Discussion. Eight-coordinate molecules generally fall into three idealized geometries, the D_{2d} dodecahedron, C_{2v} bicapped trigonal prism, and D_{4h} square antiprism (Hoard & Silverton, 1963; Kepert, 1978, 1982). A convenient way to illustrate the distortion from an idealized geometry is by the shape parameters δ' and φ (Porai-Koshits & Aslanov, 1972; Muetterties & Guggenberger, 1974), where δ' is the angle of intersection of the triangular faces along the line connecting the *AA* and *BB* sites in a dodecahedron and φ is the dihedral angle between two triangles constructed from the *BAAB* trapezoidal atoms. As shown in Table 3, the title compound is best described as a dodecahedron with the nitrogen atoms on the *A* sites and the chloride ligands on the B sites.

The average U—Cl bond length of 2·609 (9) Å is shorter than that found in other eight-coordinate structures: *e.g.* $[UCl_4(NCCH_3)_4]$ 2·623 (2) Å (Cotton, Marler & Schwotzer, 1984);* $[UCl_2\{(OC_6H_4)C(OH)NCH_2CH_2NC(OH)(C_6H_4O)\}(OC_4H_4)_2]$ 2·67 (2) Å (Calderazzo, Floriani, Pasquali, Cesari & Perego, 1976); $[UCl_2\{OS(CH_3)_2\}_6]^{2+}$ 2·70 (2) Å (Bombieri & Bagnall, 1975); UCl_4 2·869 (3) and 2·638 (4) Å (Taylor & Wilson, 1973). The average U—N distance of 2·79 (2) Å is substantially longer than the equivalent distance in $[UCl_4(NCCH_3)_4]$ of 2·589 (6) Å (Cotton, Marler & Schwotzer, 1984) and substantially longer than expected based upon the averaged U—P distance in (I) of 3·104 (6) Å (Edwards, Andersen & Zalkin, 1983) since the tetrahedral covalent radius of phosphorus is 0·40 Å longer than nitrogen (Pauling, 1960). The longer than expected U—N bond distance is most reasonably ascribed to intramolecular steric repulsions between the methyl groups on the nitrogen atoms and the chloride ligands since each chloride ligand has four C···Cl contact distances of *ca* 3·4 Å, close to the sum of the van der Waals radii of these two atoms (Pauling, 1960). Hence a shorter U—N bond would cause substantial atom–atom repulsions and the structure is a compromise between attractive (U—N, U—Cl) and repulsive (C···Cl) forces.

Table 3. *Shape parameters*

	δ' (°)	φ (°)
$[UCl_4\{(CH_3)_2NCH_2CH_2N(CH_3)_2\}_2]$	20·4, 21·9, 38·7, 39·6	1·6
D_{2d} dodecahedron	29·5, 29·5, 29·5, 29·5	0·0
C_{2v} bicapped trigonal prism	0·0, 21·8, 48·2, 48·2	14·1
D_{4h} square antiprism	0·0, 0·0, 52·4, 52·4	24·5

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* *Note added in proof:* see also preceding paper.

Acta Cryst. (1986). C**42**, 1482–1485

Structure of Sodium (*o*-Phenylenediamine-*N*,*N*,*N'*,*N'*-tetraacetato)cuprate(II)

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Abstract. $Na_2[Cu(C_{14}H_{12}N_2O_8)].4H_2O$, $M_r = 517·84$, monoclinic, $P2_1/n$, $a = 24·493$ (5), $b = 8·222$ (1), $c = 9·805$ (1) Å, $\beta = 90·43$ (1)°, $V = 1974·5$ (5) Å^3, $Z = 4$, $D_m = 1·75$, $D_x = 1·74$ g cm^{-3}, $\lambda(Cu\ K\alpha) = 1·5417$ Å, $\mu = 24·3$ cm^{-1}, $F(000) = 1060$, $T = 293$ K. Final $R = 0·033$ for 3143 observed reflections. The ligand is hexadentate. The coordination geometry is largely distorted from O_h and twisted towards that of a trigonal prism, owing to the planarity of the phenylenediamine chelate ring. Two Cu—N bond

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lengths are 2·253 (1) and 2·266 (2) Å, about 0·2 Å longer than those of the corresponding edta complex. This may result from reduced basicity of the nitrogen atoms and from the rigid configuration of the phenylenediamine moiety of the hexadentate ligand.

