0·079 Å from the plane defined by C(1), P(1), P(2). P(1)—Rh(1)—P(2) is 178·9 (1)° and is similar to the 178·6° found in other square-planar complexes, $C_{33}H_{38}F_6P_3Rh$ (Alcock, Brown & Jeffrey, 1977), but greater than that in $[C_{29}H_{28}ClP_2O_2Rh]_2.xCH_2Cl_2$ (Alcock, Brown & Jeffrey, 1977), $C_{33}H_{38}O_5F_6P_3Rh$ (Alcock, Brown & Jeffery, 1976) and $C_{19}H_{34}OP_2Rh$ (Young, 1983), where P—Rh—P angles of 172·9, 165·9, 174·3 and 164·1° are found respectively. Corresponding Rh—P and Rh—C(carbonyl) distances are similar also.

The acac ligand is almost planar. The dihedral angle between its mean plane and that through the distorted square-planar coordinations around Rh is 75·1°. The carbonyl bonds are *trans*, which differs from the acac complexes (I) and (II) above where both carbonyl oxygens have a chelated *cis* configuration within the distorted square-planar configuration around Rh. The Rh—O distances are 2·052 (5) Å in this compound, 2·06 and 2·05 Å in (I) and 2·029 and 2·087 Å in (II). Within the acac ligand, an enolate-type resonance is found, with the coordinated C—O distance being 1·291 (9) Å and intermediate-bond-order backbone C—C bonds of 1·378 (13), 1·423 (13) Å respectively. These are similar to the corresponding values of 1·281 (6), 1·377 (5), 1·379 Å found in (I) and 1·274, 1·275, 1·385, 1·399 Å in (II). The C—O value for the uncoordinated end, however, is much shorter: 1·238 (12) Å, and similar to the value of 1·23 Å for a ketonic C=O bond (*International Table for X-ray Crystallography*, 1962). The pairs of carbonyl oxygens and methyl groups are in *cis* positions relative to the C(2)—C(4)—C(5) backbond. The bulky trisubstituted phosphine ligands are in a *trans* arrangement which minimizes intramolecular steric interactions. Distances and angles within the six chair-shaped cyclohexane groups are normal. There are no unusually short intermolecular distances.

References

Alcock, N. W., Brown, J. M. & Jeffrey, J. C. (1976). *J. Chem. Soc. Dalton Trans.* pp. 583–588.

Alcock, N. W., Brown, J. M. & Jeffrey, J. C. (1977). *J. Chem. Soc. Dalton Trans.* pp. 888–893.

Frenz, B. A. (1982). *Enraf–Nonius Structure Determination Package (SDP) for Utilization on the PDP* 11/60 *Computer.* Enraf–Nonius, Delft.

Huq, F. & Skapski, A. C. (1974). *J. Cryst. Mol. Struct.* **4**, 411–418.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

Leipoldt, J. G., Basson, S. S., Bok, L. D. C. & Gerber, T. I. A. (1978). *Inorg. Chim. Acta*, pp. L35–L37.

Young, D. A. (1983). Private communication.

Acta Cryst. (1986). C**42**, 1518–1520

Structure of (2,2′-Bipyridyl)salicylaldehydatocopper(II) Perchlorate

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Abstract. $[Cu(C_7H_5O_2)(C_{10}H_8N_2)]ClO_4$, $M_r = 440·3$, triclinic, $P\bar{1}$, $a = 8·513$ (5), $b = 9·453$ (8), $c = 11·826$ (6) Å, $\alpha = 77·93$ (5), $\beta = 69·71$ (6), $\gamma = 83·10$ (4)°, $V = 872$ (1) Å^3, $Z = 2$, $D_x = 1·677$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 14·504$ cm^{-1}, $F(000) = 446$, $T = 291$ K. Final $R = 0·051$ for 2381 unique observed reflections. The structure consists of a dimeric unit involving two (2′,2′-bipyridyl)salicylaldehydatocopper(II) cations and two perchlorate anions. The coordination sphere of copper can be described as an elongated octahedron due to the Jahn–Teller effect. The basal plane is formed by the two N atoms of the 2,2′-bipyridyl and by the two O atoms of the salicylaldehydate. Two large apical Cu—O distances are found, one towards the O atom of the perchlorate anion and the other towards the O atom of the nearest salicylaldehyde molecule.

