as: relative intensity $\delta(^{11}\text{B})$ (p.p.m.) $\{\delta(^{1}\text{H})$ (p.p.m.) $[^{1}J(^{11}\text{B}–^{1}\text{H})/\text{Hz}]\}$: 1BH $+6{\cdot}0$ $[+3{\cdot}55\,(144)]$; 1BH $+3{\cdot}6$ $[+2{\cdot}64\,(144)]$; 2BH *ca* $-5{\cdot}3$ $[+2{\cdot}43$ (not resolved)]; 2BH $-6{\cdot}1$ $[+2{\cdot}04\,(139)]$; 2BH $-16{\cdot}7$ $[+1{\cdot}55\,(\geq ca\ 158)]$; 1BH $-21{\cdot}2$ $[+1{\cdot}60$ (not resolved)]; 2CH $-[+3{\cdot}19\,(—)]$. 1HCS$_2$ $-\{+11{\cdot}42\,[^{3}J(^{103}\text{Rh}–^{1}\text{H})$ and $^{4}J(^{31}\text{P}–^{1}\text{H})$ 7·3 and 3·8 Hz]}. These data are entirely consistent with the structure derived from our X-ray study, confirming that the crystal selected for the X-ray analysis was indeed representative of the bulk sample.

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Tetraaqua-μ_4-(phenylenediaminetetracetato-O^1:O^2:O^3,O^4,N:O^5,O^6,N^1)-dicopper(II) Dihydrate

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Abstract. $[\text{Cu}(\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_8)(\text{H}_2\text{O})_4].2\text{H}_2\text{O}$, $M_r = 571{\cdot}45$, orthorhombic, *Pnab*, $a = 10{\cdot}020\,(1)$, $b = 12{\cdot}065\,(1)$, $c = 16{\cdot}589\,(1)$ Å, $V = 2005{\cdot}3\,(2)$ Å^3, $D_x = 1{\cdot}893$ g cm^{-3}, $Z = 4$, $F(000) = 1168$, $\lambda(\text{Cu}\ K\alpha) = 1{\cdot}54178$ Å, $\mu = 32{\cdot}92$ cm^{-1}. Room temperature. Final $R = 0{\cdot}06$ for 1549 unique observed reflections. The Cu ions have a highly distorted octahedral coordination geometry, with the *p*-phenylenediamine-*N*,*N*,*N*′,*N*′-tetraacetic (*p*-phdta) ligand and the O*W*1 water molecule at the vertices of the square and the O*W*2 water molecule and the O11 (through symmetry operation $x+\frac{1}{2}$, $-y$, z) occupying the apical positions. The conformations of the five-membered chelate rings appear to depend on hydrogen bonding and van der Waals interactions.

Introduction. The behaviour of aromatic diamines as coordinating agents depends on the relative positions of N atoms in the aromatic ring. Thus, for derivatives of *o*-phenylenediamine, the two vicinal nitrogens may become coordinated to the same metallic cation, in a single sphere of coordination, as has been established for the complexes of *o*-phenylenediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid with Co$^{\text{II}}$ (McCandlish, Michael, Neal, Lingafelter & Rose, 1978), Mn$^{\text{II}}$ (Nakasuka, Azuma, Katayama,

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

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Cu1	−0·00480 (9)	0·12933 (7)	0·22359 (5)	0·0370 (3)
N4	−0·0935 (5)	0·1620 (4)	0·1129 (3)	0·020 (1)
O7	0·1614 (5)	0·3686 (4)	0·0966 (3)	0·040 (2)
O8	0·1381 (4)	0·2214 (4)	0·1787 (3)	0·029 (1)
O9	−0·1699 (4)	0·0482 (3)	0·2439 (3)	0·029 (1)
O11	−0·3851 (5)	0·0453 (4)	0·2061 (3)	0·037 (2)
C1	0·1021 (6)	0·0245 (5)	−0·0532 (4)	0·026 (2)
C2	0·0567 (6)	0·1044 (5)	0·0003 (4)	0·024 (2)
C3	−0·0476 (6)	0·0809 (5)	0·0546 (3)	0·020 (2)
C5	−0·0471 (6)	0·2771 (5)	0·0964 (4)	0·026 (2)
C6	0·0981 (7)	0·2910 (5)	0·1255 (4)	0·029 (2)
C10	−0·2673 (7)	0·0756 (5)	0·1981 (4)	0·027 (2)
C12	−0·2393 (6)	0·1551 (5)	0·1298 (4)	0·026 (2)
O*W*1	0·0911 (5)	0·1018 (5)	0·3279 (3)	0·034 (2)
O*W*2	−0·0933 (5)	0·2844 (4)	0·2837 (3)	0·045 (2)
O*W*3	0·4070 (5)	0·4477 (5)	0·0618 (3)	0·052 (2)

Table 2. *Bond distances* (Å), *bond angles* (°) *and selected torsion angles* (°) *with e.s.d.'s in parentheses*

