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Copper 3-Methylanthranilate [Bis(2-amino-3-methylbenzoato)copper(II)]

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Abstract. $[Cu(C_8H_8NO_2)_2]$, $M_r = 363{\cdot}9$, orthorhombic, *Pbca*, $a = 9{\cdot}580\,(2)$, $b = 7{\cdot}213\,(1)$, $c = 21{\cdot}867\,(3)$ Å, $V = 1511{\cdot}1\,(6)$ Å^3, $Z = 4$, $D_x = 1{\cdot}60$, $D_m = 1{\cdot}67$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 15{\cdot}3$ cm^{-1}, $F(000) = 748$, $T = 293\,(1)$ K, $R = 0{\cdot}055$ for 1307 reflections. The coordination of the Cu atom is square planar, with four methyl-amino-benzoate ligands acting as bridging bidentate ligands. Each Cu atom is bonded to two carboxylate O atoms of two different ligands and to two N atoms of two other ligands. The O and N atoms are in *trans* positions. The bridging ligands lead to a two-dimensional polymeric network parallel to the (010) plane, strengthened further by hydrogen bonding between adjacent molecules. The molecular packing, constrained by the methyl group, produces a cavity elongated in the [010] direction. The Cu—ligand distances are 1·954 (3) Å for Cu—O and 2·054 (3) Å for Cu—N.

Introduction. Anthranilic acid (*o*-aminobenzoic acid) is a precursor of tryptophan, a biologically important α-amino acid. This acid, and related acids with a carboxylate O atom and an N atom in *ortho* position, form highly stable and insoluble complexes with a variety of divalent and trivalent metal ions. The structures of Cu (Lange & Haendler, 1975), Y (Boudreau & Haendler, 1981), and Zn (Boudreau, Boudreau & Haendler, 1983) anthranilates have been determined, as has the structure of the Cu complex of quinaldinic acid, a metabolite of tryptophan (Haendler, 1986). Substitution on the aromatic ring may have an effect on the anti-inflammatory properties of the Cu complexes (Sorenson, 1978). Introduction of a methyl group into anthranilic acid, as in the title compound, has radically affected structure and packing. Copper anthranilate shows distorted octahedral coordination due to the Jahn–Teller effect. The methyl analog exhibits only square-planar coordination, and its packing arrangement reveals an intermolecular cavity. Copper quinaldinate monohydrate is pentacoordinate.

Experimental. Single crystals prepared by diffusion of aqueous solutions of copper nitrate and sodium 2-amino-3-methylbenzoate over ten days (Martin & Haendler, 1978); density of bulk sample by flotation in mixture of carbon tetrachloride and bromoform; dark green rectangular platelet, 0·48 × 0·40 × 0·10 mm, used; Nicolet four-circle diffractometer, graphite-monochromatized Mo *K*α radiation. 15 reflections ($2\theta > 20°$) for measurement of lattice parameters at 293 (1) K; empirical absorption correction, using ψ scan with four reflections, range $= 14{\cdot}6° < 2\theta < 31{\cdot}9°$, transmission factors 0·56–1·00; maximum $\sin\theta/\lambda = 0{\cdot}650$ Å^{-1}, h 0 to 12, k 0 to 9, l 0 to 28; six check reflections, frequency 300, no indication of deterioration or misalignment; 1738 reflections measured, 431 unobserved with $I < 3\sigma(I)$.

Structure solved with *DIRDIF* (Beurskens & Noordik, 1971; Gould, van den Hark & Beurskens, 1975; van den Hark, Prick & Beurskens, 1976). Least-squares refinement on *F*, block-diagonal approximation. Non-H atoms refined anisotropically; H atoms located from a difference Fourier map or by superposition of a Dreiding model on a scaled unit-cell projection, with further block-diagonal refinement. Final refinement using full-matrix least squares, 1307 reflections, anomalous dispersion for Cu, $B = 5{\cdot}0$ Å^2 for H atoms, converged to $R = 0{\cdot}055$, $wR = 0{\cdot}030$, $w = 1/\sigma^2(F_o)$. $(\Delta/\sigma)_{\max} = 0{\cdot}030$, exclusive of H shifts; $S = 1{\cdot}72$. Final difference map showed max. and min. peaks of 0·49 and −0·39 e Å^{-3}. No systematic errors as fuctions of $\sin^2\theta$ or F_o. No significant correlations. Atomic scattering factors for the non-H atoms from Hanson, Herman, Lee & Skillman (1964), and for H from Stewart, Davidson & Simpson (1965). Correction terms for Cu anomalous dispersion from *International Tables for X-ray Crystallography* (1974). Most computations performed with National Research Council of Canada programs (Ahmed, 1973). *ORXFLS*3 (Busing, Martin & Levy, 1971) used for full-matrix least-squares calculation and *ORTEP*II (Johnson, 1976) for the thermal-ellipsoid plot.

