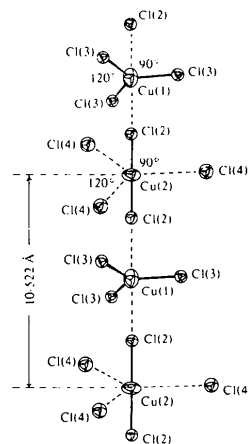

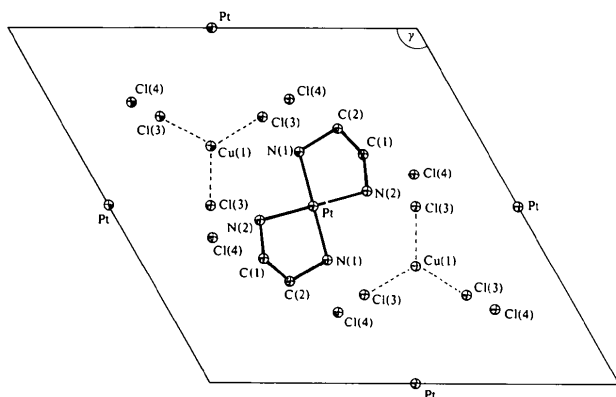Fig. 3. Representation of bond distances, angles and the numbering scheme in the 'Cu—Cl' part of the solid.

Fig. 4. Projection parallel to the two different chains into the *ab* plane. The two different trigonally coordinated Cu^I ions in the $Cl–Cu–Cl\cdots Cu\cdots Cl$ chains and the square-planar platinum-(II,IV) complex units are shown.

types of trigonal bipyramids [type 1: Cu(1)–Cl(2) apical = 3·10 (1) Å, Cu(1)–Cl(3) equatorial = 2·291 (9) Å; type 2: Cu(2)–Cl(2) apical = 2·16 (1) Å, Cu(2)–Cl(4) equatorial = 3·48 (1) Å] sharing their apices. The repeating distance in the Cu system is 10·522 (7) Å, the *c* axis of the unit cell. As the Pt–Pt distance is exceedingly short for this class of compounds, it may be argued that the distances along the Cu–halogen chains are responsible for the short *c*-axis

length, and that the Pt complex units arrange themselves accordingly. The arrangement of the parallel chains is shown in Fig. 4.

Another example of Cu–*X*–Cu chains running parallel to the Pt–*X*–Pt chains was reported recently (Keller, Martin & Traeger, 1978).

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The Crystal Structures of [1,2-Bis(diphenylphosphino)ethane]trichloro-(η-cyclopentadienyl)niobium(IV) Bistoluene Solvate and μ-Oxo-bis[aquatrichloro-(η-methylcyclopentadienyl)niobium(V)]

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Abstract

The structures of two new halo monocyclopentadienyl derivatives of Nb have been determined. They crystallize in the triclinic system, space group $P\bar{1}$, $a = 9\cdot112$ (3), $b = 11\cdot996$ (3), $c = 17\cdot113$ (5) Å, $\alpha = 70\cdot40$ (2), $\beta = 87\cdot41$ (2), $\gamma = 80\cdot32$ (2)°, $Z = 2$, for $C_{31}H_{29}Cl_3NbP_2\cdot2C_7H_8$, $[Nb(C_5H_5)(C_{26}H_{24}P_2)Cl_3]\cdot2C_7H_8$ (I), and $a = 7\cdot352$ (1), $b = 11\cdot094$ (2), $c = 12\cdot973$ (1) Å, $\alpha = 75\cdot12$ (1), $\beta = 75\cdot50$ (1), $\gamma = 86\cdot28$ (1)°, $Z = 2$, for $C_{12}H_{18}Cl_6Nb_2O_3$, $[Nb_2(C_6H_7)_2Cl_6(H_2O)_2O]$ (II). The structures were refined to $R = 0\cdot057$ (I) and $R = 0\cdot045$ (II). Both complexes contain *quasi*-octahedrally coordinated Nb atoms with a cyclopentadienyl ring at one apex, η^5-bonded to Nb, three Cl atoms at three of the apices of the equatorial plane and the remaining sites occupied by P atoms of a chelating

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