of thioxanthene 135·3 (1)°; Gillean, Phelps & Cordes (1973)], only the *trans* dication has been reported (Lee *et al.*, 1980) although a recent reexamination of the ^{13}C NMR spectra of the dication of thioxanthene shows two CH_2 carbon signals. Work on such reactions with folded heterocycles is currently underway.

Coordination by the (η^5-Cp)Fe^{II} moiety results in flattening of phenoxathiin which has a dihedral angle of 147·71 (9)° (Kimura, 1981). In addition, asymmetric C—O bond lengths are observed with the shorter bond being to the C atom of the coordinated ring. The internal angles of the central ring of phenoxathiin increase upon coordination with the C—C—S(O) angles increasing by greater than 3° while the S···O distance increases from 3·049 (2) to 3·212 (3) Å in (2). These changes are consistent with previous results that indicate that electron-withdrawing groups substituted in or on the aromatic ring(s) of phenoxathiins result in a flattening of the molecule together with substantial changes in the geometry of the central ring (Lynch, Simonsen, Martin, Puig-Torres & Smith, 1984). Although the crystal structure of phenoxazine has not been reported, its geometry is expected to be similar to that of dibenzodioxin (where O replaces NH) which is planar (Singh & McKinney, 1978). It would appear that, insofar as the dihedral angle of the molecule is concerned, coordination by (η^5-Cp)Fe^{II} has little effect.

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Structure of Dinitratobis(triphenylphosphine oxide)copper(II) Toluene Solvate (1/1)

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Abstract. $C_{36}H_{30}CuN_2O_8P_2.C_7H_8$, $M_r = 836·27$, monoclinic, $P2_1/c$, $a = 12·933$ (3), $b = 15·532$ (3), $c = 10·285$ (3) Å, $\beta = 100·68$ (3)°, $U = 2030·2$ (9) Å^3, $Z = 2$, $D_x = 1·37$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1·54178$ Å, $\mu = 1·94$ mm^{-1}, $F(000) = 866$, room temperature, final $R = 0·050$ for 1759 unique observed reflections. The Cu atom lies on a symmetry centre and is six coordinated with two *trans* unidentate triphenylphosphine oxide (tppo) ligands and two *trans* bidentate nitrate groups. The nitrate groups are coordinated unsymmetrically. The CuO_6 chromophore has elongated rhombic octahedral stereochemistry in agreement with spectroscopic results.

Introduction. In the course of our studies on the synthesis of chlorobis[1-phenyl-3-(2-pyridyl)thiourea]-Cu^I, obtained by the reaction of the ligand with tetrameric $[Cu(PPh_3)Cl]_4$ and copper(II) nitrate (Belicchi Ferrari, Gasparri Fava, Pelizzi & Tarasconi, 1985) in toluene solution, $[Cu(NO_3)_2(tppo)_2]$ (tppo

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= triphenylphosphine oxide) was also found, as a by-product, in very small yield.

As an extension of our work, it was of interest to determine the crystal structure of this compound with the aim of establishing a correlation with the results of electronic studies, such as electronic and EPR spectra.