Introduction. The hexadentate ligand of the title complex, *o*-phenylenediamine-*N*,*N*,*N'*,*N'*-tetraacetato (phdta), can be derived by substitution of the phenylene group for the ethylenic backbone in ethylenediaminetetraacetic acid (H_4edta). The substitution lowers the basicity of the N atoms considerably (Grimes, Huggard & Wilford, 1963; Nakasuka, Kunimatsu, Matsumura & Tanaka, 1985) and significantly distorts the structural configuration of the corresponding metal complexes from O_h (McCandlish, Michael, Neal, Lingafelter & Rose, 1978; Azuma, Nakasuka & Tanaka, 1986). Copper(II)–edta complexes show a variety of crystal structures in the solid state. CaCu(edta) consists of infinite chains with hexacoordinate Cu^{II} ions bridged by a carboxylate O and an amino N (Nesterova, Porai-Koshits & Logvinenko, 1979; Nesterova & Porai-Koshits, 1984). Dimeric chelate Cu_2(edta) contains tetracoordinate Cu^{II} ions of planar configuration (Filippova, Polynova, Porai-Koshits, Novozhilova & Martynenko, 1973). The Cu^{II} ion is hexacoordinate in Mn[Cu(edta)] (Solans, Font-Altaba, Oliva & Herrera, 1983) and K_2[Cu(edta)] (Porai-Koshits, Novozhilova, Polynova, Filippova & Martynenko, 1973), though the coordination geometry is distorted from an octahedral configuration. The diprotonated complex [Cu(H_2edta)(H_2O)] shows only a slight distortion from O_h, because H_2edta acts as a pentadentate ligand (Stephens, 1969). The same situation has also been found for K_2[Zn(phdta)] and [Zn(H_2phdta)(H_2O)] (Azuma, Nakasuka & Tanaka, 1986). The coordination geometry of the present complex will also be much deformed because phdta may act as a hexadentate ligand.

Experimental. Crystal prepared by half-neutralization of aqueous H_4phdta with NaOH, followed by addition of copper(II) acetate and then of ethanol. Well-formed, transparent blue crystal 0·23 × 0·23 × 0·20 mm. Elemental analysis: calcd for $C_{14}H_{20}N_2O_{12}Na_2Cu$: C 32·47, N 5·41, H 3·89, Na 8·88, Cu 12·27%; found: C 32·69, N 5·01, H 3·79, Na 8·9 (flame photometry), Cu 12·25% (chelatometry). D_m by flotation in C_6H_{12}/$C_2H_4Br_2$. Rigaku AFC-5A automated four-circle diffractometer. Cell dimensions from 20 selected reflections with $30·0 < \theta < 30·2°$. Total of 3797 reflections measured, $2\theta_{max} = 126°$, $-28 \leq h \leq 28$, $0 \leq k \leq 10$, $0 \leq l \leq 11$, $R_{int} = 0·015$. Three standard reflections after every 100 reflections, no variation in intensity. Structure solved by the Monte Carlo direct method (Furusaki, 1979) with the aid of *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) using 3143 non-zero unique reflections $[I > 3\sigma(I)]$, refined on F^2 by full-matrix least-squares program with an analytical absorption correction (Katayama, Sakabe & Sakabe, 1972). Transmission factors 0·57 to 0·61. Non-H atoms refined anisotropically. All H atoms located from difference synthesis and refined with isotropic temperature factors equivalent to those for bonded atoms. $R = 0·033$, $wR = 0·039$, $S = 2·18$, $w = 1/\sigma^2(F^2)$, $(\Delta/\sigma)_{max} = 0·14$ for *x* of C(10) and O(22), $\Delta\rho_{max} = 0·39$ e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Calculations made on a FACOM 382 computer at the Computation Center, Nagoya University.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters*

