

The observation of only a single form of the iodide in solution is consistent with increasing preference for a *trans* geometry as the halogen co-ligands become heavier. Under high resolution the ^{125}Te and ^{195}Pt NMR resonances show small splittings which are attributable to *RR/SS* and *RS/SR* enantiomers, which will interconvert by pyramidal inversion at Te. As shown by the present X-ray study, the *trans* structure is also favoured in the solid state.

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Structure of Copper(II) Salicylates: Bis(3-pyridylmethanol)bis(salicylato)copper(II)

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Abstract. $[\text{Cu}(\text{C}_7\text{H}_5\text{O}_3)_2(\text{C}_6\text{H}_7\text{NO})_2]$, $M_r = 556.03$, orthorhombic, *Pbca*, $a = 12.947$ (1), $b = 9.401$ (3), $c = 20.005$ (3) Å, $V = 2435.16$ Å³, $Z = 4$, $D_m = 1.50$, $D_x = 1.52$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.54178$ Å, $\mu = 16.949$ cm⁻¹, $F(000) = 1148$, $T = 293$ K, final $R = 0.044$ for 1122 observed reflections. The crystal structure consists of molecules bonded together into layers parallel to (100). The coordination polyhedron of Cu^{II} is a distorted octahedron built up by four short bonds in the equatorial plane [two Cu—N and two Cu—O bonds with bond lengths 1.944 (4) and 2.029 (4) Å] and two longer apical Cu—O bonds [2.622 (4) Å]. The O atoms forming apical bonds belong to the different molecules of 3-pyridylmethanol.

Introduction. Reports of complexes formed between copper(II) and salicylate ligands have given rise to several problems. For example, the ligand shows

monodentate (Pajunen & Pajunen, 1982; Hanic & Michalov, 1960) or bidentate (Ablov, Kiosse, Dimitrova, Malinovski & Popovich, 1974; Muhonen & Hämäläinen, 1978; Hoang, Valach, Dunaj-Jurčo & Melník, 1992) carboxylate coordination and also bidentate coordination through the carboxylic and phenolic O atoms (Jagner, Hazell & Larsen, 1976; Pajunen & Pajunen, 1982). In order to investigate further the structural properties of the salicylate ligand, we have examined the crystal structure of bis(3-pyridylmethanol)bis(salicylato)copper(II).

Experimental. Blue monocrystals of $\text{Cu}(\text{sal})_2 \cdot (3\text{-pyMe})_2$ (sal = salicylate, 3-pyMe = 3-pyridylmethanol) were prepared as described by Melník, Macášková & Mrozinski (1988). A prismatic crystal with dimensions $0.25 \times 0.20 \times 0.20$ mm (D_m by flotation in $\text{CHBr}_3/\text{CH}_3\text{OH}$) was used for data collection on a Syntex P_2 diffractometer, with

Table 1. Coordinates and equivalent isotropic thermal parameters (\AA^2) for non-H atoms
$$B_{eq} = (4/3) \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	x	y	z	B_{eq}
Cu	0.5	0.0	0.5	2.91 (3)
N	0.9777 (3)	0.3011 (4)	0.5380 (2)	2.6 (1)
O(1)	0.4463 (3)	0.0611 (4)	0.5861 (2)	3.27 (9)
O(2)	0.5789 (3)	0.1899 (4)	0.6222 (2)	4.02 (1)
O(3)	0.2776 (3)	0.0536 (5)	0.6482 (2)	4.6 (1)
O(4)	0.6886 (3)	0.0926 (4)	0.5195 (2)	3.9 (1)
C(1)	1.0479 (4)	0.2426 (6)	0.5782 (3)	3.2 (1)
C(2)	1.0345 (4)	0.1107 (6)	0.6056 (3)	3.9 (2)
C(3)	0.9449 (4)	0.0362 (5)	0.5922 (3)	3.7 (2)
C(4)	0.8720 (4)	0.0935 (5)	0.5503 (3)	2.9 (2)
C(5)	0.8915 (4)	0.2266 (5)	0.5235 (3)	2.7 (1)
C(6)	0.7758 (4)	0.0103 (6)	0.5339 (3)	3.5 (2)
C(7)	0.4885 (4)	0.1480 (5)	0.6274 (2)	2.8 (2)
C(8)	0.4222 (4)	0.1949 (5)	0.6836 (3)	3.0 (1)
C(9)	0.4602 (5)	0.2940 (6)	0.7301 (3)	3.8 (2)
C(10)	0.3964 (6)	0.3420 (7)	0.7814 (3)	4.4 (2)
C(11)	0.2970 (6)	0.2901 (9)	0.7877 (3)	5.2 (3)
C(12)	0.2599 (6)	0.1920 (8)	0.7445 (3)	4.7 (2)
C(13)	0.3201 (5)	0.1470 (6)	0.6915 (3)	4.2 (2)

