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## A Platinum Zigzag Chain in Bis(ethylenediamine)copper(II) Bis(oxalato)platinate(II): the Crystal Structure of $[\text{Cu}(\text{C}_2\text{N}_2\text{H}_8)_2][\text{Pt}(\text{C}_2\text{O}_4)_2]$

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The title compound, obtained by mixing aqueous solutions of  $\text{K}_2[\text{Pt}(\text{C}_2\text{O}_4)_2]$  and  $[\text{Cu}(\text{C}_2\text{N}_2\text{H}_8)_2]\text{Cl}_2$  in equimolar amounts, is triclinic, space group  $P\bar{1}$ , with  $a=6.978$  (4),  $b=9.418$  (6),  $c=12.351$  (8) Å,  $\alpha=73.14$  (5),  $\beta=100.59$  (4),  $\gamma=111.73$  (4)°,  $Z=2$ . The structure was solved by Patterson and Fourier methods and refined by least squares to  $R=0.079$  for 4035 observed reflexions. The structure is built up of zigzag chains of  $[\text{Pt}(\text{C}_2\text{O}_4)_2]^{2-}$  anions running in channels formed by  $[\text{Cu}(\text{C}_2\text{N}_2\text{H}_8)_2]^{2+}$  cations.

### Introduction

Much of the recent interest in linear-chain, transition metal compounds is connected with investigations of the direct metal-to-metal contacts (Interrante, 1974; Keller, 1975; Miller & Epstein, 1975). Pt compounds of this type with very weak intermolecular interactions can be prepared, as well as others which show evidence of strong exchange, leading finally to quasi one-dimensional metallic behaviour. Metal interactions in crystals of the former group of complexes, e.g. in the Magnus

green salt (MGS) type materials, can be studied by ESR after doping the diamagnetic lattice with sterically very similar but paramagnetic  $\text{Cu}^{\text{II}}$  ions, e.g.  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  (Fritz & Keller, 1965; Soos, Huang, Valentine & Hughes, 1973).

When we tried to dope linear-chain bis(oxalato)platinate(II) with paramagnetic tetraamminecopper(II) cations we found a red-brown 1:1 compound of bis(ethylenediamine)copper(II) and bis(oxalato)platinate(II) with a new type of structure, which is reported here.

### Experimental

$[\text{Cu}(\text{C}_2\text{N}_2\text{H}_8)_2]\text{Cl}_2$  was prepared as described by Werner, Spruch, Megerle & Pastor (1899).  $\text{K}_2[\text{Pt}(\text{C}_2\text{O}_4)_2] \cdot \text{H}_2\text{O}$  was obtained by reacting  $\text{K}_2\text{PtCl}_4$  with  $\text{K}_2\text{C}_2\text{O}_4$  (Werner, 1899).

When aqueous solutions of  $\text{K}_2\text{Pt}(\text{ox})_2 \cdot \text{H}_2\text{O}$  and of the deep-blue  $[\text{Cu}(\text{en})_2]\text{Cl}_2$  are mixed in equimolar amounts, red-brown glittering needles of formula  $[\text{Cu}(\text{en})_2][\text{Pt}(\text{ox})_2]$  are formed. The latter can be recrystallized from water showing again the deep blue colour of the  $[\text{Cu}(\text{en})_2]^{2+}$  ion in the solution. After being washed with small quantities of water the solid is dried in vacuum. Analysis: 17.4% C (calculated 17.3% C), 2.97% H (2.88% H), 10.2% N (10.05% N).

Photographs taken with  $\text{Co K}\alpha$  radiation showed the crystal to be triclinic. Determination of a lattice matrix and intensity measurements ( $\theta$ - $2\theta$  scan, five-value method) with filtered  $\text{Mo K}\alpha$  radiation were carried out on a computer-controlled Siemens single-crystal

diffractometer. In a  $\theta$  range up to  $30^\circ$ , 4040 independent reflexions were observed, reflexions with intensity  $I < 2.58\sigma(I)$  being regarded as unobserved. The observed intensities were corrected with Lorentz and polarization factors; further corrections were not applied. Lattice constants with their standard deviations were determined from the  $\theta$  values of 39 reflexions by a least-squares procedure (Berdesinski & Nuber, 1966) and are listed in Table 1.

