

The Crystal Structure of *trans*-Dichlorobis(ethylenediamine)- platinum(IV) Tetrachlorocuprate(II) Monohydrate

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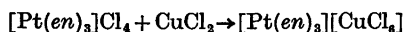
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trans-Dichlorobis(ethylenediamine)platinum(IV) tetrachlorocuprate(II) monohydrate, *trans*-Pt[(en)₂Cl₂][CuCl₄].H₂O, is monoclinic, *P*2/*c* with *a* = 7.788(6) Å, *b* = 7.369(7) Å, *c* = 15.080(20) Å, β = 114.4(1)°, and *Z* = 2. The structure has been solved by Patterson and Fourier methods from three dimensional X-ray data and refined by the method of least squares to an *R*-value of 0.051. The refinement was based on 1359 independent reflections. The coordination around Pt is nearly octahedral with an average Pt—N distance of 2.081(8) Å; the Pt—Cl distance is 2.313(4) Å. The [CuCl₄]²⁻ configuration is a strongly distorted tetrahedron with Cu—Cl distances of 2.239(5) and 2.276(4) Å; the dihedral angle is 35.7(2)°. The strong deformation may in part be due to hydrogen bonding.

Complex ions of the type [CuCl_{*n*}]^{(*n*-2)-}, *n* = 3, 4, and 5, have received much interest recently,¹⁻⁷ mainly because of the variety of coordination polyhedra they exhibit. However, isolated [CuCl_{*n*}]^{(*n*-2)-} complexes with *n* = 6, the most frequent coordination number in 3*d*-transition metal complexes, have not been reported in the literature.

In [Cr(NH₃)₆][CuCl₅] the uncommon CuCl₅³⁻ ion is stabilised by the large [Cr(NH₃)₆]³⁺ cation.⁸ This suggests that a suitable cation, *i.e.* with respect to size and charge, might facilitate the existence of an isolated CuCl₆⁴⁻ complex. [Pt(en)₃]⁴⁺ was chosen as cation and the reaction assumed to take place was



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However, this attempt led to the formation of *trans*-[Pt(en)₂Cl₂][CuCl₄].H₂O, exclusively. For *n* = 4, at least three distinct coordination polyhedra are known of which examples are given in Table 1. The present compound contains [CuCl₄]²⁻ complexes of type 1, but a strong distortion of the tetrahedron brings it close to type 2.

EXPERIMENTAL

Chemistry. [Pt(en)₃]Cl₄.3H₂O: A modification of Smirnov's method⁹ was used to prepare this compound. (Found: C 12.35; H 4.11; N 14.49; Calc. for [Pt(C₂H₈N₂)₃]Cl₄.3H₂O: C 12.61; H 4.25; N 14.71). *trans*-[Pt(en)₂Cl₂][CuCl₄].H₂O: A mixture of 0.3 g [Pt(en)₃]Cl₄.3H₂O in 1.5 ml water was added dropwise to a solution of 2.0 g LiCl and 0.2 g CuCl₂.2H₂O in a mixture of 2 ml ethanol and 3 ml 4 M hydrochloric acid. A brown salt precipitated after a few seconds. Recrystallization from hot conc. HCl gave grass-green prismatic crystals. Yield 0.2 g. (Found: C 7.57; H 2.89; N 8.79; Cl 34.48. Calc. for [Pt(C₂H₈N₂)₂Cl₂][CuCl₄].H₂O: C 7.88; H 2.98; N 9.19; Cl 34.89). The density of the crystals was determined by flotation in a mixture of CCl₄ and CHBr₃.