Table 2. Bond lengths (\AA) and bond angles ($^\circ$)

Coordination sphere of Cu ^{II}			
Cu—N ⁱ	2.039 (4)	N ⁱ —Cu—O(1)	90.5 (2)
Cu—O(1)	1.944 (4)	N ⁱ —Cu—O(4)	89.2 (2)
Cu—O(4)	2.622 (4)	O(1)—Cu—O(4)	96.0 (3)
Cu—O(2)	3.194 (5)	Cu—O(1)—C(7)	127.3 (3)
3-Pyridylmethanol ligand			
N—C(1)	1.332 (7)	Cu ⁱⁱ —N—C(1)	120.5 (3)
N—C(5)	1.349 (6)	N—C(1)—C(2)	122.0 (5)
C(1)—C(2)	1.367 (8)	C(1)—C(2)—C(3)	119.3 (5)
C(2)—C(3)	1.381 (7)	C(2)—C(3)—C(4)	119.8 (5)
C(3)—C(4)	1.372 (8)	C(3)—C(4)—C(5)	117.8 (5)
C(4)—C(5)	1.385 (7)	C(3)—C(4)—C(6)	119.9 (5)
C(4)—C(6)	1.507 (7)	C(4)—C(5)—N	122.5 (5)
C(6)—O(4)	1.399 (7)	C(1)—N—C(5)	118.7 (4)
C—N(av.)	1.341 (6)	C(4)—C(6)—O(4)	115.1 (4)
C—C(av.)	1.376 (1)	C(6)—O(4)—Cu	126.7 (4)
		N—C—C(av.)	122.3 (2)
		C—C—C(av.)	118.96 (1)
Salicylate ligand			
C(7)—O(1)	1.284 (6)	O(1)—C(7)—O(2)	123.4 (4)
C(7)—O(2)	1.239 (6)	O(1)—C(7)—C(8)	115.5 (4)
C(7)—C(8)	1.482 (7)	O(2)—C(7)—C(8)	121.1 (5)
C(8)—C(9)	1.406 (8)	C(7)—C(8)—C(9)	119.8 (5)
C(9)—C(10)	1.393 (9)	C(7)—C(8)—C(13)	122.3 (5)
C(10)—C(11)	1.38 (1)	C(8)—C(9)—C(10)	119.7 (6)
C(11)—C(12)	1.35 (1)	C(9)—C(10)—C(11)	120.3 (6)
C(12)—C(13)	1.382 (9)	C(10)—C(11)—C(12)	120.9 (6)
C(13)—C(8)	1.405 (8)	C(11)—C(12)—C(13)	119.9 (7)
C(13)—O(3)	1.351 (7)	C(12)—C(13)—C(8)	121.2 (6)
C—C(av.)	1.386 (2)	C(12)—C(13)—O(3)	117.5 (6)
		O(3)—C(13)—C(8)	121.3 (5)
		C(13)—C(8)—C(9)	117.8 (5)
		C—C—C(av.)	119.97 (2)

Symmetry code: (i) $-\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$; (ii) $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$.