### Determination and refinement of the structure

The number and height of the Pt-Cu vectors in the Patterson synthesis made it evident that the crystal structure is centrosymmetric. The position of the metal atoms could then be evaluated from the Patterson synthesis. Pt lies on a twofold general position whereas the two Cu atoms occupy centres of symmetry at  $0, \frac{1}{2}, \frac{1}{2}$  and  $\frac{1}{2}, 0, 0$  respectively.  $R$ , calculated with the metal atoms and individual isotropic temperature factors, was 0.211. The positions of the light atoms excluding H were found from a series of Fourier syntheses. Least-squares refinement of all atoms with isotropic temperature factors led to  $R = 0.152$ . Further refinement

Table 1. *Crystal data*

Formula $[\text{Pt}(\text{C}_2\text{O}_4)_2][\text{Cu}(\text{C}_2\text{N}_2\text{H}_8)_2]$		Reduced cell	
Formula weight 554.9			
Triclinic, space group $P\bar{1}$			
$a$	6.978 (4) Å	$b$	9.419 Å
$b$	9.418 (6)	$c$	13.182
$c$	12.351 (8)	$\alpha$	12.351
$\alpha$	73.14 (5)°	$\beta$	136.86°
$\beta$	100.59 (4)	$\gamma$	98.85
$\gamma$	111.73 (4)	$V$	111.97
$Z$	2		
$d_c$	2.59 g cm <sup>-3</sup>		

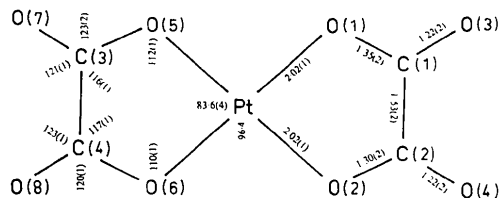


Fig. 1. Bond lengths (Å) and angles (°) in the  $[\text{Pt}(\text{C}_2\text{O}_4)_2]^{2-}$  anion (averaged).

Table 2. *Atomic parameters*

The positional parameters of Pt and Cu are multiplied by  $10^4$ , those of the non-metal atoms by  $10^3$ . The expression for the temperature factor is  $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$ . The  $U_{ij}$  have been multiplied by  $10^3$ .

	$x$	$y$	$z$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Pt	2358 (1)	4301 (1)	291 (1)	34.7 (3)	41.2 (3)	22.8 (2)	13.4 (2)	-9.1 (2)	-12.7 (2)
Cu(1)	0	5000	5000	42 (2)	52 (2)	31 (1)	21 (1)	-16 (1)	-17 (1)
Cu(2)	5000	0	0	42 (2)	47 (2)	32 (1)	19 (1)	-7 (1)	-10 (1)
C(1)	378 (2)	398 (2)	259 (1)	32 (8)	83 (12)	27 (6)	27 (8)	-13 (6)	-22 (7)
C(2)	444 (3)	575 (2)	205 (1)	39 (8)	59 (10)	36 (7)	11 (7)	-15 (6)	-31 (7)
C(3)	10 (2)	284 (2)	-144 (1)	30 (7)	50 (8)	32 (7)	11 (6)	-9 (6)	-20 (6)
C(4)	77 (2)	461 (2)	-198 (1)	46 (9)	60 (10)	22 (6)	26 (8)	-13 (6)	-14 (6)
C(5)	67 (4)	204 (3)	562 (2)	87 (17)	87 (16)	52 (11)	55 (14)	-22 (11)	-27 (11)
C(6)	159 (4)	830 (3)	484 (2)	90 (17)	70 (13)	53 (11)	33 (13)	-23 (11)	-28 (10)
C(7)	437 (3)	928 (3)	783 (1)	60 (12)	77 (13)	37 (8)	28 (10)	-7 (8)	-23 (8)
C(8)	223 (3)	904 (2)	815 (2)	48 (10)	52 (10)	60 (11)	17 (8)	-14 (8)	-28 (8)
N(1)	189 (2)	376 (2)	527 (1)	54 (9)	74 (10)	28 (6)	48 (8)	-20 (6)	-17 (6)
N(2)	228 (3)	708 (2)	464 (1)	58 (10)	61 (10)	38 (7)	17 (8)	-14 (7)	-18 (7)
N(3)	566 (3)	900 (2)	893 (1)	51 (9)	73 (10)	42 (7)	33 (8)	-11 (6)	-25 (7)
N(4)	249 (3)	9 (2)	891 (1)	54 (9)	75 (11)	43 (8)	35 (8)	-19 (7)	-27 (7)
O(1)	264 (2)	302 (1)	190 (1)	56 (7)	40 (6)	37 (5)	24 (5)	-1 (5)	-9 (4)
O(2)	383 (2)	617 (1)	99 (1)	59 (8)	52 (7)	36 (5)	13 (6)	-17 (5)	-23 (5)
O(3)	420 (2)	342 (2)	360 (1)	72 (9)	72 (9)	29 (5)	48 (8)	-18 (6)	-20 (6)
O(4)	547 (3)	669 (2)	262 (1)	92 (12)	75 (10)	62 (8)	28 (9)	-45 (8)	-43 (7)
O(5)	83 (2)	244 (1)	-39 (1)	62 (8)	42 (6)	32 (5)	15 (6)	-15 (5)	-16 (4)
O(6)	212 (2)	556 (1)	-134 (1)	57 (7)	40 (6)	39 (5)	25 (5)	-7 (5)	-14 (4)
O(7)	-97 (2)	190 (1)	-198 (1)	65 (9)	62 (8)	52 (7)	11 (7)	-22 (6)	-31 (6)
O(8)	23 (2)	518 (2)	-295 (1)	89 (11)	65 (8)	28 (5)	32 (8)	-20 (6)	-13 (5)

of the metal atoms with anisotropic temperature factors yielded an  $R$  of 0.087. Refinement of all atoms with anisotropic temperature factors converged at  $R=0.083$ . Then five poor reflexions were removed and final refinement gave  $R=0.079$  for 4035 observed re-