X-Ray technique. Lattice parameters and space group were determined from Weissenberg and precession photographs using Cu and Mo radiation (*λ*_{Cu} = 1.5418 Å, *λ*_{Mo} = 0.7109 Å). Preliminary intensity data were collected in the *h*0*l* plane from Weissenberg photographs using the multiple film technique and visual intensity estimation. Ni-filtered Cu radiation was employed, and the crystal, which was bounded by {100}, {001}, and {010}, had the linear dimensions 0.11 × 0.10 × 0.30 mm³. Three

Table 1.

| Type | Compound | Coordination polyhedron | Ref. |
|------|--|---------------------------|------|
| 1 | $[(C_2H_5)_3NH]_2[CuCl_4]$ | flattened tetrahedron | 4 |
| 2 | $[(C_2H_5)_2C_2H_4NH_2(CH_3)]_2[CuCl_4]$ | square plane ^a | 7 |
| 3 | $[(C_2H_5)_3NH]_2[CuCl_4]$ | elongated octahedron | 6 |

^a Room temperature modification.

dimensional intensity data were obtained by means of a semi-automatic Supper diffractometer controlled by an RC4000 computer. This computer was also used for the data reduction. Graphite monochromatized MoK α radiation was used and data were collected out to $\sin \theta/\lambda = 0.7 \text{ \AA}^{-1}$, yielding 1570 independent reflections. No correction was applied for absorption.

CRYSTAL DATA

Crystal system: monoclinic (*b*-axis unique).
 Unit cell: $a = 7.788(6) \text{ \AA}$, $b = 7.369(7) \text{ \AA}$, $c = 15.080(20) \text{ \AA}$, $\beta = 114.4(1)^\circ$, $Z = 2$, $d_{\text{obs}} = 2.54 \text{ g/cm}^3$, $d_{\text{calc}} = 2.56 \text{ g/cm}^3$, $\mu_{\text{MoK}\alpha} = 116.8 \text{ cm}^{-1}$.
 Systematic absences: $h0l$. $l = 2n + 1$.
 Space group: $P2_1/c$ (or Pc).

STRUCTURE DETERMINATION

A Patterson function based on the $h0l$ film data confirmed that the platinum and copper atoms were in special positions. The position of the three chlorine atoms could also be determined, whereas the lighter atoms were undetectable both in Patterson and Fourier maps.

The *R*-value at this stage was 0.21, ($R = (\sum ||F_{\text{obs}}| - k|F_{\text{calc}}||) / \sum |F_{\text{obs}}|$). This part of the structure analysis constituted an undergraduate course in X-ray crystallography.

The three dimensional data confirmed the positions of the heavy atoms and the ethylenediamine molecule was easily found from a Fourier map. The structure was refined by the full matrix least squares program LINUS.¹⁰ An *R*-value of 0.065 based on all reflections was obtained when anisotropic thermal parameters were included. A difference Fourier map showed the oxygen atom of the water molecule and to some extent the hydrogen atoms. The criterion $F_{\text{obs}}^2 \leq 3\sigma(F_{\text{obs}}^2)$ was then applied and reflections with $k^2 + l^2 \leq 8$ were deleted due to the diffractometer geometry. This reduced the number of reflections to 1359 and they were in the further refinement weighted by $w = 1/[\mu(F)]^2$, where $\mu(F) = [\sigma(F)_{\text{count}} + 1.03F_{\text{obs}}^2]^{1/2} - |F_{\text{obs}}|$. Hydrogen atoms were inserted in fixed calculated positions with constant *B*-values of 4.0. The scattering factors used for Pt, Cu, Cl, N, C, and O were those given by Cromer and Mann,¹¹ and for hydrogen the scattering curve

Table 2. Atomic coordinates with standard deviations $\times 10^4$ in parentheses. Calculated hydrogen positions under the assumption of sp^3 hybridized atoms and N-H = 1.00 \AA , C-H = 1.05 \AA , O-H = 0.95 \AA .

