

- BRESSAN, M., MORANDINI, F. & RIGO, P. (1983). *Inorg. Chim. Acta*, **77**, L139–L142.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- KILLEAN, R. C. G. & LAWRENCE, J. L. (1969). *Acta Cryst.* **B25**, 1750–1753.
- MCGINNETY, J. A., PAYNE, N. C. & IBERS, J. A. (1969). *J. Am. Chem. Soc.* **91**, 6301–6310.
- NOLTE, M. J., SINGLETON, E. & LAING, M. (1975). *J. Am. Chem. Soc.* **97**, 6396–6400.
- STEPHAN, D. W. (1984). *Inorg. Chem.* **23**, 2207–2210.
- VALENTINE, J. S. (1973). *Chem. Rev.* **73**, 235–245.
- VÁŠKA, L. (1976). *Acc. Chem. Res.* **9**, 175–183.

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Structure of (1,10-Phenanthroline)(salicylaldehydato)copper(II) Nitrate

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Abstract. [Cu(C₇H₅O₂)(C₁₂H₈N₂)]NO₃, $M_r = 426.9$, triclinic, $P\bar{1}$, $a = 11.739$ (3), $b = 9.062$ (2), $c = 8.773$ (2) Å, $\alpha = 95.74$ (2), $\beta = 112.78$ (2), $\gamma = 79.87$ (1)°, $V = 846.5$ (6) Å³, $Z = 2$, $D_x = 1.67$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 1.379$ mm⁻¹, $F(000) = 434$, room temperature. $R = 0.043$ for 2380 observed reflections. The Cu ion displays a distorted square-pyramidal coordination, being linked to two O atoms of the salicylaldehydato and two N atoms of the 1,10-phenanthroline ligand and an O atom of the nitrate group. There is a weak interaction between Cu and an O atom of another salicylaldehydato ligand. The (1,10-phenanthroline)-(salicylaldehydato)copper(II) ion is roughly planar, the phenyl group of the salicylaldehydato ligand deviating most from this plane. Deviations in metal–ligand lengths are due to the different characters of the C–O bonds.

Introduction. The behaviour of mixed-chelate complexes (Griesser & Sigel, 1970) has been of great interest for inorganic and bioinorganic chemists in the last few years because their synthesis is a challenge itself, as is their characterization. A series of compounds of formula $M(\text{N–N})(\text{O–O})$ ($M = \text{Cu}$, $\text{N–N} = o\text{-phenanthroline}$, bipyridine or $\text{substituted phenanthroline}$, $\text{O–O} = \text{salicylaldehydato}$ or acetylacetonato) have been synthesized, characterized and their stability constants determined by potentiometric methods (Gasque, 1984; Ruiz-Ramirez & Gasque,

1986). The title compound is a member of this series of complexes and its crystal structure is determined in order to obtain the ligand arrangement around the Cu ion.

Experimental. Dark-green pinacoids (0.5 × 0.4 × 0.1 mm), Philips PW 1100 diffractometer, Mo $K\alpha$, graphite monochromator, cell parameters from 25 reflections ($4 \leq \theta \leq 12^\circ$), ω -scan technique, scan width 1° , scan speed $0.03^\circ \text{ s}^{-1}$. 2982 independent reflections with $\theta \leq 25^\circ$; 2380 with $I \geq 2.5\sigma(I)$, hkl range -12 to 12 , 0 to 10 , and 0 to 10 . Three standard reflections were measured every 2 h, significant intensity decay was not observed, L_p correction, absorption ignored.

The structure was solved by direct methods (*MULTAN*80, Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Full-matrix least-squares refinements (*SHELX*76, Sheldrick, 1976), $\sum w(|F_o| - |F_c|)^2$ minimized, $w = [\sigma^2(F_o) + 0.004|F_o|^2]^{-1}$, f , f' and f'' from *International Tables for X-ray Crystallography* (1974). An O atom of the NO₃ group was located in a disordered position, an occupancy factor of 0.5 was assigned according to peak heights of Fourier synthesis. All H atoms from $\Delta\rho$ map and refined with an overall isotropic temperature factor, remaining atoms refined anisotropically, final $R = 0.043$ ($wR = 0.048$) for all observed reflections, max. shift/e.s.d. = 0.27 in U_{12} of Cu, max. and min. peaks in final $\Delta\rho$ map 0.4 [1.05 Å away from N(32)] and $-0.3 \text{ e } \text{Å}^{-3}$, respectively; IBM-3082 computer.