$$B_{eq} = \tfrac{8}{3}\pi^2 \textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j.$$

	x	*y*	*z*	B_{eq}(Å^2)
Cu(1)	0·37267 (1)	0·67675 (3)	0·75761 (3)	1·586 (9)
Na(2)	0·32442 (3)	0·06937 (11)	1·11578 (9)	2·60 (1)
Na(3)	0·28522 (4)	0·85508 (14)	0·50692 (10)	3·54 (2)
C(10)	0·49635 (7)	0·59782 (24)	0·77566 (18)	1·61 (3)
C(20)	0·47370 (8)	0·44994 (23)	0·73401 (18)	1·67 (3)
C(30)	0·50823 (9)	0·31994 (25)	0·70467 (21)	2·32 (4)
C(40)	0·56437 (9)	0·33335 (29)	0·72359 (22)	2·64 (4)
C(50)	0·58648 (9)	0·47774 (32)	0·77148 (22)	2·63 (4)
C(60)	0·55302 (8)	0·60998 (27)	0·79574 (21)	2·21 (4)
N(10)	0·46138 (6)	0·73735 (19)	0·79305 (16)	1·60 (3)
C(11)	0·46139 (8)	0·80040 (25)	0·93381 (20)	2·02 (4)
C(12)	0·41157 (8)	0·90896 (24)	0·95799 (20)	1·93 (4)
O(11)	0·37093 (6)	0·89185 (19)	0·87701 (16)	2·37 (3)
O(12)	0·41355 (6)	1·00460 (20)	1·05534 (17)	2·88 (3)
C(31)	0·47213 (8)	0·86640 (25)	0·69169 (22)	2·26 (4)
C(32)	0·42546 (8)	0·89490 (24)	0·58991 (20)	1·91 (4)
O(31)	0·38351 (6)	0·80241 (18)	0·59414 (14)	2·19 (2)
O(32)	0·43135 (6)	1·00521 (21)	0·50639 (17)	2·96 (3)
N(20)	0·41470 (6)	0·43519 (20)	0·72168 (16)	1·75 (3)
C(21)	0·39690 (9)	0·39378 (27)	0·58225 (21)	2·32 (4)
C(22)	0·33724 (8)	0·43976 (24)	0·55692 (20)	2·05 (4)
O(21)	0·31554 (6)	0·54493 (19)	0·63195 (15)	2·39 (3)
O(22)	0·31427 (7)	0·37279 (20)	0·45674 (18)	2·91 (3)
C(41)	0·39076 (9)	0·32602 (25)	0·82599 (23)	2·36 (4)
C(42)	0·34852 (8)	0·40849 (26)	0·91742 (20)	2·09 (4)
O(41)	0·34574 (6)	0·56327 (18)	0·91524 (15)	2·41 (3)
O(42)	0·32043 (7)	0·32197 (21)	0·99207 (19)	3·20 (4)
O(1)	0·28223 (9)	0·99168 (37)	0·71162 (23)	5·14 (6)
O(2)	0·26834 (7)	0·65502 (22)	0·34188 (17)	2·64 (3)
O(3)	0·70848 (7)	0·21366 (23)	0·90685 (17)	3·00 (4)
O(4)	0·83540 (7)	0·44280 (23)	0·86027 (17)	2·99 (3)

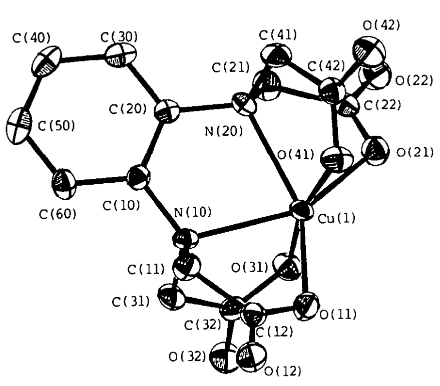

Fig. 1. *ORTEP* plot (Johnson, 1965) of Cu(phdta) showing the atom-numbering scheme. The thermal ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity.