| Atom | <i>x</i> | <i>y</i> | <i>z</i> | Atom | <i>x</i> | <i>y</i> | <i>z</i> |
|-----------------|------------|-------------|-------------|----------------|----------|----------|----------|
| Pt | 0.0000 | 0.0000 | 0.0000 | H ₁ | 0.192 | -0.235 | 0.131 |
| Cu | 0.5000 | 0.2955(3) | 0.2500 | H ₂ | 0.327 | -0.060 | 0.139 |
| Cl ₁ | 0.2043(6) | 0.2194(5) | -0.0092(3) | H ₃ | 0.104 | -0.071 | -0.140 |
| Cl ₂ | 0.2715(6) | 0.4966(7) | 0.2301(3) | H ₄ | -0.080 | -0.196 | -0.155 |
| Cl ₃ | 0.3566(6) | 0.0759(6) | 0.3014(3) | H ₅ | 0.396 | -0.358 | 0.073 |
| N ₁ | 0.2328(18) | -0.1453(17) | 0.0930(9) | H ₆ | 0.413 | -0.158 | 0.019 |
| N ₂ | 0.0435(19) | -0.1497(16) | -0.1064(8) | H ₇ | 0.092 | -0.411 | -0.045 |
| C ₁ | 0.3209(23) | -0.2451(22) | 0.0338(13) | H ₈ | 0.232 | -0.356 | -0.105 |
| C ₂ | 0.1704(24) | -0.3067(21) | -0.0590(12) | H ₉ | 0.095 | -0.248 | 0.245 |
| O | 0.0000 | -0.1717(33) | 0.2500 | | | | |

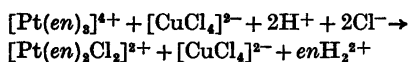
Table 3. Thermal parameters with standard deviations in parentheses, both × 10⁴. The *u*_{ij} are defined by exp [−2π²(*u*₁₁*a*²*h*² + ⋯ 2*u*₁₂*a*^{*}*b*^{*}*h**k* + ⋯)].

| Atom | <i>u</i> ₁₁ | <i>u</i> ₂₂ | <i>u</i> ₃₃ | <i>u</i> ₁₂ | <i>u</i> ₁₃ | <i>u</i> ₂₃ |
|-----------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|
| Pt | 287 (3) | 162(16) | 214(3) | 0(5) | 135(2) | 23(5) |
| Cu | 423(15) | 241(19) | 384(14) | 0 | 216(12) | 0 |
| Cl ₁ | 445(21) | 244(21) | 535(23) | 21(16) | 300(19) | −64(19) |
| Cl ₂ | 652(24) | 338(21) | 643(24) | 105(30) | 369(21) | 81(27) |
| Cl ₃ | 454(22) | 341(22) | 380(19) | 16(16) | 240(17) | 38(15) |
| N ₁ | 451(76) | 270(58) | 357(64) | 33(54) | 195(60) | 35(50) |
| N ₂ | 514(78) | 293(55) | 281(58) | 10(54) | 259(59) | −23(58) |
| C ₁ | 345(82) | 414(84) | 506(93) | 108(68) | 208(76) | 86(71) |
| C ₂ | 567(101) | 309(74) | 447(87) | 30(69) | 355(82) | −24(67) |
| O | 652(140) | 742(169) | 1404(224) | 0 | 570(152) | 0 |

given by Stewart, Davidson and Simpson¹² was used. A final *R*-value of 0.051 was obtained; no attempt has been made to use the non-centrosymmetric space group *Pc*. Atomic coordinates are listed in Table 2 and anisotropic thermal parameters in Table 3; a list of observed and calculated structure factors is available on request.

DISCUSSION

Chemistry. The compound *trans*-[Pt(en)₂Cl₂]-[CuCl₄].H₂O is prepared according to the following overall reaction scheme:



This is a rather unusual reaction because the ion [Pt(en)₃]⁴⁺ is normally kinetically inert. The formation of the *trans* isomer suggests a mechanism involving the planar [Pt(en)₂]⁴⁺ ion as a simple splitting off of one *en* molecule would lead to the *cis* isomer. It is possible⁹ that the starting material [Pt(en)₃]Cl₄.3H₂O contained small amounts of [Pt(en)₂]Cl₂; furthermore, it is known¹³ that chlorocomplexes of Cu(II) are able to oxidize Pt(II) to Pt(IV). It is therefore suggested that the dark brown salt isolated first contains both Cu(I) and Cu(II); salts of this type have been described by Mori.¹⁴ When this salt is recrystallized from hydrochloric acid, copper(I) is reoxidized to copper(II) by molecular oxygen, and [Pt(en)₃]⁴⁺ is converted to *trans*-[Pt(en)₂Cl₂]²⁺. It is presumed that Cu(I) here acts as a catalyst. The details of this last reaction are under further investigation.