Introduction. Among the ternary complexes containing 3*d* ions, those with copper(II) have been by far the best studied in solution (Sigel, 1973). Some ligand combinations lead to a discriminating behaviour and an

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increasing stability. This is especially pronounced if the mixed-ligand complex is formed by a heteroaromatic N base and an O donor. It has been concluded that the stability of the ternary complex depends on the π-accepting ability of the heteroaromatic N base.

However, relatively little has been done to determine the crystal and molecular structure of ternary complexes (Garland, Le Marouille & Spodine, 1985, 1986). Since (di-2-pyridylamine)salicylaldehydatocopper(II) perchlorate and (di-2-pyridylamine)salicylidineaminatocopper(II) perchlorate have been prepared and their structures determined, we decided to synthesize and characterize the (2,2′-bipyridyl)salicylaldehydatocopper(II) perchlorate, in order to continue the study of the chemical properties of mixed-ligand Cu^{II} complexes. 2,2′-Bipyridyl and di-2-pyridylamine are two heteroaromatic N bases, the latter being a pyridyl moiety with an enhanced electron density on the ring, due to the interaction of the nitrogen lone pair with the π system of the aromatic ring. Therefore the π-acceptor ability should be better in the 2,2′-bipyridyl than the di-2-pyridylamine ligand (Fischer & Sigel, 1979).

Experimental. The mixed copper(II) complex, $[Cu(bp)(sal)]ClO_4$, was prepared similarly to the di-2-pyridylamine salicylaldehydatocopper(II) complex (Garland, Le Marouille & Spodine, 1985). The hydrolysis reaction permits the growth of single crystals of the ternary Cu^{II} complex. The direct reaction with salicylaldehyde gives a green microcrystalline solid. The crystals were identified by microanalysis and an infrared spectrum.

Crystal dimensions: $0{\cdot}24 \times 0{\cdot}19 \times 0{\cdot}12$ mm; Nonius CAD-4 four-circle diffractometer, cell dimensions from high 2θ angles of 25 reflections; 3195 integrated reflections with $\sin\theta/\lambda < 0{\cdot}595$ Å^{-1}, ω–2θ scan, scan width $(1{\cdot}0 + 0{\cdot}35\tan\theta)°$; $0 < h < 10$, $-10 < k < 10$, $-13 < l < 13$; no significant decline in intensities of three standard reflections; decay 3·6% during 46 h of irradiation; absorption and time decay corrections ignored; 2873 unique reflections after averaging ($R_{\rm int} = 0{\cdot}016$); 2381 with $F^2 > 3\sigma(F^2)$; structure solution by *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), full-matrix least squares based on F_o, weights based on counting statistics: $1/w = \sigma^2(F) = \frac{1}{4}\{[\sigma^2(I) + (0{\cdot}06I)^2]/I\}$ (Stout & Jensen, 1968); atomic scattering factors for neutral atoms from *International Tables for X-ray Crystallography* (1974); hydrogen atoms placed at idealized positions and refined with fixed thermal parameters (5 Å^2); anisotropic thermal parameters for all other atoms; $R = 0{\cdot}051$ and $wR = 0{\cdot}065$; goodness of fit $S = 1{\cdot}811$ for 283 refined parameters; $(\Delta/\sigma)_{\rm max} = 0{\cdot}25$; max. $\Delta\rho$ in final map 0·504 e Å^{-3} and a residual peak 1·0 e Å^{-3} found in neighbourhood of the copper atom. All computer programs from Enraf–Nonius *SDP* described by Frenz (1978).