Experimental. Green-blue plates, dimensions (mm) 0·03 × 0·13 × 0·29; Siemens AED single-crystal computer-controlled diffractometer; Ni-filtered Cu $K\alpha$ radiation; cell parameters from angular values of 17 reflections ($7{\cdot}0 \leq \theta \leq 62{\cdot}2°$) accurately measured on diffractometer; data collected at room temperature with modified version (Belletti, Ugozzoli, Cantoni & Pasquinelli, 1979) of Lehmann & Larsen (1974) procedure; one check reflection every 50 measurements without significant variation; no correction for absorption; 4220 collected reflections ($2{\cdot}5 \leq \theta \leq 70{\cdot}0°$; $-15 \leq h \leq 15$; $0 \leq k \leq 18$; $0 \leq l \leq 12$), 1855 observed at 2σ level, 1759 unique ($R_{\rm int} = 0{\cdot}028$). Atomic positions of all non-H atoms from Patterson and Fourier syntheses; anisotropic block-matrix least squares with *SHELX76* (Sheldrick, 1976), $\sum(\Delta F)^2$ minimized; H atoms (from ΔF map) isotropic, included in calculations but not refined; final $R = 0{\cdot}050$, $wR = 0{\cdot}056$; no peaks > 0·16 and < $-0{\cdot}16$ e Å^{-3} in last ΔF map; $S = 1{\cdot}74$; unit weights. Max. $(\Delta/\sigma) = 2{\cdot}58$ (for thermal parameter U_{11} of C atom of disordered toluene molecule). Atomic scattering factors from *SHELX76*. Calculations for *SHELX76*, *PARST* (Nardelli, 1983) on the Gould-SEL 77/22 computer of Centro di Studio per la Strutturistica Diffrattometrica del CNR (Parma), those for *PLUTO* (Motherwell, 1976) on the CDC Cyber 76 of CINECA, Casalecchio (Bologna).

Discussion. Final atomic parameters are in Table 1* with Fig. 1 showing the atom numbering. Selected bond distances and angles are in Table 2.

The centrosymmetric CuO_6 chromophore, involving two *trans* nitrate chelate ligands and two *trans* tppo molecules, has elongated rhombic octahedral stereochemistry with a tetragonality T of 0·867† (Hathaway, Duggan, Murphy, Mullane, Power, Walsh & Walsh, 1981).

The nitrate groups are coordinated to the Cu^{II} ion unsymmetrically with Cu—O bond distances of 2·099 (6) and 2·331 (6) Å. This unsymmetrical bidentate coordination is clearly reflected in the N—O bond distances. The strongly bound O(2) atom has an N—O

Table 1. *Fractional atomic coordinates* (×10^4) *with equivalent isotropic thermal parameters for the non-hydrogen atoms, with e.s.d.'s in parentheses*

$B_{\rm eq} = \frac{8}{3}\pi^2 \,\text{trace}\, \tilde{\mathbf{U}}$.

	x	y	z	$B_{\rm eq}$(Å^2)
Cu	0	½	½	3·08 (3)
P	1976 (1)	4567 (1)	3564 (2)	3·13 (5)
O(1)	1349 (3)	4603 (3)	4663 (4)	3·6 (1)
O(2)	513 (4)	4732 (3)	7017 (6)	5·5 (2)
O(3)	965 (5)	5962 (4)	6491 (6)	6·8 (2)
O(4)	1530 (5)	5507 (5)	8441 (6)	8·9 (2)
N	1030 (5)	5398 (5)	7341 (6)	4·2 (2)
C(1)	1427 (5)	3855 (5)	2238 (6)	3·5 (2)
C(2)	1499 (6)	2961 (5)	2488 (7)	4·7 (3)
C(3)	1028 (7)	2398 (5)	1535 (9)	5·6 (3)
C(4)	513 (6)	2665 (6)	332 (8)	5·1 (3)
C(5)	434 (6)	3551 (6)	77 (7)	5·4 (3)
C(6)	900 (6)	4161 (5)	1009 (7)	4·6 (2)
C(7)	3261 (5)	4161 (4)	4267 (7)	3·7 (2)
C(8)	3582 (7)	4145 (7)	5606 (8)	6·9 (3)
C(9)	4585 (9)	3857 (8)	6146 (10)	9·1 (4)
C(10)	5246 (7)	3565 (7)	5402 (12)	6·8 (4)
C(11)	4950 (8)	3581 (8)	4082 (11)	7·9 (4)
C(12)	3954 (7)	3875 (7)	3495 (8)	7·0 (3)
C(13)	2126 (5)	5621 (4)	2894 (6)	3·3 (2)
C(14)	1767 (5)	6333 (4)	3464 (7)	3·7 (2)
C(15)	1877 (6)	7161 (5)	2989 (7)	4·2 (2)
C(16)	2360 (6)	7266 (5)	1880 (8)	4·6 (2)
C(17)	2742 (6)	6551 (6)	1341 (7)	5·0 (3)
C(18)	2621 (6)	5732 (5)	1785 (7)	4·2 (2)
C(19)	5872 (14)	4775 (19)	808 (16)	12·3 (8)
C(20)	5110 (23)	4180 (14)	493 (19)	13·6 (8)
C(21)	4164 (18)	4314 (19)	−374 (22)	13·9 (10)
C(22)	3361 (22)	3764 (20)	−701 (28)	11·3 (12)

