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***trans*-Diperchloratobis(pyridine-2-carboxamide-*N*¹,*O*)copper(II)**

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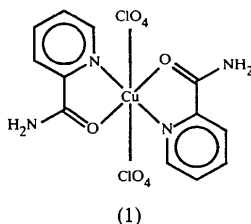
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Abstract

Crystals of the title compound, [Cu(ClO₄)₂(C₆H₆N₂O)₂], consist of centrosymmetric complex molecules of [Cu(ClO₄)₂(paa)₂] linked by hydrogen bonding (paa is picolinic acid amide or pyridine-2-carboxamide, C₆H₆N₂O). The paa ligands are coordinated through their ring N and amide O atoms to form the base of an elongated octahedron [Cu—N 1.967 (2) and Cu—O 1.937 (2) Å]. The axial Cu—O distance is 2.649 (3) Å. The sparse structural literature on copper(II)–pyridine-2-carboxamide chelate complexes is discussed.

Comment

This work forms the continuation of our study of the preparation, properties and structure of copper(II) complexes with pyridine-2-carboxamide (Sieroń & Bukowska-Strzyżewska, 1997). The structure of the title compound, (1), is shown in Fig. 1. The complex displays inversion symmetry. The Cu atom is in an elongated octahedral environment with four short and two long bonds. The short bonds [Cu—N 1.967 (2) and Cu—O 1.937 (2) Å] are formed by the chelating paa ligand which bonds through its amide O and ring N atoms. Selected geometric parameters are given in Table 1.



lengths of the equatorial Cu—N chelate bonds are very similar: the average value of 1.967 (2) Å is identical to that found in the title compound. The Cu—O chelate bonds show more variation [from 1.937 (2) Å in (1) to 1.981 (1) Å in structures (2) and (3)]. We observe that elongation of this bond is connected with the shortening of the axial Cu—O bonds, as shown in Fig. 2.

The complexes lie in the plane (010) and are connected along [101] and $[\bar{1}01]$ by N—H...O(ClO₄⁻) hydrogen bonds, forming a two-dimensional network. A

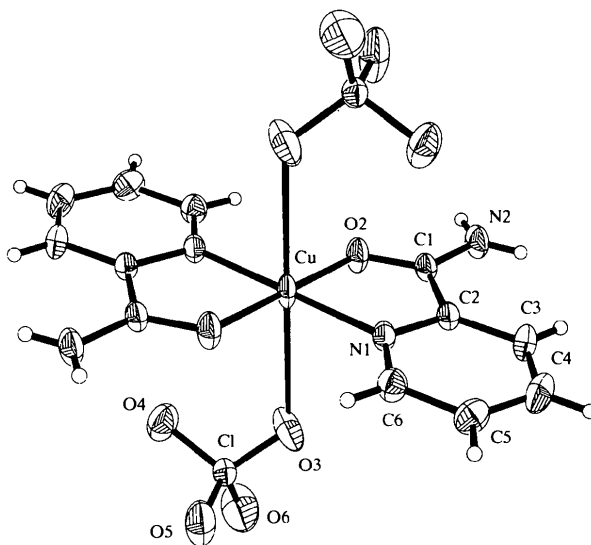


Fig. 1. Centrosymmetric *trans*-diperchloratobis(pyridine-2-carboxamide)copper(II). Displacement ellipsoids are drawn at the 30% probability level.

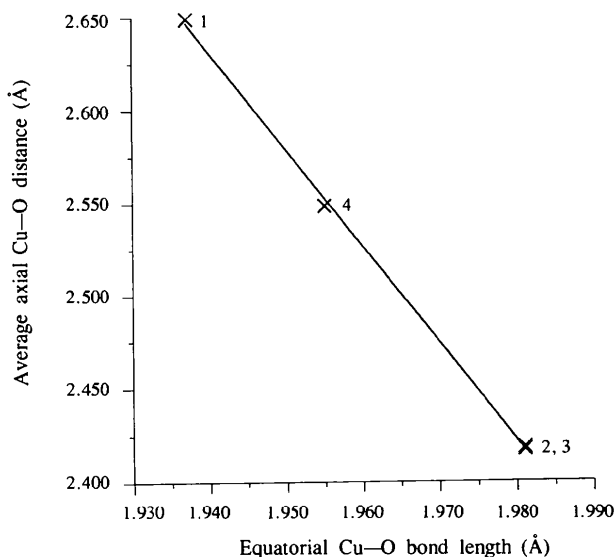


Fig. 2. The correlation between equatorial Cu—O bond lengths and the average axial Cu—O distances in complexes where the paa chelate ring is equatorial [(1)–(4) relate to compounds in Table 3].

centrosymmetric 12-membered ring is formed by four such hydrogen bonds (see Table 2). We can observe the influence of hydrogen bonds and the weak Cu—O3(ClO₄⁻) coordination on the Cl—O bond lengths and the displacement parameters of the O atoms of the ClO₄⁻ groups. The observed Cl—O bonds range from 1.395 (3) to 1.433 (2) Å and the U_{eq} values for perchlorate O atoms vary from 0.119 (1) to 0.078 (1) Å². The longest Cl—O bond and smallest U_{eq} value are for the O4 atom which participates in the stronger of the two hydrogen bonds. The long Cu—O3 bond of 2.649 (3) Å causes a similar elongation of Cl—O3 [1.414 (2) Å], as does the weak hydrogen bond N—H...O5 of 2.23 (3) Å, which elongates Cl—O5 to 1.411 (2) Å.