Cu1—O8	1·959 (4)	Cu1—O9	1·951 (4)
Cu1—N4	2·078 (5)	Cu1—O*W*1	2·007 (5)
Cu1—O*W*2	2·298 (5)	Cu1—O11*	2·442 (5)
O8—C6	1·283 (8)	C9—O9	1·280 (8)
N4—C3	1·451 (7)	N4—C5	1·490 (8)
N4—C12	1·490 (8)	O7—C6	1·228 (8)
O11—C10	1·243 (8)	C1—C3	1·408 (8)
C1—C2	1·387 (8)	C5—C6	1·541 (9)
C10—C12	1·510 (9)		
O*W*1—Cu1—O*W*2	86·9 (2)	N4—Cu1—O*W*2	93·7 (2)
N4—Cu1—O*W*1	176·6 (2)	O9—Cu1—O*W*2	90·7 (2)
O9—Cu1—O*W*1	100·0 (2)	O9—Cu1—N4	83·4 (2)
O8—Cu1—O*W*2	89·1 (2)	O8—Cu1—O*W*1	94·1 (2)
O8—Cu1—N4	82·5 (2)	O8—Cu1—O9	165·8 (2)
O*W*2—Cu1—O11*	160·7 (2)	O*W*1—Cu1—O11*	74·0 (2)
N4—Cu1—O11*	105·6 (2)	O9—Cu1—O11*	90·2 (2)
O8—Cu1—O11*	94·9 (2)	Cu1—O8—C6	113·9 (4)
Cu1—O9—C10	114·5 (4)	Cu1—N4—C12	104·0 (4)
Cu1—N4—C5	101·9 (4)	Cu1—N4—C3	109·0 (4)
C5—N4—C12	113·2 (4)	C3—N4—C12	113·5 (5)
C3—N4—C5	114·0 (5)	N4—C3—C2	121·7 (5)
C3—C2—C1	120·9 (5)	N4—C5—C6	109·8 (5)
O7—C6—C5	116·6 (5)	O8—C6—C5	116·1 (5)
O8—C6—O7	127·3 (6)	N4—C12—C10	111·0 (5)
O10—C10—C12	116·3 (6)	O9—C10—C12	117·9 (6)
O8—Cu1—N4—C5	−34·5 (3)	O9—Cu1—N4—C12	26·3 (3)
N4—Cu1—O8—C6	26·2 (4)	N4—Cu1—O9—C10	−19·5 (4)
Cu1—O8—C6—C5	−9·8 (7)	Cu1—O9—C10—C12	6·8 (7)
N4—C5—C6—O8	−21·3 (7)	N4—C12—C10—O9	17·0 (8)
Cu1—N4—C5—C6	37·6 (5)	Cu1—N4—C12—C10	−29·2 (5)

Honda, Tanaka & Tanaka, 1985), Zn^{II} (Azuma, Nakasuka & Tanaka, 1986) and Cu^{II} (Nakasuka, Azuma & Tanaka, 1986).

For *m*- and *p*-phenylenediamine derivatives, the participation of both (1,3 or 1,4) N atoms in the same sphere of coordination seems to be precluded by the greater distance between them. These ligands can, therefore, coordinate in two spheres and are potentially tridentate. This is in accordance with our studies in aqueous solution of the coordinating capacity of *m*- and *p*-phenylenediamine-*N*,*N*,*N*,*N*′-tetraacetic acid with Cu^{II} (Mederos, Felipe, Brito & Bazdikian, 1986) and with the structure of the title compound, described in this work.

Experimental. The compound was synthesized by the liquid–liquid diffusion reaction between aqueous solutions of Cu(NO$_3$)$_2$.6H$_2$O and (*p*-phdta)Na$_2$.H$_2$O (2:1 ratio). Green crystals of [Cu$_2$(*p*-phdta)(H$_2$O)$_4$].2H$_2$O were formed directly at the interphase between the two solutions. Crystal used for data collection had dimensions 0·2 × 0·4 × 0·7 mm.

Data were collected with a Siemens AED diffractometer using graphite-monochromated Cu $K\alpha$ radiation. Lattice parameters and their e.s.d.'s were derived from the setting angles of 19 reflections with $3 < 2\theta < 40°$. Intensity data for 1615 reflections (h 0:12, k 0:14, l 0:19; $2 < 2\theta < 128°$) were collected in the ω/θ scan mode. 1615 unique, 1548 observed [$I > 3\sigma(I)$]. Two reference reflections (024, 123) measured every hour showed no significant decrease during the exposure. The intensity data were corrected for Lp and, after isotropic refinement, for absorption (correction range 0·855 to 1·731) with *DIFABS* (Walker & Stuart, 1983). The space group was derived from the systematic absences. Structure solved by Patterson method (*SHELXS*86; Sheldrick, 1986) followed by Fourier synthesis (*SHELX*76; Sheldrick, 1976). The centre of the benzene ring is at the centre of symmetry. Refinement by full-matrix least squares (*XRAY*80; Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1980), anisotropic thermal parameters for all non-H atoms. After this refinement all H atoms, except those of the water molecules, which could not be found, were located from a ΔF map and were included in the refinement with fixed positional parameters and isotropic temperature factors. $\sum(F_o - F_c)$ minimized, unit weights. Scattering factors and anomalous-dispersion terms