Table 1. *Fractional atomic coordinates and equivalent isotropic B* (Å^2) *with e.s.d.'s in parentheses*

$$B_{\rm eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
Cu	0·51673 (6)	0·39833 (6)	0·89042 (5)	3·30 (1)
Cl	0·7787 (1)	0·1910 (1)	0·6627 (1)	3·60 (2)
O(1)	0·4039 (4)	0·2327 (4)	1·0066 (3)	4·01 (8)
O(2)	0·6678 (4)	0·4052 (3)	0·9755 (3)	3·64 (7)
O(3)	0·7047 (7)	0·1959 (5)	0·7901 (4)	7·7 (1)
O(4)	0·8518 (5)	0·3260 (4)	0·6015 (4)	6·1 (1)
O(5)	0·6526 (5)	0·1682 (6)	0·6173 (4)	8·8 (1)
O(6)	0·8980 (7)	0·0784 (5)	0·6482 (6)	8·7 (2)
N(1)	0·3590 (5)	0·4133 (4)	0·7977 (3)	3·50 (8)
N(2)	0·6168 (4)	0·5621 (4)	0·7583 (3)	3·14 (8)
C(1)	0·2282 (6)	0·3313 (6)	0·8245 (4)	4·2 (1)
C(2)	0·1268 (6)	0·3487 (6)	0·7543 (5)	4·6 (1)
C(3)	0·1578 (6)	0·4563 (7)	0·6526 (5)	4·8 (1)
C(4)	0·2907 (6)	0·5448 (6)	0·6241 (4)	4·3 (1)
C(5)	0·3877 (5)	0·5216 (5)	0·6983 (4)	3·4 (1)
C(6)	0·5337 (5)	0·6085 (5)	0·6774 (4)	3·3 (1)
C(7)	0·5826 (6)	0·7262 (6)	0·5845 (4)	4·3 (1)
C(8)	0·7239 (7)	0·7950 (6)	0·5714 (5)	4·9 (1)
C(9)	0·8112 (6)	0·7455 (6)	0·6518 (5)	4·5 (1)
C(10)	0·7554 (6)	0·6299 (5)	0·7434 (4)	3·8 (1)
C(11)	0·7130 (6)	0·2927 (5)	1·0465 (4)	3·4 (1)
C(12)	0·8590 (6)	0·2985 (6)	1·0754 (5)	4·2 (1)
C(13)	0·9074 (7)	0·1836 (7)	1·1521 (5)	5·3 (1)
C(14)	0·8145 (7)	0·0608 (7)	1·2037 (6)	6·3 (2)
C(15)	0·6704 (7)	0·0518 (6)	1·1792 (5)	5·0 (1)
C(16)	0·6178 (6)	0·1669 (5)	1·0997 (4)	3·5 (1)
C(17)	0·4677 (6)	0·1482 (5)	1·0783 (4)	3·9 (1)

Discussion. Final atomic parameters are given in Table 1,[*] bond distances and angles in Table 2. The atomic numbering is shown in Fig. 1.

The coordination sphere of Cu is N_2O_4-type and can be described as an elongated octahedron. The basal plane is formed by the two N atoms from the 2,2′-bipyridyl and by the two O atoms of the salicylaldehydate, while the apical distance Cu—O provided by the oxygen atom of the perchlorate group is Cu—O(3) = 2·555 (4) Å and the other apical distance Cu—O(2′) is 2·690 (3) Å, compared with the basal Cu–ligand bonds: Cu—N(1) = 1·981 (3), Cu—N(2) = 1·983 (3), Cu—O(1) = 1·948 (3) and Cu—O(2) = 1·897 (3) Å. These values are comparable with those found (Garland, Le Marouille & Spodine, 1985) in (di-2-pyridylamine)salicylaldehydatocopper perchlorate with a slight tendency to be shorter, in agreement with Fischer (Fischer & Sigel, 1979), in the sense that the 2,2′-bipyridyl should be a better π-acceptor ligand than the di-2-pyridylamine. The C—N bonds of the 2,2′-bipyridyl molecule range from 1·339 (5) to 1·357 (5) Å, the corresponding bonds of the di-2-pyridylamine molecule from 1·348 (4) to 1·372 (4) Å. The Cu—O distance that links the two monomeric units