Discussion. Final fractional coordinates are given in Table 1.* The atom numbering appears in Fig. 1, while bond lengths and bond angles are listed in Table 2. The coordination geometry around the Cu^{II} ion is twisted much more from an octahedral configuration than that of Mn[Cu(edta)] (Solans, Font-Altaba, Oliva & Herrera, 1983). This is well illustrated in Fig. 2, where perspective views of the six donor atoms along the N—N direction are compared. The Cu(phdta) complex takes an intermediate form between O_h and a trigonal prism. A similar type of polyhedron has also been found for zinc(II) (Azuma *et al.*, 1986) and cobalt(II) (McCandlish *et al.*, 1978) complexes of phdta. Table 3 shows that the sum of interior angles in the diamine chelate ring is 539·8°. This value corresponds well to planarity (540°), which is observed for most phdta complexes. As expected from a lower value of 536·8°, a perspective projection shows considerable kinking in the terminal glycinate chelate rings in contrast to the planar form in the edta complexes (Motherwell, 1978). The mean Cu—N distance is 0·217(7) Å longer than that in $[Cu(edta)]^{2-}$ (Table 3). This may result from the reduced electron density on the N atoms and from the geometrical restriction imposed by the planar configuration of the phenylenediamine ring.

Table 2. *Pertinent lengths* (Å) *and angles* (°) *for the* Cu–phdta *complex*

Cu(1)—N(10)	2·253 (1)	Cu(1)—N(20)	2·266 (2)
Cu(1)—O(31)	1·927 (1)	Cu(1)—O(21)	2·150 (2)
Cu(1)—O(11)	2·121 (2)	Cu(1)—O(41)	1·926 (2)
C(10)—N(10)	1·443 (2)	C(20)—N(20)	1·454 (2)
N(10)—C(31)	1·479 (3)	N(20)—C(21)	1·472 (3)
N(10)—C(11)	1·474 (3)	N(20)—C(41)	1·485 (3)
C(31)—C(32)	1·530 (3)	C(21)—C(22)	1·528 (3)
C(11)—C(12)	1·532 (3)	C(41)—C(42)	1·532 (3)
C(32)—O(31)	1·279 (2)	C(32)—O(32)	1·231 (3)
C(22)—O(21)	1·256 (2)	C(22)—O(22)	1·255 (3)
C(12)—O(11)	1·276 (2)	C(12)—O(12)	1·237 (3)
C(42)—O(41)	1·275 (3)	C(42)—O(42)	1·234 (3)
N(10)—Cu(1)—N(20)	77·20 (6)	N(10)—Cu(1)—O(31)	82·61 (6)
N(10)—Cu(1)—O(21)	145·29 (6)	N(10)—Cu(1)—O(11)	75·79 (6)
N(10)—Cu(1)—O(41)	108·58 (6)	N(20)—Cu(1)—O(31)	105·98 (6)
N(20)—Cu(1)—O(21)	76·35 (6)	N(20)—Cu(1)—O(11)	145·85 (6)
N(20)—Cu(1)—O(41)	81·88 (6)	O(31)—Cu(1)—O(21)	83·48 (6)
O(31)—Cu(1)—O(11)	90·89 (6)	O(31)—Cu(1)—O(41)	167·77 (6)
O(21)—Cu(1)—O(11)	136·08 (6)	O(21)—Cu(1)—O(41)	89·47 (6)
O(11)—Cu(1)—O(41)	87·28 (6)		
Cu(1)—N(10)—C(10)	112·2 (1)	N(10)—C(10)—C(20)	119·5 (2)
C(10)—C(20)—N(20)	119·3 (2)	C(20)—N(20)—Cu(1)	111·5 (1)
Cu(1)—N(10)—C(31)	103·3 (1)	N(10)—C(31)—C(32)	114·4 (2)
C(31)—C(32)—O(31)	118·9 (2)	C(32)—O(31)—Cu(1)	117·5 (1)
Cu(1)—N(10)—C(11)	102·4 (1)	N(10)—C(11)—C(12)	110·8 (2)
C(11)—C(12)—O(11)	117·3 (2)	C(12)—O(11)—Cu(1)	114·6 (1)
Cu(1)—N(20)—C(21)	102·4 (1)	N(20)—C(21)—C(22)	111·7 (2)
C(21)—C(22)—O(21)	119·0 (2)	C(22)—O(21)—Cu(1)	114·0 (1)
Cu(1)—N(20)—C(41)	103·9 (1)	N(20)—C(41)—C(42)	114·0 (2)
C(41)—C(42)—O(41)	117·9 (2)	C(42)—O(41)—Cu(1)	118·6 (1)
C(10)—N(10)—C(31)	112·5 (2)	C(10)—N(10)—C(11)	113·2 (2)
C(20)—N(20)—C(21)	112·6 (2)	C(20)—N(20)—C(41)	113·0 (2)
O(31)—C(32)—O(32)	123·9 (2)	O(21)—C(22)—O(22)	124·8 (2)
O(11)—C(12)—O(12)	125·1 (2)	O(41)—C(42)—O(42)	123·7 (2)