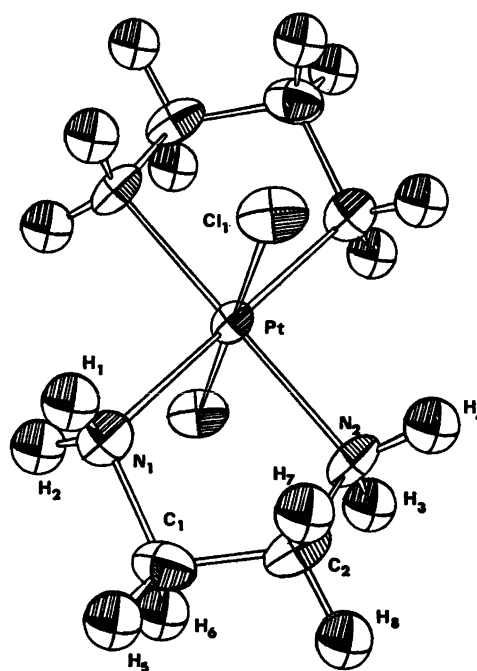


Fig. 1. Perspective drawing of *trans*-[Pt(en)₂Cl₂]²⁺ in *trans*-[Pt(en)₂Cl₂][CuCl₄].H₂O. Thermal ellipsoids enclose 50% probability (ORTEP II).¹⁵

Structure. The platinum atom lies at a centre of symmetry which causes the four nitrogen atoms and the platinum to be exactly in a plane and the chlorines to be in *trans* position (Fig. 1). The two Pt–N distances (Table 4) are equal within one standard deviation, and apart from the N₁–Pt–N₂ angle only slight devia-

Table 4. Interatomic angles and distances in *trans*-[Pt(en)₂Cl₂][CuCl₄].H₂O calculated with the program ORFFE¹⁸ including variance-covariance matrix and cell parameter errors. Standard deviations in parentheses.^a

| Angle | Degrees | Distance | Å |
|---|------------|--------------------------------|-----------|
| N ₁ -Pt-Cl ₁ | 88.3(4) | Pt-Cl ₁ | 2.313(4) |
| N ₂ -Pt-Cl ₁ | 89.4(3) | Pt-N ₁ | 2.074(12) |
| N ₁ -Pt-N ₂ | 82.7(5) | Pt-N ₂ | 2.087(11) |
| Pt-N ₁ -C ₁ | 109.4(9) | N ₁ -C ₁ | 1.522(20) |
| N ₁ -C ₁ -C ₂ | 109.3(1.2) | C ₁ -C ₂ | 1.478(23) |
| C ₁ -C ₂ -N ₁ | 108.9(1.2) | C ₂ -N ₁ | 1.497(20) |
| C ₂ -N ₁ -Pt | 109.0(9) | | |
| Cl ₂ -Cu-Cl ₃ ' | 97.1(3) | Cu-Cl ₂ | 2.239(5) |
| Cl ₂ -Cu-Cl ₃ ' | 89.4(2) | Cu-Cl ₃ | 2.276(4) |
| Cl ₂ -Cu-Cl ₃ | 92.4(2) | | |
| Cl ₂ -Cu-Cl ₃ ' | 154.1(2) | | |
| Dihedral angle (Cl ₂ -Cu-Cl ₃ ')-(Cl ₂ -Cu-Cl ₃) 35.7(2)°. | | | |

^a (') Symmetry operation $\bar{x}, y, \frac{1}{2} - z$.