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[*] Lists of structure factors, anisotropic thermal parameters, H-atom parameters and least-squares-planes calculations have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43093 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Intramolecular bond lengths* (Å) *and bond angles* (°) *and selected intermolecular bond lengths* (Å) *with e.s.d's in parentheses*

Cu–O(1)	1·948 (3)	C(4)–C(5)	1·368 (5)
Cu–O(2)	1·897 (2)	C(5)–C(6)	1·489 (5)
Cu–O(3)	2·555 (4)	C(6)–C(7)	1·377 (5)
Cu–N(1)	1·981 (3)	C(7)–C(8)	1·378 (6)
Cu–N(2)	1·983 (3)	C(8)–C(9)	1·374 (6)
Cl–O(3)	1·427 (3)	C(9)–C(10)	1·363 (6)
Cl–O(4)	1·422 (3)	C(11)–C(12)	1·405 (5)
Cl–O(5)	1·408 (3)	C(11)–C(16)	1·422 (5)
Cl–O(6)	1·374 (4)	C(12)–C(13)	1·382 (6)
O(1)–C(17)	1·256 (5)	C(13)–C(14)	1·387 (7)
O(2)–C(11)	1·316 (4)	C(14)–C(15)	1·368 (7)
N(1)–C(1)	1·339 (5)	C(15)–C(16)	1·417 (6)
N(1)–C(5)	1·357 (5)	C(16)–C(17)	1·420 (6)
N(2)–C(6)	1·350 (6)		
N(2)–C(10)	1·348 (5)		
C(1)–C(2)	1·365 (6)		
C(2)–C(3)	1·370 (7)		
C(3)–C(4)	1·389 (6)		

O(1)–Cu–O(2)	93·6 (6)	N(1)–C(5)–C(6)	114·1 (3)
O(1)–Cu–O(3)	81·6 (1)	C(4)–C(5)–C(6)	124·1 (4)
O(1)–Cu–N(1)	91·2 (1)	N(2)–C(6)–C(5)	114·1 (3)
O(1)–Cu–N(2)	172·7 (1)	N(2)–C(6)–C(7)	121·8 (3)
O(2)–Cu–O(3)	89·2 (1)	C(5)–C(6)–C(7)	124·1 (3)
O(2)–Cu–N(1)	174·1 (1)	C(6)–C(7)–C(8)	118·9 (4)
O(2)–Cu–N(2)	93·5 (1)	C(7)–C(8)–C(9)	119·4 (4)
O(3)–Cu–N(1)	94·9 (1)	C(8)–C(9)–C(10)	119·2 (4)
O(3)–Cu–N(2)	96·9 (1)	N(2)–C(10)–C(9)	122·2 (4)
N(1)–Cu–N(2)	81·8 (1)	O(2)–C(11)–C(12)	118·8 (3)
C(1)–N(1)–C(5)	118·1 (3)	O(2)–C(11)–C(16)	123·2 (3)
C(6)–N(2)–C(10)	118·4 (3)	C(12)–C(11)–C(16)	118·0 (4)
N(1)–C(1)–C(2)	122·9 (4)	C(11)–C(12)–C(13)	120·1 (4)
C(1)–C(2)–C(3)	118·9 (4)	C(12)–C(13)–C(14)	121·8 (4)
C(2)–C(3)–C(4)	119·3 (4)	C(13)–C(14)–C(15)	119·9 (5)
C(3)–C(4)–C(5)	119·0 (4)	C(14)–C(15)–C(16)	119·9 (4)
N(1)–C(5)–C(4)	121·8 (4)	C(11)–C(16)–C(15)	120·3 (4)
		C(11)–C(16)–C(17)	123·4 (3)
		C(15)–C(16)–C(17)	116·3 (4)
		O(1)–C(17)–C(16)	126·7 (4)