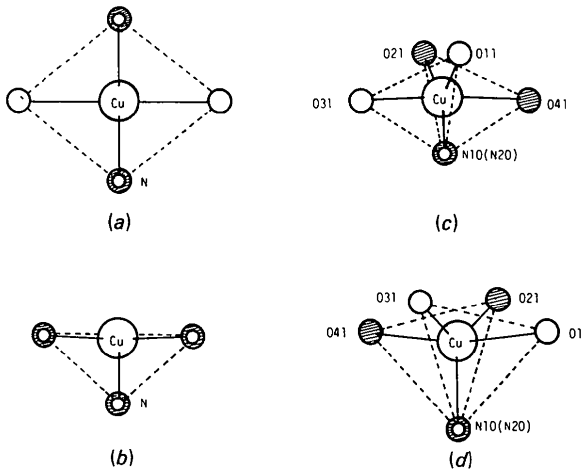

Fig. 2. Comparison of the perspectives of donor atoms (2N, 4O) and a central metal ion down the line from one N atom to the other. The double circle shows overlapping of two atoms, and the shaded circle denotes an atom behind the plane of the page, on which the copper ion lies. (*a*) O_h, (*b*) trigonal prism, (*c*) Cu(edta) in $[(H_2O)_4Mn(edta)Cu].2H_2O$, (*d*) Cu(phdta).

Table 3. *Comparison of the bond lengths and angles of* phdta *and* edta *complexes*

	K_2[Zn(phdta)][a]	H[Zn(Hphdta)][a]	Mg[Zn(edta)][b]	Na_2[Cu(phdta)][c]	Mn[Cu(edta)][b]	Cd_2(phdta)[d]	Mg[Cd(edta)][e]
Bond length (metal–N) (Å)	2·191 (2) 2·184 (3)	2·252 (3) 2·136 (3)	2·163 (6) 2·145 (8)	2·253 (1) 2·266 (2)	2·042 (5) 2·042 (5)	2·455 (8) 2·464 (6)	2·382 (9) 2·414 (7)
Sum of angles* (diamine)	539·6	539·9 538·9	518·2	539·8 (3)	514·4	539·9	508·1
(glycinate)†	536·6	535·4	539·5	536·8 (3)	539·5	525·7	530·1

(*a*) Azuma *et al.* (1986). (*b*) Solans, Font-Altaba, Oliva & Herrera (1983). (*c*) This work. (*d*) Nakasuka *et al.*, unpublished results. (*e*) Solans, Galí, Font-Altaba, Oliva & Herrera (1983).