Discussion. Atomic coordinates and equivalent isotropic thermal coefficients are given in Table 1. Fig. 1 shows a view of the molecule with the numbering of atoms. The bond distances and angles are listed in Table 2.*

The Cu ion displays a distorted square-pyramidal coordination being linked to two O atoms of the salicylaldehydato and two N atoms of the 1,10-phenanthroline ligand, these four atoms being roughly planar [largest deviation $-0.259(5)$ Å for N(10), distance from Cu atom to mean plane $-0.811(3)$ Å], and an O atom of a nitrate group in the apex site with a large contact distance [$2.402(3)$ Å]. This distance is $2.15(4)$ Å in bis(2,9-dimethyl-1,10-phenanthroline)-nitrate(trichloroacetato)copper(II) trichloroacetic acid solvate (Van Meerssche, Germain, Declercq & Wilputte-Steinert, 1981). The loss of planarity of the Cu ion and the increase in the Cu...ONO₂ length can be explained by a Jahn–Teller effect. The π -bond character of the C(1)–O(1) bond produces a lengthening of the Cu–O(1) bond distance, $1.952(3)$ Å with respect to

$1.898(3)$ Å observed for Cu–O(8). This effect is also observed in bis(salicylaldehydato)copper(II) (McKinnon, Waters & Hall, 1964) where these distances are 1.98 and 1.86 Å, respectively (the different values for

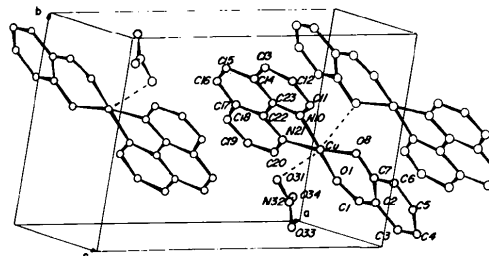


Fig. 1. View of the molecule with the atom-numbering scheme.

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and bond lengths and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43475 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final atomic coordinates ($\times 10^4$, for Cu $\times 10^5$) and equivalent isotropic thermal parameters

$$B_{eq} = \frac{1}{3} \pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	$B_{eq}(\text{Å}^2)$
Cu	87727 (4)	40207 (5)	46940 (5)	2.77 (2)
O(1)	9974 (3)	2394 (3)	5986 (3)	3.2 (1)
C(1)	10674 (4)	1495 (4)	5430 (5)	2.9 (2)
C(2)	10846 (3)	1600 (4)	3945 (5)	2.9 (2)
C(3)	11630 (4)	400 (5)	3503 (6)	3.8 (2)
C(4)	11836 (5)	416 (5)	2089 (6)	4.3 (2)
C(5)	11305 (4)	1637 (5)	1075 (6)	3.9 (2)
C(6)	10580 (4)	2841 (5)	1485 (5)	3.3 (2)
C(7)	10316 (3)	2865 (4)	2913 (5)	2.4 (1)
O(8)	9632 (3)	4042 (3)	3258 (4)	3.4 (1)
N(10)	7517 (3)	5779 (4)	3596 (4)	2.9 (1)
C(11)	7367 (4)	6467 (5)	2270 (5)	3.5 (2)
C(12)	6448 (5)	7677 (6)	1673 (6)	4.5 (2)
C(13)	5646 (4)	8206 (5)	2454 (7)	4.7 (2)
C(14)	5776 (4)	7485 (5)	3868 (6)	3.9 (2)
C(15)	4989 (4)	7890 (6)	4796 (8)	4.8 (2)
C(16)	5150 (5)	7142 (7)	6115 (8)	4.9 (2)
C(17)	6129 (4)	5911 (5)	6688 (6)	3.8 (2)
C(18)	6362 (5)	5044 (6)	8066 (7)	4.5 (2)
C(19)	7333 (5)	3912 (6)	8494 (6)	4.9 (2)
C(20)	8065 (4)	3570 (5)	7564 (5)	3.7 (2)
N(21)	7873 (3)	4330 (4)	6241 (4)	3.0 (1)
C(22)	6905 (4)	5484 (5)	5813 (5)	3.1 (2)
C(23)	6731 (4)	6273 (4)	4391 (5)	3.0 (2)
O(31)	12355 (3)	-1996 (4)	6701 (4)	4.8 (1)
N(32)	12938 (3)	-1941 (4)	8206 (4)	3.6 (1)
O(33)	13689 (4)	-3106 (5)	8816 (5)	6.4 (2)
O(34)	12995 (22)	-866 (27)	9083 (25)	9.4 (9)
O(34')	12552 (23)	-950 (27)	8945 (23)	9.5 (12)

Table 2. Bond lengths (Å) and angles (°)