graphite-monochromated Cu $K\alpha$ radiation, $\theta/2\theta$ scans to $2\theta_{\max} = 110^\circ$, and a time per reflection of ca 60 s. Two standard reflections showed variation by 0.4%. 25 reflections with $8 \leq 2\theta \leq 33^\circ$ were used for refinement of lattice parameters. An absorption correction was applied with maximum and minimum transmission factors of 0.796 and 0.564. For the index range $0 \leq h \leq 9, 0 \leq k \leq 13, 0 \leq l \leq 21$, 1849 reflections were measured. 1530 reflections were unique, of which 1122 were observed [$F \geq 3\sigma(F)$]. Data reduction was performed by program *XP21*

(Pavelčík, 1987). All non-H atoms were located by direct methods using the program *SHELXS86* (Sheldrick, 1990). Refinement was by full-matrix least squares based on F values (169 parameters), using the program *SHELX76* (Sheldrick, 1976). Scattering factors and f' , f'' values were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). An absorption correction was applied after isotropic refinement by the program *DIFABS* (Walker, 1983). After anisotropic refinement all H atoms were located from a difference map (held

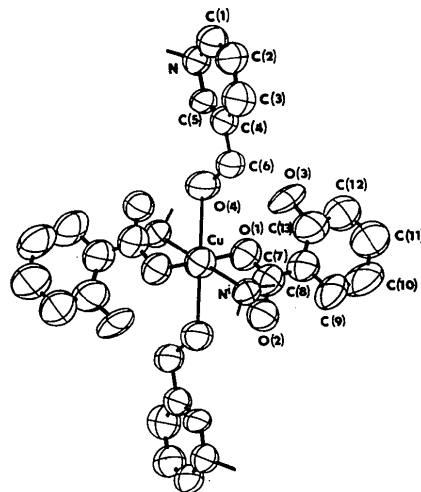


Fig. 1. A fragment of the structure drawn by *ORTEP* (Johnson, 1965). H atoms are omitted. Symmetry code: (i) $-\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$.

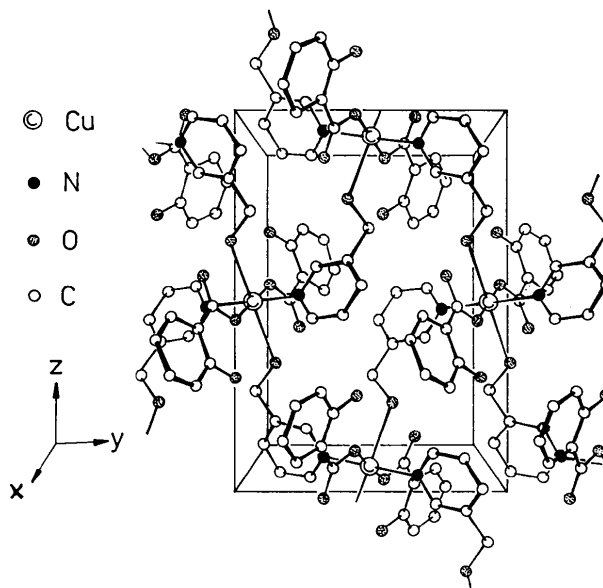


Fig. 2. The structure of one layer perpendicular to \mathbf{a} . H atoms are omitted for clarity.

Table 3. Structural data for copper(II) salicylates

Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parentheses following an average value is the maximal e.s.d., and the second number is the maximum deviation from the mean.

Compound	Chromophore	Cu—L* (Å)	cis-L—Cu—L (°)	Reference
Cu(sal)(C ₈ H ₂₂ N ₂ O)†	CuN ₂ O ₃	N 2.059 (4,9) O 2.107 (4,413)	85.1 (2,0) 93.3 (1,3.23)	Pajunen & Pajunen (1982)
Cu(sal) ₂ (H ₂ O) ₂ ‡	CuO ₆	O 2.142 (2,583)	90.6 (6,3.8)	Jagner, Hazell & Larsen (1976)
[Cu(sal) ₂ (H ₂ O) ₂].2H ₂ O§	CuO ₄	O 1.948 (4,34)	91.51 (5,0)	Rissanen <i>et al.</i> (1987)
Cu(sal) ₂ (C ₆ H ₁₆ N ₂)¶	CuN ₂ O ₄	N 2.030 (10,10) O 2.273 (9,323)	86.9 (4,0) 76.52 (3,15.6)	Muhonen & Hämäläinen (1978)
Cu ₂ (sal) ₂ (C ₆ H ₄ O ₂).2H ₂ O¶	CuO ₅	O 1.98–2.03**		Ablov <i>et al.</i> (1974)
Cu(sal) ₂ (2-pyMe) ₂ §	CuN ₂ O ₄	N 1.981 (1,0) O 2.156 (1,175)	Not present 95.13 (5,0)	Hoang <i>et al.</i> (1992)
Cu(sal) ₂ (3-pyMe) ₂ §	CuN ₂ O ₄	N 2.039 (4,0) O 2.283 (4,339)	Not present 96.0 (3,0)	This work