* Sum of the interior angles for the diamine chelate ring (°).

† The maximum value of sums of the interior angles for glycinate rings (°).

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* Lists of structure factors, fractional atomic coordinates of H atoms, anisotropic thermal parameters, normal intermolecular distances, non-essential bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43106 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The Structure of Tetramethylphosphonium Dicopper Pentachloride

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Abstract. $[(CH_3)_4P]Cu_2Cl_5$, $M_r = 395{\cdot}46$, monoclinic, $P2_1/n$, $a = 10{\cdot}967\ (1)$, $b = 12{\cdot}023\ (1)$, $c = 10{\cdot}211\ (1)$ Å, $\beta = 109{\cdot}86\ (7)^\circ$, $V = 1266{\cdot}3\ (2)$ Å^3, $Z = 4$, $D_x = 2{\cdot}074$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 45{\cdot}22$ cm^{-1}, $F(000) = 776$, $T = 293$ K, $wR = 0{\cdot}024$ for 2176 reflections. The compound consists of chains of edge-sharing $CuCl_5$ pyramids, with approximate site symmetry C_{4v}. One Cl of each pyramid bridges to a neighbouring chain. In this way planes of interconnected chains are formed, which are held together by the large tetramethylphosphonium (TMP) cations.

Introduction. Part of the investigations carried out in our group are focused on structural and magnetic properties of ternary halides in the system AX–BX_2 and more specifically of compounds with the formula ABX_3, the hexagonal perovskite (2L). In the systems under consideration, $B = Cu^{2+}$, $X = Cl^-$ and $A = Rb^+$, Cs^+, $(CH_3)_4N^+$ (Crama & Maaskant, 1983; Weenk & Spek, 1976). In these compounds the A ion is important for the manifestation of the cooperative $E \otimes \varepsilon$ Jahn–Teller effect of the $CuCl_6$ octahedra. In order to investigate the effect of a still larger cation, $(CH_3)_4P^+$ was used. The synthesis yielded a new compound with the composition $[(CH_3)_4P]Cu_2Cl_5$ in which copper is coordinated to five chlorines.

Experimental. Single crystals were grown from an aqueous solution, acidified with concentrated hydrochloric acid, containing equimolar amounts of (TMP)-Cl and $CuCl_2$. The solution yielded reddish-brown and yellow oblique crystals. From the crystal structure determination it was found that the reddish-brown TMP compound was $(TMP)Cu_2Cl_5$. It is known that the composition of this kind of crystal depends on the concentration of both hydrochloric acid and starting materials (Weenk, 1976).

Reddish-brown oblique crystals, 0·43 × 0·17 × 0·14 mm, Enraf–Nonius four-circle diffractometer, graphite-monochromated Mo $K\alpha$ radiation, 24 reflections used for determination of unit-cell dimensions ($-14{\cdot}25 < \theta < 14{\cdot}25^\circ$), from systematic absence of $hk0$, $h + k = 2n$, and $00l$, $l = 2n$, it was concluded that the space group is $P2_1/n$, 7691 reflections measured $2 < \theta < 30^\circ$, 3852 independent reflections, $R_{\rm int} = 0{\cdot}036$, 2176 significant, 584 non-significant [observed, $I > 2\sigma(I)$], 1092 unobserved reflections, h −15 to 15, k 0 to 16, l −14 to 14, 3 standard reflections ($\bar{4}35$, $\bar{6}06$, $2\bar{6}3$), decay scattering power 5·77%, observed reflections were corrected for this variation; e.s.d. of standard reflections 1·4%. Lp correction, absorption correction (de Graaff, 1973), min. and max. transmission 0·6097, 0·7351, scattering factors from *International Tables*

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