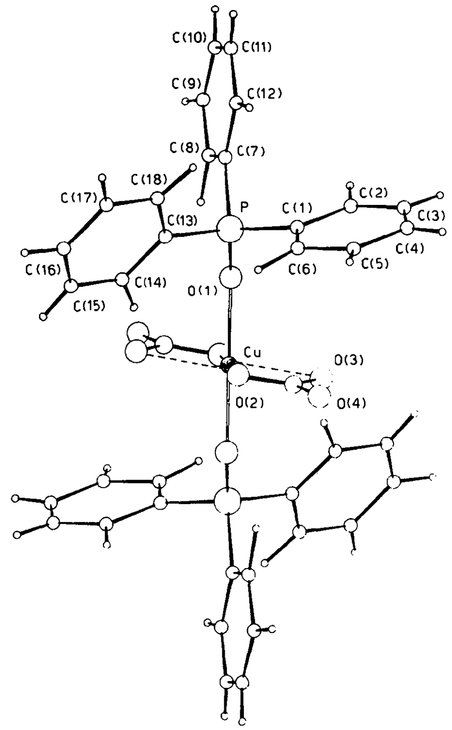

Fig. 1. Molecular structure and numbering scheme for the title compound.

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* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42981 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† T = mean in-plane Cu–L distance/mean out-of-plane Cu–L distance.

distance of 1·243 (9) Å, while weakly bound O(3) has an N—O distance of 1·229 (9) Å. The free atom O(4) has a short N—O distance of 1·206 (8) Å.

The P—O distance of 1·509 (5) Å is somewhat longer than in the free oxide (1·46 Å) (Bandoli, Bortolozzo, Clemente, Croatto & Panattoni, 1970) but similar to that found in other compounds (Ciani, Manassero & Sansoni, 1972; Bertrand & Kalyanaram, 1971).

The Cu—O—P arrangement is bent; the bond angle at the oxygen, of 140·4 (2)°, is less than 150·9 (3)° found for $Cu(tppo)_2Cl_2$ (Bertrand, Graham, Deutsch & VanDerveer, 1976) and 169° for the $Fe(S_2C_4F_6)_2(tppo)^{1-}$ anion (Epstein & Bernal, 1970) and does not differ significantly from that found in trialkylphosphine oxide complexes studied (Cotton & Soderberg, 1963). The P—C distance is 1·799 (7) Å and O—P—C and C—P—C angles are in the range 107–113°. The mean distances and angles of the aromatic rings are normal [1·39 (1); 1·37 (1); 1·39 (1) Å; 120·0 (7), 120·0 (7); 120·6 (7)°].

The structure consists of discrete molecular units of $[Cu(NO_3)_2(tppo)_2]$ and toluene. Cavities centred at $\frac{1}{2},\frac{1}{2},0$ are occupied by toluene molecules, which have a disordered methyl group.

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

Cu—O(1)	1·941 (4)	N—O(4)	1·207 (8)
Cu—O(2)	2·099 (6)	P—O(1)	1·509 (5)
Cu—O(3)	2·331 (6)	P—C(1)	1·797 (7)
N—O(2)	1·243 (9)	P—C(7)	1·799 (6)
N—O(3)	1·229 (9)	P—C(13)	1·801 (7)
O(1)—Cu—O(2)	89·1 (2)	Cu—O(1)—P	140·4 (3)
O(2)—Cu—O(3)	56·2 (2)	O(1)—P—C(1)	113·6 (3)
O(1)—Cu—O(3)	86·1 (2)	O(1)—P—C(7)	107·3 (3)
O(2)—N—O(3)	116·1 (7)	O(1)—P—C(13)	111·3 (3)
O(2)—N—O(4)	122·4 (7)	C(1)—P—C(13)	108·9 (3)
O(3)—N—O(4)	121·4 (8)	C(7)—P—C(13)	108·4 (3)
		C(1)—P—C(7)	107·2 (3)