tions from pseudo octahedral symmetry are observed. Several papers¹⁷⁻²¹ report Pt-Cl and Pt-N distances and they all lie in the ranges 2.30-2.34 Å and 2.01-2.10 Å, respectively. The structure of *cis*-[Pt(en)₂Cl₂Cl₂] (Ref. 22) contains two independent Pt-Cl distances with an average value of 2.306(5) Å, and this value is within one standard deviation of the distance found in the present study. The average Pt-N distance in the *cis* complex is 2.057(12) Å as compared with 2.081(8) Å in the present complex. The geometry of the ethylenediamine molecule, which is quite similar in the two isomers, shows only slight deviations from the expected configuration. The water molecule lies on the two-fold axis through $(x, z) = (0, 1/4)$ and from the calculated hydrogen positions there seems to be weak hydrogen bonding between the water molecule and the ethylenediamine moiety, *cf.* Table 5.

Table 5. Probable hydrogen bonds in *trans*-[Pt(en)₂Cl₂][CuCl₄].H₂O.^a

| A...B | Distance (Å) | H...B | Distance (Å) |
|-------------------------------------|--------------|-------------------------------------|--------------|
| N ₁ ...Cl ₃ ' | 3.35(1) | H ₂ ...Cl ₃ ' | 2.46 |
| N ₁ ...Cl ₃ | 3.31(1) | H ₂ ...Cl ₃ | 2.55 |
| N ₂ ...Cl ₃ | 3.50(1) | H ₄ ...Cl ₃ | 2.63 |
| N ₂ ...O | 3.13(2) | H ₃ ...O | 2.35 |

^a (') Symmetry operation $\bar{x}, y, \frac{1}{2} - z$.

The [CuCl₄]²⁻ ion (Fig. 2a,b) is situated on the two-fold axis through $(x, z) = (1/2, 1/4)$. The two independent Cu-Cl distances (Table 4) seem to be significantly different, but they agree with previously obtained values^{1-4, 6, 7, 22, 24} which normally lie in the range 2.20-2.34 Å. The Cl-Cu-Cl angles, *cf.* Table 4, show a large distortion of the [CuCl₄]²⁻ ion from tetrahedral towards square planar configuration. The deformation, expressed by the dihedral angle as defined in Table 4, seems to be the most pronounced so far reported. Table 6 shows a selection of dihedral angles in distorted [CuCl₄]²⁻ ions along with the extreme cases, *i.e.* the tetrahedral and the square planar configurations.

Theoretical calculations^{5, 20-22} on the geometry of the [CuCl₄]²⁻ ion predict the flattened tetrahedron (approx. *D_{2d}* symmetry) to be the most stable coordination polyhedron. However,

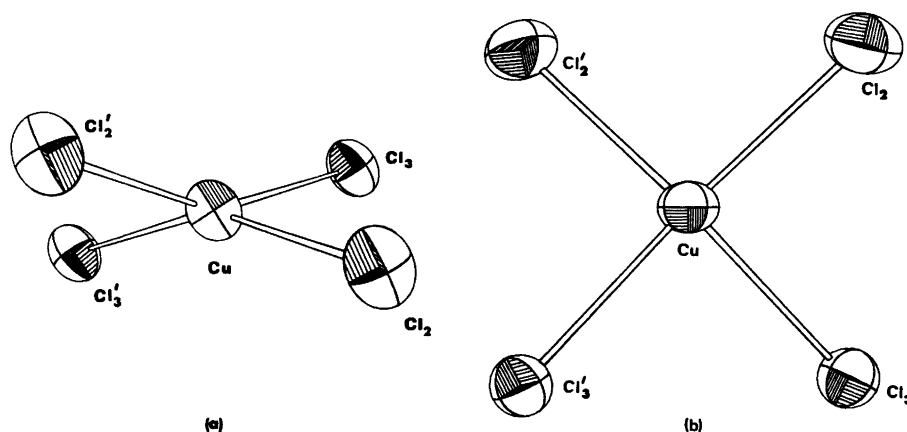


Fig. 2. Perspective drawing of [CuCl₄]²⁻ in *trans*-[Pt(en)₂Cl₂][CuCl₄].H₂O. a. Viewed along the twofold axis. b. Viewed perpendicular to the twofold axis. Thermal ellipsoids enclose 50 % probability.