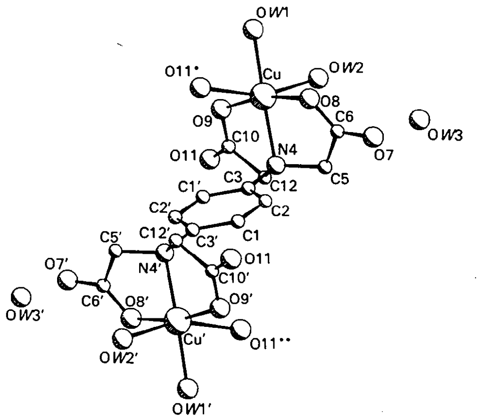

Fig. 1. Structure of the complex showing atomic numbering scheme. Symmetry codes: * ($x + \frac{1}{2}$, $-y$, z); ** ($-x - \frac{1}{2}$, y, $-z$).

from *International Tables for X-ray Crystallography* (1974). Final R was 0·06. The ratio of maximum least-squares shift to e.s.d. in final refinement cycle was 0·009, maximum electron density in final difference Fourier synthesis was 0·62 e Å^{-3}.

Discussion. Final parameters are shown in Table 1.* The molecular structure of the complex including the atomic numbering scheme is illustrated in Fig. 1. Associated bond parameters for the structure and selected torsion angles are present in Table 2.

The Cu atoms have a highly distorted octahedral coordination geometry with the *p*-phdta ligand and the O*W*1 water molecule at the vertices of the square and the O*W*2 water molecule and the O11 (through the symmetry operation $x+\frac{1}{2}, -y, z$) occupying the apical positions. The Cu···O11($x+\frac{1}{2}, -y, z$) bond distance is 2·442 (5) Å and the angle O(O*W*2)···Cu^{II}···O11($x+\frac{1}{2}, -y, z$) is 160·7 (2)°. The Cu^{II} −O*W*2 and the Cu^{II} −O11($x+\frac{1}{2}, -y, z$) axial bonds are, respectively, 0·33 and 0·47 Å longer than the average Cu^{II}—O in-plane bond length, owing to the Jahn–Teller effect. The Cu^{II}—O*W*1 bond distance, 2·007 Å, *trans* to N4, is shorter than those observed for Cu—O*W*2, 2·298 (5) Å. The Cu—N bond length, 2·078 (5) Å, compares well with that observed in methylenetriaminepentaacetate cuprate(II) monohydrate (Seccombe, Lee & Henry, 1975) [average 2·049 (2) Å]. The Cu—O—C—C—N five-membered chelate rings have envelope conformations with the common N atom (N4) out of plane.

The hydrate water molecule (O*W*3) participates in intermolecular hydrogen bonds: O*W*3···O7 (x, y, z) 2·702 (5) Å and O*W*3···O*W*1 ($x-\frac{1}{2}, -y+\frac{1}{2}, -z+\frac{1}{2}$) 2·666 (5) Å. The O*W*2 is hydrogen bonded: O*W*2···O8 ($x+\frac{1}{2}, -y+\frac{1}{2}, -z+\frac{1}{2}$) 2·764 (5) Å.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52759 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of Tetraphenylphosphonium Tetracyanooxo[*N*-*o*-tolylhydroxylaminato-(2−)-*O*,*N*]molybdate(VI)

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Abstract. $[P(C_6H_5)_4]_2[Mo(CN)_4(O)(C_7H_7NO)]$, M_r = 1016, monoclinic, $P2_1/n$, a = 11·332 (4), b = 13·698 (4), c = 36·06 (1) Å, β = 92·04 (5)°, V = 5594 (6) Å^3, Z = 4, D_x = 1·21 g cm^{-3}, $F(000)$ = 2096, Mo $K\alpha$, λ = 0·71069 Å, μ = 3·26 cm^{-1}, T = 293 K, R = 0·085 for 1743 unique diffractometer data with $I > 3\sigma(I)$. The seven-coordinate metal structure is compared to diverse oxo–peroxo or oxaziridine Mo complexes. Crystals of the title compound are composed of $[Mo(CN)_4(O)(C_7H_7NO)]^{2-}$ anions and $[P(C_6H_5)_4]^+$ cations, packed without any remarkable features.

Introduction. Transition-metal-catalyzed reduction of nitric oxide (NO) is important for industrial applications (*Ullmanns Encyklopädie der Technischen Chemie*, 1981) such as exhaust-gas treatment as well as for understanding enzymatic reactions (Hughes,

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