Experimental

The title crystals were grown from an aqueous solution of 2-pyridinecarbonitrile and copper(II) perchlorate, indicating that copper-assisted hydrolysis of 2-pyridinecarbonitrile to pyridine-2-carboxamide (Watanabe *et al.*, 1973) had occurred. A pale-blue solution formed when Cu(ClO₄)₂ (1 mmol) was added to an aqueous solution (50 ml) containing 2-pyridinecarbonitrile (2 mmol). After heating to boiling point, the solution became dark blue. After a few days, pale-blue prismatic crystals of the title compound were obtained.

Crystal data

[Cu(ClO₄)₂(C₆H₆N₂O)₂]
 $M_r = 506.70$
 Triclinic
 $P\bar{1}$
 $a = 5.8839$ (11) Å
 $b = 9.104$ (2) Å
 $c = 9.205$ (2) Å
 $\alpha = 92.60$ (2)°
 $\beta = 101.697$ (15)°
 $\gamma = 107.608$ (14)°
 $V = 457.26$ (15) Å³
 $Z = 1$
 $D_x = 1.840$ Mg m⁻³
 D_m not measured

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 41 reflections
 $\theta = 3.7$ – 15.8 °
 $\mu = 1.549$ mm⁻¹
 $T = 293$ K
 Prism
 $0.76 \times 0.15 \times 0.13$ mm
 Pale blue

Data collection

Siemens P3 diffractometer $\theta_{max} = 25.98$ °
 ω - 2θ scans $h = 0 \rightarrow 7$
 Absorption correction: none $k = -11 \rightarrow 11$
 1984 measured reflections $l = -11 \rightarrow 11$
 1799 independent reflections 3 standard reflections
 1629 reflections with every 96 reflections
 $I > 2\sigma(I)$ intensity decay: none
 $R_{int} = 0.012$

Refinement

Refinement on F^2 $(\Delta/\sigma)_{max} < 0.01$
 $R(F) = 0.036$ $\Delta\rho_{max} = 0.59$ e Å⁻³
 $wR(F^2) = 0.095$ $\Delta\rho_{min} = -0.42$ e Å⁻³
 $S = 1.07$ Extinction correction: SHELXL93
 1799 reflections Extinction coefficient: 0.016 (2)
 158 parameters Scattering factors from International Tables for Crystallography (Vol. C)
 All H atoms refined
 $w = 1/[\sigma^2(F_o^2) + (0.0428P)^2 + 0.56P]$ where $P = (F_o^2 + 2F_c^2)/3$

Table 1. Selected geometric parameters (Å, °)

Cu—O2	1.937 (2)	Cl—O6	1.395 (3)
Cu—O3	2.649 (3)	O2—C1	1.255 (3)
Cu—N1	1.967 (2)	N1—C2	1.343 (3)
Cl—O3	1.414 (2)	N1—C6	1.327 (3)
Cl—O4	1.433 (2)	N2—C1	1.302 (3)
Cl—O5	1.411 (2)	Cl—C2	1.494 (3)
O2—Cu—O3	90.30 (7)	C2—N1—C6	119.9 (2)
O2—Cu—N1	83.27 (8)	N1—C2—C1	112.2 (2)
O3—Cu—N1	80.89 (8)	N1—C2—C3	121.5 (2)
Cl—O2—Cu	113.7 (2)	N1—C6—C5	121.1 (2)
C2—N1—Cu	112.6 (2)	N2—C1—C2	121.0 (2)
C6—N1—Cu	127.5 (2)	C1—C2—C3	126.2 (2)

Table 2. Hydrogen-bonding geometry (Å, °)

D—H...A	D—H	H...A	D...A	D—H...A
N2—H1...O4 ⁱ	0.85 (3)	2.08 (3)	2.919 (4)	171 (3)
N2—H2...O5 ⁱⁱ	0.80 (3)	2.23 (3)	2.977 (3)	155 (3)

Symmetry codes: (i) $1 - x, -y, -z$; (ii) $x, y, z - 1$.