O(1)–Cu	1.952 (3)	C(13)–C(12)	1.364 (8)
O(8)–Cu	1.898 (3)	C(14)–C(13)	1.403 (7)
N(10)–Cu	2.005 (3)	C(15)–C(14)	1.433 (7)
N(21)–Cu	1.991 (3)	C(23)–C(14)	1.394 (5)
O(31)–Cu	2.402 (3)	C(16)–C(15)	1.333 (8)
Cu–Cu	3.486 (1)	C(17)–C(16)	1.426 (7)
C(1)–O(1)	1.254 (4)	C(18)–C(17)	1.418 (7)
C(2)–C(1)	1.409 (6)	C(22)–C(17)	1.389 (5)
C(3)–C(2)	1.421 (5)	C(19)–C(18)	1.352 (7)
C(7)–C(2)	1.428 (5)	C(20)–C(19)	1.378 (6)
C(4)–C(3)	1.355 (6)	N(21)–C(20)	1.333 (6)
C(5)–C(4)	1.389 (7)	C(22)–N(21)	1.362 (5)
C(6)–C(5)	1.370 (6)	C(23)–C(22)	1.428 (6)
C(7)–C(6)	1.400 (5)	N(32)–O(31)	1.230 (5)
O(8)–C(7)	1.302 (4)	O(33)–N(32)	1.265 (5)
C(11)–N(10)	1.312 (5)	O(34)–N(32)	1.174 (17)
C(23)–N(10)	1.351 (5)	O(34')–N(32)	1.183 (17)
C(12)–C(11)	1.379 (7)	O(34')–O(34)	0.504 (40)
O(8)–Cu–O(1)	93.6 (1)	C(23)–C(14)–C(15)	117.8 (4)
N(10)–Cu–O(1)	173.8 (1)	C(16)–C(15)–C(14)	121.8 (4)
N(10)–Cu–O(8)	91.6 (1)	C(17)–C(16)–C(15)	121.5 (4)
N(21)–Cu–O(1)	91.9 (1)	C(18)–C(17)–C(16)	125.4 (4)
N(21)–Cu–O(8)	171.4 (1)	C(22)–C(17)–C(16)	118.1 (5)
N(21)–Cu–N(10)	82.5 (1)	C(22)–C(17)–C(18)	116.5 (4)
C(1)–O(1)–Cu	122.6 (3)	C(19)–C(18)–C(17)	119.5 (4)
C(2)–C(1)–O(1)	126.9 (4)	C(20)–C(19)–C(18)	120.2 (5)
C(3)–C(2)–C(1)	117.4 (4)	N(21)–C(20)–C(19)	122.7 (4)
C(7)–C(2)–C(1)	123.4 (3)	C(20)–N(21)–Cu	129.9 (3)
C(7)–C(2)–C(3)	119.2 (4)	C(22)–N(21)–Cu	112.7 (3)
C(4)–C(3)–C(2)	120.8 (4)	C(22)–N(21)–C(20)	117.4 (3)
C(5)–C(4)–C(3)	119.9 (4)	N(21)–C(22)–C(17)	123.6 (4)
C(6)–C(5)–C(4)	121.1 (4)	C(23)–C(22)–C(17)	120.6 (4)
C(7)–C(6)–C(5)	121.2 (4)	C(23)–C(22)–N(21)	115.8 (3)
C(6)–C(7)–C(2)	117.7 (3)	C(14)–C(23)–N(10)	122.9 (4)
O(8)–C(7)–C(2)	123.4 (3)	C(22)–C(23)–N(10)	117.1 (3)
O(8)–C(7)–C(6)	118.9 (3)	C(22)–C(23)–C(14)	120.1 (4)
C(7)–O(8)–Cu	123.3 (2)	O(33)–N(32)–O(31)	116.0 (4)
C(11)–N(10)–Cu	129.6 (3)	O(34)–N(32)–O(31)	126.4 (13)
C(23)–N(10)–Cu	111.9 (3)	O(34)–N(32)–O(33)	116.7 (13)
C(23)–N(10)–C(11)	118.4 (3)	O(34')–N(32)–O(31)	115.8 (12)
C(12)–C(11)–N(10)	122.4 (4)	O(34')–N(32)–O(33)	126.3 (12)
C(13)–C(12)–C(11)	120.5 (4)	O(34')–N(32)–O(34)	24.7 (19)
C(14)–C(13)–C(12)	118.4 (4)	O(34')–O(34)–N(32)	78.7 (37)
C(15)–C(14)–C(13)	124.8 (4)	O(34)–O(34')–N(32)	76.6 (35)
C(23)–C(14)–C(13)	117.4 (4)		

the Cu—O bond lengths are explained by the different *trans* atoms). This fact explains the shortening of the Cu—N(21) bond distance [1.991 (3) Å, *trans* to O(8)] with respect to 2.005 (3) Å observed for Cu—N(10) [*trans* O(1)]. The Cu ion is also weakly linked to O(8ⁱ) of another cation [Cu...O(8ⁱ) 2.781 (3) Å, symmetry code: (i) 2-x, 1-y, 1-z], being located at the opposite side from O(31) (Fig. 1).