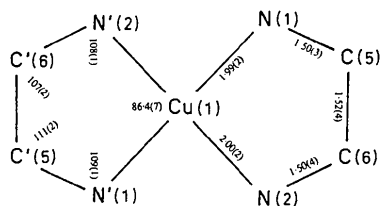


Fig. 2. Bond lengths (Å) and angles (°) in the  $[\text{Cu}(\text{C}_2\text{N}_2\text{H}_8)_2]^{2+}$  cation with Cu(1) at  $0, \frac{1}{2}, \frac{1}{2}$ .

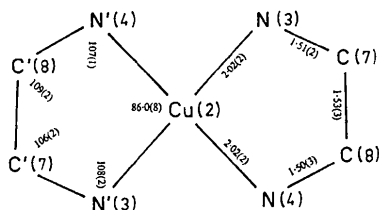


Fig. 3. Bond lengths (Å) and angles (°) in the  $[\text{Cu}(\text{C}_2\text{N}_2\text{H}_8)_2]^{2+}$  cation with Cu(2) at  $\frac{1}{2}, 0, 0$ .

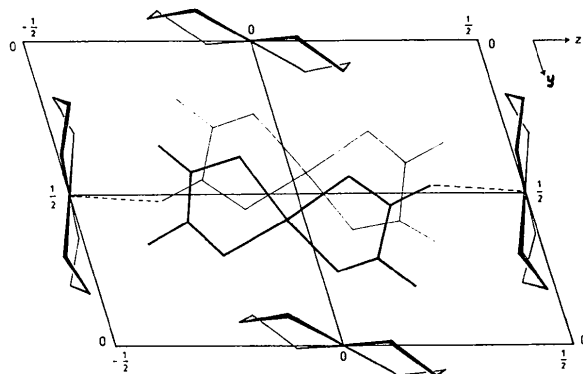


Fig. 4. Projection of one  $[\text{Pt}(\text{C}_2\text{O}_4)_2]^{2-}$  strand and the surrounding  $[\text{Cu}(\text{C}_2\text{N}_2\text{H}_8)_2]^{2+}$  cations on the  $bc$  plane. Projection parallel to  $a$ .

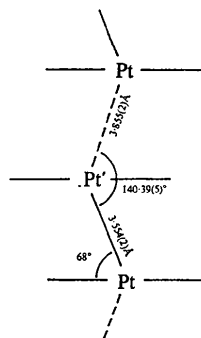


Fig. 5. The geometry of the Pt zigzag chain.

flexions ( $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ ; maximum shift/error 0.28; average shift/error 0.04). The atomic parameters are listed in Table 2.\*

### Description of the structure

The unit cell contains two centrosymmetrically related planar  $[\text{Pt}(\text{C}_2\text{O}_4)_2]^{2-}$  anions and two crystallographically non-equivalent  $[\text{Cu}(\text{C}_2\text{N}_2\text{H}_8)_2]^{2+}$  cations. Bond lengths and angles are summarized in Figs. 1 to 3. Though the Pt atom is not occupying a centre of symmetry, the  $[\text{Pt}(\text{C}_2\text{O}_4)_2]^{2-}$  anion is found to be centrosymmetric within the standard deviation. In Fig. 1 averaged values are given for bond lengths and angles, with the molecule regarded to be centrosymmetric. Table 3 gives the deviations of the atoms from the best plane through the  $[\text{Pt}(\text{C}_2\text{O}_4)_2]^{2-}$  anion.

Table 3. Deviations of the atoms (Å) from the best plane through the  $[\text{Pt}(\text{C}_2\text{O}_4)_2]^{2-}$  anion

Pt	0.050	O(4)	0.005	O(8)	-0.118
O(1)	-0.045	O(5)	0.123	C(1)	-0.009
O(2)	-0.077	O(6)	0.191	C(2)	-0.022
O(3)	-0.008	O(7)	-0.074	C(3)	-0.005
				C(4)	-0.008

The equation of the plane is  $px + qy + rz - s = 0$  with  $p = 6.767$ ,  $q = 4.104$ ,  $r = 5.040$ ,  $s = 0.367$ .