Table 3. Selected bond lengths (Å) in copper(II) pyridine-2-carboxamide (paa) complexes

No.	Compound	Equatorial bonds		Axial bonds	
		Cu—N(paa)	Cu—O(paa)	L	Cu—O(L)
(1) ^a	Cu(ClO ₄) ₂ (paa) ₂	1.967 (2)	1.937 (2)	ClO ₄ ⁻	2.649 (3)
(2) ^b	CuCl ₂ (H ₂ O) ₂ (paa) ₂	1.960 (1)	1.981 (1)	H ₂ O	2.418 (2)
(3) ^b	CuBr ₂ (H ₂ O) ₂ (paa) ₂	1.965 (2)	1.981 (1)	H ₂ O	2.417 (3)
(4) ^c	Cu(NO ₃) ₂ (H ₂ O) ₂ (paa) ₂	1.976 (3)	1.955 (2)	H ₂ O	2.265 (4)
	Average value	1.967 (2)		NO ₃ ⁻	2.832 (4)
		Cu—N(paa)	Cu—N(pyCO) ₂		
(5) ^d	Cu(ClO ₄)[(pyCO) ₂ N](H ₂ O)(paa)	2.001 (4)	from 1.931 (4) to 2.018 (4)	paa	2.316 (3)
				ClO ₄ ⁻	2.73 (6)

References: (a) this work; (b) Sieroń & Bukowska-Strzyżewska (1997); (c) Castro *et al.* (1990); (d) Cantarero *et al.* (1988) (pyCO = NC₅H₄CO).

All non-H atoms were refined anisotropically. All H atoms were located from a difference synthesis and refined isotropically. Corrections for absorption were considered unnecessary; transmission factors were estimated to be in the range 0.577–0.649.

Data collection: Siemens P3 software. Cell refinement: Siemens P3 software. Data reduction: *SHELXTLPC XDISK* (Sheldrick, 1990b). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990a). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTLPC XP*. Software used to prepare material for publication: *SHELXL93*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: MU1350). Services for accessing these data are described at the back of the journal.

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Monosodium 3-(Dimethylammonio)-1-hydroxy-1,1-propanedioldiphosphonate Monohydrate (Monosodium Olpadronate Monohydrate)

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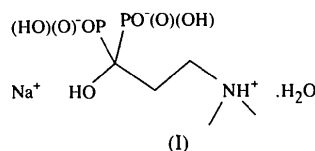
Abstract

The crystal structure of the title compound, Na⁺.C₅H₁₄NO₇P₂⁻.H₂O, contains zwitterionic olpadronate anions coordinated to Na⁺ cations. The interactions in the crystal define broad chains which have Na⁺ ions at their core and bis-phosphonate groups near the Na⁺ centres, with the positively charged ends of the zwitterions

extending outwards. Strong hydrogen bonds provide both intra- and interchain connectivity.

Comment

The title compound, (I), has been shown to be a highly effective drug for preventing or reverting bone loss (Van Beek *et al.*, 1994) and is much more soluble than other bis-phosphonates in common use, suggesting better digestive tolerance. Its dimethylated side chain offers unique properties for modulating bone-mass metabolism (Boonekamp *et al.*, 1986, 1987; Löwik *et al.*, 1988; Van Der Pluijm *et al.*, 1991; Feretti *et al.*, 1995; Vega *et al.*, 1994) without disturbing cell vitality and bone quality, according to experimental assays.



A number of structural studies of drugs containing bis-phosphonate groups have been known for some time, in particular, that of olpadronate free acid (Shkol'nikova *et al.*, 1987). This knowledge has not diminished our interest in the structures of sodium salts of bis-phosphonates and, in particular, that of olpadronate, mainly because among the recent related literature (Coiro & Lamba, 1989; Leroux *et al.*, 1989; Shkol'nikova *et al.*, 1990; Rachdaoui *et al.*, 1990; Vega *et al.*, 1996) only a few sodium salts are to be found, in spite of their favourable bio-availability. We report here the crystal and molecular structure of monosodium olpadronate monohydrate, (I). Unfortunately, the precision of the results previously reported for the free acid (Shkol'nikova *et al.*, 1987) precluded any detailed analysis, making meaningful comparisons possible only in qualitative terms.

A view of the molecule and its surroundings in the lattice is shown in Fig. 1. The molecule exists as a zwitterion with an overall charge of -1; the protonated dimethylamine group bears a positive charge and the two phosphonate groups each have a single negative charge. Each phosphonate has one protonated O atom, the extra electronic charge being shared by the remaining two non-protonated O atoms. This fact defines two distinct types of P—O bonds, as shown by the mean values of the following bond lengths and angles: P—OH 1.579 (7), P—O 1.496 (8) Å, O—P—OH 109.0 (24), O—P—O 116.9 (19)°; these are in accord with the results found for related molecules (Coiro & Lamba, 1989; Vega *et al.*, 1996) and confirms the partial double-bond character of the non-protonated O atoms.

As in the free acid, the phosphonate groups have staggered conformations with atoms O11, P1, C1, P2 and O21 nearly coplanar [O11—P1—C1—P2 -168.9 (2)