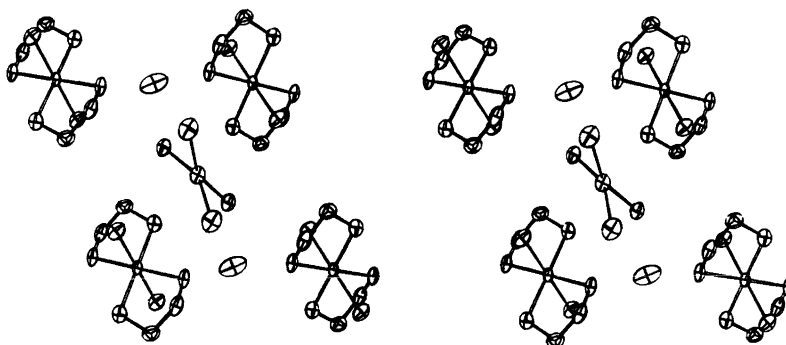


Fig. 3. Stereoscopic drawing of the *b*-projection in *trans*-[Pt(en)₂Cl₂][CuCl₄].H₂O. Hydrogen atoms have been omitted for clarity.

Table 6. Dihedral angles in [CuCl₄]²⁻ ions.

| Compound | Angle (degrees) | Ref. |
|---|-----------------|------|
| Tetrahedron | 90.0 | |
| [(C ₆ H ₅)C ₂ H ₄ NH ₂ (CH ₃) ₂][CuCl ₄] ^a | 80.0 | 7 |
| Cs ₂ CuCl ₄ | 73.6 | 25 |
| [(CH ₃) ₄ N] ₂ [CuCl ₄] | 68.6 | 26 |
| [(C ₆ H ₅ NCH ₂) ₂][CuCl ₄] | 67.6 | 27 |
| [(C ₆ H ₅)CH ₂ N(CH ₃) ₃] ₂ [CuCl ₄] | 66.6 | 28 |
| [(C ₆ H ₅) ₂ NH] ₂ [CuCl ₄] | 63.7 | 4 |
| [C ₁₃ H ₁₉ N ₂ OS] ₂ [CuCl ₄] | 49.5 | 29 |
| [Pt(en) ₂ Cl ₂][CuCl ₄].H ₂ O | 35.7 | |
| Square plane | 0.0 | |

^a High temperature modification.

in many of the structures solved so far, hydrogen bonding seems to be of importance in determining the final geometry of the $[\text{CuCl}_4]^{2-}$ ion. This is so also in the present compound where several short distances which may correspond to hydrogen bonds are found, *cf.* Table 5. The interaction between $[\text{CuCl}_4]^{2-}$ and $[\text{Pt}(\text{en})_2\text{Cl}_2]^{2+}$ through hydrogen bonds might be taken as an explanation of the stronger distortion towards square planar configuration in the present compound than in the other compounds in Table 6. Further evidence for the importance of hydrogen bonds in this type of compounds is given by the complex $[(\text{C}_6\text{H}_5)_2\text{C}_2\text{H}_4\text{NH}_2(\text{CH}_3)]_2[\text{CuCl}_4]$ which exists in two modifications.⁷ At room temperature the configuration of the $[\text{CuCl}_4]^{2-}$ ion is a square plane with substantial hydrogen bonding, while the modification at 80 °C, *i.e.* at higher thermal energy, contains $[\text{CuCl}_4]^{2-}$ as a flattened tetrahedron. This seems to indicate that with weak hydrogen bonding or completely without, as is the case in Cs_2CuCl_4 (Refs. 25, 33), the most favourable geometry of the $[\text{CuCl}_4]^{2-}$ ion is in fact the moderately flattened tetrahedron as predicted by theory. It is therefore likely that the strong deformation of the $[\text{CuCl}_4]^{2-}$ ion in the present compound is due only to packing forces and hydrogen bonding and not to any inherent feature of the $[\text{CuCl}_4]^{2-}$ ion itself.

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