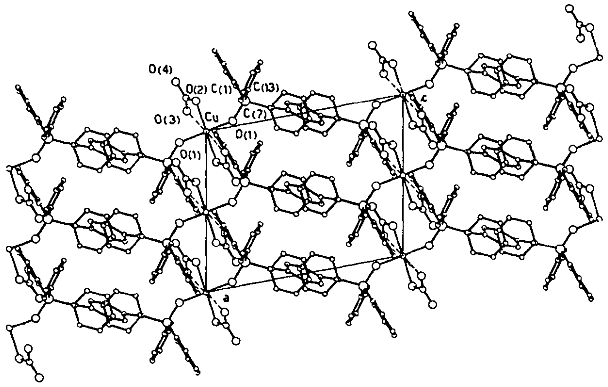

Fig. 2. Unit-cell contents projected down **b**.

The shortest intermolecular distances are between the O and C atoms (Fig. 2) [C(3)···O(2)(x, $\frac{1}{2}-y$, $z-\frac{1}{2}$) = 3·43 (1); C(14)···O(2)(x, $1-y$, $1-z$) = 3·34 (1); C(16)···O(3)(x, $\frac{3}{2}-y$, $z-\frac{1}{2}$) = 3·28 (1); C(19)···O(4)($1-x$, $1-y$, $1-z$) = 3·33 (2) Å] and indicate the presence of weak C···O bonds probably through the H atoms of the corresponding C atoms.

The room-temperature EPR spectrum was recorded on a JEOL PE-3X spectrometer and the spin Hamiltonian parameter values obtained on a polycrystalline sample are in the range expected for similarly distorted octahedral compounds ($g_\perp = 2{\cdot}075$, $g_\parallel = 2{\cdot}349$, $10^4A = 126\ \mathrm{cm}^{-1}$) (Hathaway, 1984). The reflectance electronic spectrum of the solid complex is characterized by a large band at 845 nm while the infrared spectrum obtained using KBr discs shows two strong bands at 1490 and 1280 cm^{-1} attributable to $\nu(NO_3)_{as}$ and $\nu(NO_3)_s$ respectively.

The $\Delta\nu$ (210 cm^{-1}) of asymmetric and symmetric stretching modes of the NO_3 group is in agreement with other IR absorptions reported for bidentate nitrato complexes (Addison, Logan, Wallwork & Garner, 1971; Potts, Sharma, Carty & Walker, 1974). The triphenylphosphine oxide in the complex formation gives rise to a shift (45 cm^{-1}) of the P—O band active in IR to lower values with respect to the stretching frequency of the free ligand [ν(P—O) = 1185 cm^{-1}] (Cotton, Barnes & Bannister, 1960). From these analyses, the results agree well with the X-ray data for the presence of a CuO_6 chromophore in an elongated octahedral structure, showing good correlation between structure and spectroscopic properties.

The $[Cu(NO_3)_2(tppo)_2]$ complex has also been studied by X-ray K-absorption-edge spectrometry (Prasad, Shah & Srivastava, 1982). The average metal–ligand bond distance calculated from these measurements (1·93 Å) is shorter than the mean value of the Cu—O distances (2·124 Å) of the present work. Moreover, the coordination stoichiometry (1:4) related to edge-widths does not correspond well to the structural data (1:6).