Discussion. The final positional parameters are given in Table 1,* and principal bond distances and angles in Table 2. One half of the unit cell is shown in projection

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* Lists of structure factors, ring bond distances and angles, and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42866 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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in Fig. 1; the thermal-ellipsoid plot is in Fig. 2. The coordination around the Cu atom is square planar, with the methyl-amino-benzoate ligand acting as a bridging bidentate ligand coordinating through amino N atoms and carboxylate O atoms. The sites of attachment on a ligand are not associated with the same Cu atom, each ligand bridging two Cu atoms. Two carboxylate O atoms, O(1), each belonging to a different ligand, are in *trans* positions, and the remaining two sites are occupied by two *trans* amino N atoms, also from two separate ligands. This leads to a two-dimensional polymeric network parallel to the (010) plane. Similar networks resulting from bridging Cu atoms have been reported in bis(*o*-aminobenzoato)copper(II) (Lange & Haendler, 1975), copper(II) aminobutyrate dihydrate (Takenaka, Oshima, Yamada & Watanabe, 1973), and bis(6-aminohexanoato)copper(II) dihydrate (Sjöberg, Österberg & Söderquist, 1973).

Table 1. *Final positional parameters and equivalent Debye–Waller factors*

$$B_{\rm eq} = \tfrac{8}{3}\pi^2 \textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$(Å^2)
Cu	0·0000	0·0000	0·0000	1·87
O(1)	0·0976 (3)	0·0917 (4)	−0·0724 (1)	2·28
O(2)	0·2674 (3)	0·0155 (5)	−0·0091 (1)	2·65
N	0·5009 (4)	0·2333 (5)	−0·0329 (1)	2·11
C(1)	0·2266 (4)	0·0731 (6)	−0·0599 (2)	2·14
C(2)	0·3287 (4)	0·1242 (5)	−0·1091 (2)	1·95
C(3)	0·4612 (4)	0·1948 (5)	−0·0958 (2)	2·03
C(4)	0·5547 (4)	0·2374 (6)	−0·1432 (2)	2·58
C(5)	0·5137 (6)	0·2029 (7)	−0·2025 (2)	3·27
C(6)	0·3833 (6)	0·1324 (8)	−0·2157 (2)	3·33
C(7)	0·2896 (5)	0·0956 (7)	−0·1696 (2)	2·73
C(8)	0·6953 (6)	0·3208 (7)	−0·1294 (3)	3·93
H(1)	0·585 (5)	0·197 (8)	−0·019 (2)	
H(2)	0·438 (6)	0·188 (8)	−0·013 (3)	
H(5)	0·575 (5)	0·230 (7)	−0·236 (2)	
H(6)	0·359 (6)	0·109 (8)	−0·253 (2)	
H(7)	0·206 (5)	0·051 (8)	−0·180 (2)	
H(81)	0·673 (7)	0·414 (8)	−0·114 (3)	
H(82)	0·754 (6)	0·246 (9)	−0·112 (2)	
H(83)	0·730 (5)	0·407 (8)	−0·176 (2)	

Table 2. *Selected bond distances* (Å) *and angles* (°)

The dotted line represents a bond between atoms in different molecules.

Cu–O(1)	1·954 (3)	C(4)–C(5)	1·378 (4)
Cu···N	2·054 (3)	C(5)–C(6)	1·379 (5)
C(1)–O(1)	1·273 (3)	C(6)–C(7)	1·376 (5)
C(1)–O(2)	1·249 (3)	C(7)–C(2)	1·390 (4)
C(1)–C(2)	1·500 (4)	N–H(1)	0·90 (4)
C(2)–C(3)	1·398 (4)	N–H(2)	0·81 (4)
C(3)–C(4)	1·404 (4)	H(1)···O(2)	2·18 (5)
C(3)–N	1·454 (3)	N···O(2)	2·999 (3)
C(4)–C(8)	1·506 (5)		
O(1)–Cu···N	88·0 (4)	C(1)–C(2)–C(7)	118·1 (4)
Cu–O(1)–C(1)	104·8 (4)	C(2)–C(3)–N	120·3 (4)
O(1)–C(1)–O(2)	122·0 (4)	H(1)–N–H(2)	111 (5)
O(1)–C(1)–C(2)	116·9 (4)	C(4)–C(8)–H(83)	106 (5)
O(2)–C(1)–C(2)	121·0 (4)	C(3)–N–H(1)	119 (5)
C(3)–C(4)–C(8)	120·7 (5)	N–H(1)···O(2)	152 (5)
C(1)–C(2)–C(3)	122·2 (4)		

The metal-to-ligand distances Cu—O(1), 1·954 Å, and Cu···N, 2·054 Å, are comparable to the corresponding average values 1·96 (6) and 2·00 (8) Å reported for a large number of Cu$^{\rm II}$ complexes with amino acids and peptides (Freeman, 1966; Karlin & Zubieta, 1983). There is indication of hydrogen bonding between the N atom and an adjacent O(2). The metal anthranilates have the same crosslinking in the polymeric network. The N···O(2) distance is 2·999 Å and the N—H(1)···O(2) angle is 152°, within the range found for hydrogen bonds between amine groups and oxygen (2·57–3·22 Å). There are two Cu···O(2) distances, 2·572 Å, that lie off the axis which is perpendicular to the coordination plane. Similar out-of-plane ligands have been reported for Cu$^{\rm II}$ complexes of phenoxyacetate (Goebel & Doedens, 1971) and dichloracetate with α-picoline (Davey & Stephens, 1971).