Cu–O(2^i)	2·690 (3)
O(2)–O(2^i)	3·124 (5)
O(4)–C(4^{ii})	3·252 (5)

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

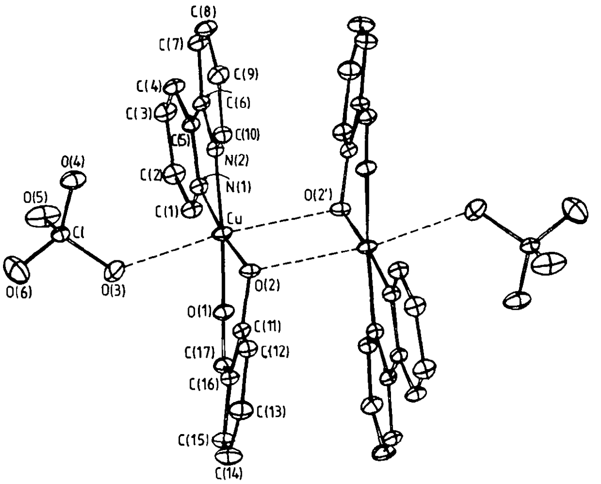

Fig. 1. A perspective view of the molecule with atom numbering; H atoms excluded for clarity.

is longer in this complex; the loss of the amine group induces here a change in the crystalline geometry giving rise to a dimeric molecule with weak intramolecular interaction [2·690 (3) Å in this work instead of 2·436 (2) Å].

The unweighted mean plane through the four donor atoms N(1), N(2), O(1) and O(2) defines a chelating plane. Displacements of the atoms from this mean plane are −0·048, 0·048, 0·044 and −0·044 Å respectively. The copper atom is out of this plane 0·014 Å in the direction of the apical O(3) atom. The dihedral angle between the planes through Cu, O(1), O(2) and through Cu, N(1), N(2) is 4·1°.

The 2,2′-bipyridyl ligand forms a planar five-membered chelate with the Cu atom and deviates from planarity by 0·022 Å. The salicylaldehydato ligand forms a six-membered chelating ring including the Cu atom with larger deviations from the mean plane (−0·160 Å).

The 2,2′-bipyridyl chelate rings deviate from planarity by 0·012 and −0·012 Å respectively and the out-of-plane displacements of Cu from these rings are 0·022 and −0·086 Å. The Cu distance from the mean plane of the benzene ring is 0·465 Å. A comparison of the structural features of the title compound with (di-2-pyridylamine)salicylaldehydatocopper perchlorate shows that the former is in general more planar.

The crystal packing is mainly determined by van der Waals forces between the O atoms of the perchlorate group and the C atoms of the 2,2′-bipyridyl (Table 2).

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References

Fischer, B. E. & Sigel, H. (1979). *Inorg. Chem.* **18**, 425–428.

Frenz, B. A. (1978). *The Enraf–Nonius CAD-4 SDP – A Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Solution.* In *Computing in Crystallography*, edited by H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld & G. C. Bassi. Delft Univ. Press.

Garland, M. T., Le Marouille, J. Y. & Spodine, E. (1985). *Acta Cryst.* C**41**, 855–858.

Garland, M. T., Le Marouille, J. Y. & Spodine, E. (1986). *Acta Cryst.* C**42**, 299–301.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press Press. (Present distributor D. Reidel, Dordrecht.)

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Sigel, H. (1973). *Metal Ions in Biological Systems.* Vol. 2, pp. 62–125. New York: Marcel Dekker.

Stout, G. H. & Jensen, L. H. (1968). In *X-ray Structure Determination.* New York: Macmillan.