The  $[\text{Cu}(\text{C}_2\text{N}_2\text{H}_8)_2]^{2+}$  cations are arranged so as to build up channels in the  $x$  direction. These channels are filled with  $[\text{Pt}(\text{C}_2\text{O}_4)_2]^{2-}$  anions so as to form centrosymmetric dimers (Fig. 4). The Pt atoms form a zigzag chain with alternating Pt-Pt distances of 3.554 (2) Å within and 3.855 (2) Å between dimers. The Pt-Pt-Pt angle is  $140.39^\circ$ , whereas the line connecting the two Pt atoms of a dimer is tilted by  $22^\circ$  with respect to the normal to the  $[\text{Pt}(\text{C}_2\text{O}_4)_2]^{2-}$  plane. Fig. 5 shows the geometry of the zigzag chain. The nearest contact between a Pt atom of one plane and an atom of an adjacent plane within a dimer is between Pt' and O(2). The distance is 3.54 Å; the angle between the Pt-O(2) connecting line and the normal of the  $[\text{Pt}(\text{C}_2\text{O}_4)_2]^{2-}$  plane is  $15.0^\circ$ .

The plane through Cu(1) at  $0, \frac{1}{2}, \frac{1}{2}$  and the adjacent N atoms forms an angle of  $74.5^\circ$  with the  $[\text{Pt}(\text{C}_2\text{O}_4)_2]^{2-}$  plane; the plane through Cu(2) at  $\frac{1}{2}, 0, 0$  and its N atoms forms an angle of  $70.1^\circ$ . The angle between the two planes through the two Cu atoms is  $72.4^\circ$ .

The coordination around the two Cu atoms is different. Besides its four N neighbours, Cu(1) is coordinated to O(8) and O(8') of two adjacent  $[\text{Pt}(\text{C}_2\text{O}_4)_2]^{2-}$  anions. The Cu-O distances are 2.55 (1) Å; the angle

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31877 (21 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

between the line  $\text{O}(8')\text{-Cu-O}(8)$  and the normal of the  $\text{Cu-N}$  plane is  $7^\circ$ . Thus the coordination around  $\text{Cu}(1)$  may be described as distorted octahedral.

For  $\text{Cu}(2)$  no relation like this can be found. The two nearest O atoms are  $3.28$  [ $\text{O}(2)$ ] and  $3.84 \text{ \AA}$  [ $\text{O}(4)$ ] from  $\text{Cu}(2)$ ; the angle between the  $\text{Cu}(2)\text{-O}(2)$  connecting line and the normal of the  $\text{Cu}(2)\text{-N}$  plane is  $25.4^\circ$ .

### Discussion

The stacking of the anions is unusual. In the case of doubly and oppositely charged *planar* Pt complexes the arrangement found most often is a MGS structure. Though the bis(oxalato)platinate(II) crystallize in a variety of ways [e.g. with isolated ions (Mattes & Krogmann, 1964) or strongly interacting ions in linear chains (Krogmann, 1968)] a zigzag chain is a new structural feature. A deviation from an exact linear arrangement of the metal ions seems to occur in the mixed-valence bis(oxalato)platinate(II,IV), however, (Krogmann & Geserich, 1974) and was found in  $\text{K}_{1.75}[\text{Pt}(\text{CN})_4] \cdot 1.5\text{H}_2\text{O}$  (Keefer, Washecheck, Enright & Williams, 1976; Reis, Peterson, Washecheck & Miller, 1976) but with a different repeating unit.

In tetracoordinated planar and bivalent Pt compounds an alternating zigzag chain is a rather unusual feature. To our knowledge the complex *cis*-dichlorodiammineplatinum(II) is the only example known so far (Milburn & Truter, 1966). The structure found for  $[\text{Cu}(\text{en})_2][\text{Pt}(\text{ox})_2]$  explains why  $[\text{Pt}(\text{ox})_2]^{2-}$  compounds surprisingly could not be doped with  $[\text{Cu}(\text{en})_2]^{2+}$ , unlike compounds of  $[\text{PtCl}_4]^{2-}$ , but offers no explanation for the unusual colour of the solid. The square-planar four-coordinated  $\text{Cu}^{\text{II}}$  unit, as well as the other  $\text{Cu}^{\text{II}}$  ion in a distorted octahedral arrangement, should absorb as usual in the red part of the visible spectrum. The colour could possibly be explained by a charge transfer from the  $\text{Pt}^{\text{II}}$  chains to the  $\text{Cu}^{\text{II}}$  complexes.

Calculations were performed on computers Siemens 301 (Anorganisch-Chemisches Institut der Universität Heidelberg) and IBM 370/168 (Universitätsrechenzentrum, Heidelberg) with X-RAY 70 (Stewart, Kundell & Baldwin, 1970). Scattering factors were those given by Hanson, Herman, Lea & Skillman (1964).

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