Parallel ligands are spaced at unit-cell distances in the [010] direction, forming a cavity, centered roughly over C(4) of each aromatic ring, and approximately 3 × 6 × 3 Å in size. This suggests that formation of inclusion compounds might be possible. A report of a similar cavity between molecules of *N,N′*-(1,1′-biphenyl)bis(salicylideneaminato)copper(II) has been published (Cheeseman, Hall & Waters, 1966).

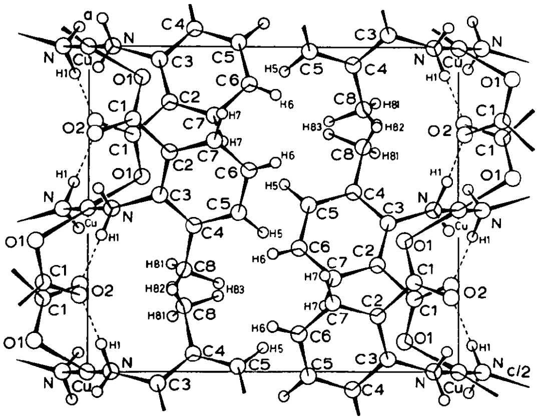

Fig. 1. Projection of one half of the unit cell of copper(II) 3-methylanthranilate, as viewed along the [010] direction.

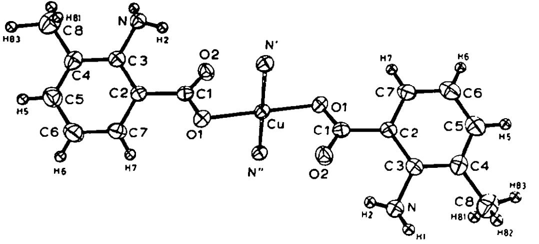

Fig. 2. Thermal-ellipsoid plot of copper(II) 3-methylanthranilate.

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Trioxalatoruthénate(III) de Potassium 4,5-Hydraté

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Abstract. $K_3[Ru(C_2O_4)_3].4\cdot5H_2O$, $M_r = 563\cdot5$, triclinic, $P\bar{1}$, $a = 6\cdot814\ (1)$, $b = 10\cdot517\ (2)$, $c = 12\cdot463\ (2)$ Å, $\alpha = 76\cdot24\ (1)$, $\beta = 84\cdot35\ (1)$, $\gamma = 85\cdot51\ (1)^\circ$, $V = 861\cdot9\ (4)$ Å^3, $Z = 2$, $D_x = 2\cdot17$ Mg m^{-3}, $\lambda(\text{Mo } K\bar{\alpha}) = 0\cdot7114$ Å, $\mu = 1\cdot69$ mm^{-1}, $F(000) = 556$, $T = 295$ K, $R = 0\cdot050$ for 3778 unique reflections. Ru atoms are six-coordinated in an asymmetrical octahedron, by three oxalato groups with $2\cdot019\ (4) \leq \text{Ru—O} \leq 2\cdot034\ (3)$ Å. The water molecules are grouped in tunnels along the [100] axis; one molecule is statistically distributed around one $\bar{1}$ center. Each of the three K atoms is surrounded by O oxalic or aquo atoms with the shortest distances: 2·674 (3), 2·700 (4), 2·669 (4) Å.

Introduction. Avec l'acide oxalique, en solution aqueuse, le ruthénium(IV) dans ses trois ions les mieux connus ($[RuCl_6]^{2-}$, $[Ru_2OCl_{10}]^{4-}$ et $[Ru_4O_6]^{4+}$) donne lieu à des réactions qui font apparaître de nombreux composés intermédiaires (Deloume, 1984) encore mal caractérisés. Les chlorocomplexes cristallisés utilisés comme réactifs sont bien connus (Deloume, Faure & Thomas-David, 1979) et nous essayons d'isoler les produits finals des réactions auxquels pourrait appartenir le trioxolatoruthénate(III) de potassium.

Partie expérimentale. Le composé a été préparé selon la méthode décrite par Charonnat (1931). Une solution d'oxalate de potassium et de pentachloroaquaruthénate(III) de potassium est chauffée pendant deux heures en ampoule scellée à 403 K; maintenue ensuite à 273 K la solution laisse déposer les cristaux vert olive du composé.

Cristallisation dans l'eau; parallélépipède taillé 0,25 × 0,50 × 0,50 mm; diffractomètre Enraf–Nonius CAD-4; monochromateur en graphite; paramètres de

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