* The chemical identity of the coordinated atom is specified in this column.

† Salicylate ligand coordinates through the carboxylate group and phenyl group bidentately. One carboxyl O atom is nonbonded.

‡ Salicylate ligand coordinates through the carboxylate group and phenyl group tridentately.

§ Salicylate ligand coordinates through the carboxylate group monodentately.

¶ Salicylate ligand coordinates through the carboxylate group bidentately.

** In this structure bond lengths and angles are not published, only range of bonds Cu—O is given.

fixed). Maximum positive and negative electron density in the final difference map were 0.3 and $-0.5 \text{ e } \text{Å}^{-3}$. Final $R = 0.044$, $wR = 0.044$, $w = 0.6694/[\sigma^2(F_o) + 0.00005F_o^2]$; $S = 0.05$; $(\Delta/\sigma)_{\text{max}} = 0.03$ in the final refinement cycle. Calculations were performed on a PC-386 computer.*

Discussion. Coordinates and equivalent isotropic thermal parameters for non-H atoms are given in Table 1, bond lengths and bond angles in Table 2. The structure is shown in Figs. 1 and 2. Each Cu atom lies on an inversion centre and is *trans*-coordinated by two carboxyl O atoms of two monodentate salicylate ligands [Cu—O(1) = 1.944 (1) Å] and by two N atoms of 3-pyMe ligands [Cu—Nⁱ = 2.039 (4) Å]. Pseudo-octahedral Cu^{II} coordination is completed by two O atoms of 3-pyMe ligands from two [Cu(sal)₂(3-pyMe)₂] units [Cu—O(4) = 2.622 (4) Å] forming infinite layers perpendicular to *a*. The deformation of the coordination octahedron of Cu is more significant in the lengths than in the angles. The average value of four equatorial bonds is 1.99 (3) Å. This value and the axial Cu—O(4) bond length [2.622 (4) Å] agree well with the equatorial bond length *versus* axial bond length curve evaluated for Cu^{II} complexes by Gažo *et al.* (1976). The variety of salicylate ligand bonding is illustrated in Table 3. The separation between the atoms Cu and O(2) [3.194 (5) Å] does not indicate any bonding. The salicylate ligands are therefore bonded to the Cu^{II} atom by only one O atom from the carboxyl group. The remaining carboxyl O atom is non-bonded,