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Structure of *N,N'*-Ethylenebis(salicylideneiminato)manganese(III) Chloride Acetonitrile Solvate

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Abstract. $Mn[C_{16}H_{14}N_2O_2]Cl.CH_3CN$, $M_r = 397\cdot7$, monoclinic, $P2_1/n$, $a = 10\cdot415$ (7), $b = 12\cdot671$ (8), $c = 13\cdot184$ (8) Å, $\beta = 96\cdot56$ (5)°, $V = 1728$ (1) Å^3, $Z = 4$, $D_x = 1\cdot529$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0\cdot7107$ Å, $\mu = 9\cdot05$ cm^{-1}, $F(000) = 816$, $T = 300$ K, $R = 0\cdot033$, $wR = 0\cdot033$ for 1791 unique reflections with $(I) > 3\sigma(I)$. The title Mn^{III}(salen)Cl complex displays a square-pyramidal geometry similar to that of Fe^{III}(salen)Cl. The bond lengths for atoms in the manganese coordination sphere are Mn(1)—O(1), 1·878; Mn(1)—O(2), 1·906; Mn(1)—N(1), 1·981; Mn(1)—N(2), 1·993; Mn(1)—Cl(1), 2·461 Å. Important angles described by the five atoms bound to Mn(1) are O(1)—Mn(1)—Cl(1), 98·7; O(2)—Mn(1)—Cl(1), 97·2; N(1)—Mn(1)—Cl(1), 94·8; O(1)—Mn(1)—N(1), 92·2; O(1)—Mn(1)—N(2), 168·6; N(2)—Mn(1)—Cl(1), 91·4; O(1)—Mn(1)—O(2), 94·8; O(2)—Mn(1)—N(1), 165·1; O(2)—Mn(1)—N(2), 89·1; N(1)—Mn(1)—N(2), 81·6°. The Mn ion lies 0·19 Å above an equatorial plane consisting of two phenolate O and two imine N atoms. This manganese out-of-plane displacement is unusually short for five-coordinate Schiff-base or porphyrin complexes. A detailed structural comparison of the Mn(salen)Cl molecule with Mn(acen)Cl [acen = *N,N'*-ethylenebis(acetylacetone imine)], *M*(tpp)Cl (*M*=Mn^{3+}, Fe^{3+}; tpp = tetraphenylporphyrin), Fe(salenCl and Mn(salen)acetate proves useful toward understanding the apparently disparate chemistry between Mn^{3+} and Fe^{3+} salen complexes. The Mn ions of adjacent Mn(salen)Cl molecules are within 3·5 Å, but do not interact.

Introduction. Study of the coordination chemistry of manganese has undergone a renaissance over the past five years due in part to the increased recognition of this element's role in biological systems. There does not appear to be a single structural type for the manganese center(s) in manganoenzymes. Indeed, the known variations already range from the mononuclear sites in a superoxide dismutase (Weisiger & Fridovich, 1973) and a sweet potato acid phosphatase (Sugiura, Kawabe, Tanaka, Fujimoto & Ohara, 1981) to the proposed multinuclear center of the thylakoid-membrane-associated oxygen-evolving complex of photosystem II (Dismukes & Siderer, 1981). Unfortunately, the chemistry of manganese in the catalytically relevant 3+ and 4+ oxidation states is less well developed than for the Mn^{2+} ion, with structural data available for only a handful of Mn^{III} compounds.

Mn^{III} Schiff-base complexes are among the simplest models for the active sites of manganoenzymes. Metal complexes of the Schiff-base ligand *N,N'*-bis(salicylideneiminato)ethylene (salen) have been extensively studied (Hobday & Smith, 1972/1973) and have been shown to adopt three main structural types. These are mononuclear (Gerloch & Mabbs, 1967*a*) *M*(salen)*X* (where *X* = halide), binuclear (Gerloch & Mabbs, 1967*b*) *M*(salen)$_2$ and bridged binuclear (Lewis, Mabbs & Richards, 1967) *M*(salen)$_2$O. The complexes of Mn^{III}(salen)*X* (*X* = I,Br,Cl) have been prepared and are soluble in aqueous and methanolic solutions. In contrast, Fe(salen)*X* has low solubility in water or methanol (Gerloch, Lewis, Mabbs & Richards, 1968). Furthermore, while Fe(salen)*X* reacts rapidly with base

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