The salicylaldehydato ligand is not planar. The phenyl ring is planar, with the largest deviation from the mean plane being 0.014 (6) Å; O(8) and O(1) deviate from this phenyl plane by 0.035 (4) and -0.086 (4) Å respectively. The dihedral angle between the phenyl ring and the O(1), O(8), N(10), N(21) plane is 18.6 (3)°. The 1,10-phenanthroline ligand is planar with the dihedral angle between this plane and the O(1), O(8) N(10), N(21) plane equal to 2.8 (3)°.

The mean Cu—N(phenanthroline) distance of 1.998 (7) Å is similar to that of 2.01 (1) Å observed in aqua(1,10-phenanthroline)(thiamine pyrophosphate)-copper(II) dinitrate hydrate (Aoki & Yamasaki, 1980), while it is shorter than those obtained in the *trans*-bis(1,10-phenanthroline)copper(II) complex [mean value 2.05 (1) Å; Boys, Escobar & Martinez-Carrera, 1981].

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References

- AOKI, K. & YAMASAKI, H. (1980). *J. Am. Chem. Soc.* **102**, 6878–6883.
 BOYS, D., ESCOBAR, C. & MARTINEZ-CARRERA, S. (1981). *Acta Cryst.* **B37**, 351–353.
 GASQUE, L. (1984). *Synthesis, Characterization and Stability Constants of Mixed-Chelate Compounds of Cu^{II}*. MSc Thesis, Univ. Nacional Autónoma de México.
 GRIESSER, T. & SIGEL, H. (1970). *Inorg. Chem.* **9**(5), 1238–1253.
International Tables for X-ray Crystallography (1974). Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
 MCKINNON, A. J., WATERS, T. N. & HALL, A. (1964). *J. Chem. Soc.* pp. 3290–3296.
 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.
 RUIZ-RAMÍREZ, L. & GASQUE, L. (1986). In preparation.
 SHELDRIK, G. M. (1976). *SHELX76*. A program for crystal structure determination. Univ. of Cambridge, England.
 VAN MEERSSCHE, M., GERMAIN, G., DECLERCQ, J.-P. & WILPUTTE-STEINERT, L. (1981). *Cryst. Struct. Commun.* **10**, 47–49.

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Structure of Tris(η -methylcyclopentadienyl)(trimethylphosphine)cerium(III)

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Abstract. [Ce(CH₃C₅H₄)₃{P(CH₃)₃}], $M_r = 453.57$, monoclinic, *Cc*, $a = 14.017$ (4), $b = 9.351$ (3), $c = 16.348$ (6) Å, $\beta = 103.92$ (3)°, $V = 2080$ (3) Å³, $Z = 4$, $D_x = 1.448$ (3) g cm⁻³, Mo $K\alpha$, $\lambda(\alpha_1) = 0.70930$ Å, $\mu = 23.0$ cm⁻¹, $F(000) = 916$, $T = 296$ K, $R = 0.024$ for 1232 reflections [$F^2 > \sigma(F^2)$]. The structure consists of Ce centered monomolecular units in which the Ce atom is coordinated in a pentahapto fashion to three cyclopentadiene rings and to the phosphorus atom of the trimethylphosphine molecule. The average Ce—C distance is 2.82 (4) Å and the Ce—P distance is 3.072 (4) Å.

Introduction. Recently we reported the structure of [U(CH₃C₅H₄)₃P(CH₃)₃] (Brennan & Zalkin, 1985) as part of a study of the relative affinity of Lewis bases

toward (CH₃C₅H₄)₃U. A parallel experiment using [Ce(CH₃C₅H₄)₃P(CH₃)₃] is being performed to study what effect a different metal atom has on the molecular structure and chemistry. Interligand contacts influence the ability of a ligand to coordinate to a metal ion and must be considered when comparing ligand basicities. As part of this study we report here the X-ray structure of [Ce(CH₃C₅H₄)₃P(CH₃)₃], which is isomorphous with the uranium complex.

Experimental. Yellow air-sensitive needles of the phosphine complex were prepared by reacting [Ce(CH₃C₅H₄)₃OC₄H₈], isolated from the reaction of CeCl₃ with three equivalents of NaCH₃C₅H₄ in tetrahydrofuran, with P(CH₃)₃ in diethyl ether and crystallizing from diethyl ether at 253 K. Crystals were