which correlates with the greater B_{eq} value of the O(2) atom compared to that of O(1) (Table 1) and with the somewhat shorter bond length for C(7)—O(2) [1.239 (6) Å] than for C(7)—O(1) [1.284 (6) Å]. Average values of C—C bond lengths and C—C—C bond angles within the salicylate ring (Table 2) are close to values found in [Cu(sal)₂(H₂O)₂].2H₂O [1.38 (2) Å and 120.0 (4)° (Rissanen, Valkonen, Kokkonen & Leskelä, 1987)], and in Cu(sal)₂(2pyMe)₂ [1.373 (1) Å and 119.9 (8)° (Hoang *et al.*, 1992)]. Average values of C—C, N—C bond lengths and N—C—C, C—C—C bond angles of the pyridine rings (Table 2) show good correlation with the values found in Cu(CH₂COO)₂(3-pyMe)₂.CH₂Cl₂ [1.378 (3) Å and 118.5 (3)° (Melník, Smolander & Sharrock, 1985)] and in Cu(sal)₂(2-pyMe)₂ [1.375 (1) Å and 119.7 (3)° (Hoang *et al.*, 1992)]. The salicylate rings are planar ($\chi^2 = 6.14 \text{ Å}^2$); the carboxyl groups are coplanar with the salicylate rings. The pyridine rings are approximately planar ($\chi^2 = 7.81 \text{ Å}^2$) and the O atoms on the methyl groups are displaced from the planes [0.58 (4) Å]. The dihedral angle between the least-squares planes of the salicylate and pyridine rings is 75 (1)°. As shown in Table 3, the salicylate ligands can be bonded to Cu^{II} atoms by O atoms from carboxyl or phenyl groups. The geometrical rigidity of the carboxylate group causes many structures to have only one bonded carboxylate O atom; the second remains non-bonded or has only hydrogen-bonding contacts. In the structures of Cu(sal)₂(2-pyMe)₂ and Cu(sal)₂(3-pyMe)₂ the coordination spheres of the Cu^{II} atoms are completed by O atoms from methanol groups of pyridyl-methanol ligands rather than by the second carboxylate O atoms. But in some cases, where the geometrical arrangements are suitable [for example, binuclear structures of the type Cu₂L₄X₂ (L = ligand having carboxylate group)], both carboxylate O atoms are bonded (Melník *et al.*, 1985).

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55308 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL0524]

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Structure of a One-Dimensional Br-Bridged Pt^{II}–Pt^{IV} Mixed-Valence Complex, *catena*-Poly[bis(ethylenediamine)platinum(II,IV)- μ -bromo bis(hydrogensulfate)]

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Abstract. [Pt^{II}(C₂H₈N₂)₂][Pt^{IV}Br₂(C₂H₈N₂)₂](HSO₄)₄, $M_r = 1178.65$, orthorhombic, *Ibam*, $a = 9.263$ (2), $b = 14.317$ (3), $c = 11.036$ (5) Å, $V = 1463.6$ (8) Å³, $Z = 2$, $D_x = 2.67$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 12.64$ mm⁻¹, $F(000) = 1116$, $T = 296$ K, $R = 0.049$, $wR = 0.079$ for 773 observed reflections [$|F_o| > 3\sigma(|F_o|)$]. The crystal contains columns composed of square-planar [Pt(en)₂]²⁺ and elongated octahedral *trans*-[PtBr₂(en)₂]²⁺ units (en = ethylenediamine) stacked alternately along the *c* axis. The Br ions bridging the adjacent Pt ions are disordered over two sites along the $\cdots\text{Br}-\text{Pt}^{\text{IV}}-\text{Br}\cdots\text{Pt}^{\text{II}}\cdots$ linear chain. The Pt^{IV}–Br and Pt^{II}–Br bonds are 2.474 (3) and 3.044 (4) Å, respectively. The structural parameter $\delta = (\text{Pt}^{\text{IV}}-\text{Br})/(\text{Pt}^{\text{II}}-\text{Br})$ bears a good correlation with

the data of the intervalence charge-transfer (IVCT) absorption edge ($\delta = 0.813$). The hydrogen bonds along the column [N \cdots O = 3.06 (3) and 3.24 (2) Å] and the intercolumn hydrogen bonds [O \cdots O = 3.13 (3) Å] stabilize the structure.

Introduction. The title compound is a one-dimensional halogen-bridged $M^{\text{II}}-M^{\text{IV}}$ mixed-valence complex analogous to Wolfram's Red Salt, [Pt-(C₂H₅NH₂)₄][PtCl₂(C₂H₅NH₂)₄]Cl₄·4H₂O. The compound exhibits an absorption band corresponding to intervalence charge-transfer (IVCT) transition from Pt^{II} to Pt^{IV}. The IVCT absorption edge depending on the mixed-valence state of the Pt ions has a strong relation to the hydrogen-bond network between amines and counter ions (Matsushita, Kojima, Ban & Tsujikawa, 1989*a,b*), and the energy of the IVCT absorption edge in the title compound is larger than

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