Rhenium phosphine chelate complexes involving other ring systems are very rare. Brown *et al.* recently reported the structure of Re$_2$(CO)$_5$(dppm)(μ-η^1,η^2-CH=CH$_2$)(μ-η^1,η^2-C=CPh) (Lee, Pennington, Cordes & Brown, 1985). The dppm and one of the rheniums form a four-membered ring. The Re—P bond lengths of 2·42–2·44 Å are normal. However, the bite angle P—Re—P of 68·9° is substantially less than that in the five-membered ring complex. The P—C—P angle of 96·4° is 13° less than the regular tetrahedral angle. H$_3$Re$_3$(CO)$_{10}$(tedip)$_2$ [tedip stands for (EtO)$_2$POP(OEt)$_2$] was also characterized to have a four-membered ring (Prest, Mays, Raithby & Orpen, 1982), but the detailed structure is not reported.

The Re(CO)$_3$Cl(tdppme) reported here is the only chelating phosphine monorhenium compound with a six-membered ring. The Re—P bond lengths of 2·445 (3)–2·480 (2) Å are slightly longer than those in the normal range. The P(1)—Re—P(2) angle 88·07 (8)° is only 6–8° larger than those in Re(dppe) complexes. However, the P(2)—C(2)—C(3) and P(1)—C(1)—C(3) angles of 118·9 (6)–121·1 (6)° are substantially larger than the normal 109°. It is an indication that the large ring strain disfavors the geometry of the six-membered ring. Dppp [1,3-bis(diphenylphosphinopropane)] has been reported to form a six-membered ring complex, RhCl$_2$(COPh)(dppp) (McGuiggan, Doughty & Pignolet, 1980). The bite angle P—Re—P 94° is 12–14° larger than that in the dppe rhenium complexes with five-membered rings. All the other angles in the six-membered ring ranging from 114–117° are larger than the expected tetrahedral angle. Thus, the six-membered ring complexes are characterized with a large ring strain as reflected in the bond angles.

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Structure of an Octacoordinate Cadmium(II) Complex: Di-μ-aqua-bis[1,1,1-triaqua-μ-(*o*-phenylenediamine-*N*,*N*,*N'*,*N'*-tetraacetato-O^1,O^2,O^3:N,N',O^1,O^2,O^4,O^5)-dicadmium(II)] Octahydrate

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Abstract. [Cd(H$_2$O)C$_{14}$H$_{12}$N$_2$O$_8$Cd(H$_2$O)$_3$]$_2$.8H$_2$O, M_r = 1410·4, triclinic, $P\bar{1}$, a = 11·357 (2), b = 12·260 (2), c = 9·905 (1) Å, α = 114·74 (1), β = 102·54 (1), γ = 101·99 (2)°, V = 1151·3 (4) Å^3, Z = 1, D_m = 2·03, D_x = 2·03 g cm^{-3}, λ(Cu $K\alpha$) = 1·5417 Å, μ = 149·7 cm^{-1}, F(000) = 700, T = 293 K. Final R = 0·055 for 3365 observed reflections. The title compound is a tetranuclear complex bridged by carboxylate and water oxygen atoms. The chelated cadmium(II) ion is dihydrated and octacoordinate, whereas

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another metal ion is trihydrated to give heptacoordination. The unusual octacoordination results from a rigid structure of the planar *o*-phenylenediamine chelate ring, which is unable to encircle such a large metal ion.

Introduction. The octahedral structure is quite common in metal complexes of potentially hexadentate aminopolycarboxylates such as ethylenediaminetetraacetate (EDTA). This is, however, not the case for the complexes of *o*-phenylenediamine-*N*,*N*,*N*′,*N*′-tetraacetate (PhDTA), of which the phenylene group substituted for the ethylenic backbone imposes a planar configuration on the diamine chelate ring and reduces the basicity of N donor atoms (Nakasuka, Kunimatsu, Matsumura & Tanaka, 1985). This new type of ligand gives a complex of Co^{II} (McCandlish, Michael, Neal, Lingafelter & Rose, 1978), Cu^{II} (Nakasuka, Azuma & Tanaka, 1986) or Zn^{II} (Azuma, Nakasuka & Tanaka, 1986) with a molecular structure which is twisted largely from the antiprismatic configuration (O_h) toward the trigonal-prismatic one. On the other hand, Mn^{II} has been found to give a heptacoordinate monoaqua complex (Nakasuka, Azuma, Katayama, Honda, Tanaka & Tanaka, 1985). The increase in coordination number has been interpreted in terms of the large ionic radius of this ion, and this is consistent with our calorimetric studies on the complexation of these metal ions with PhDTA in aqueous solution. The structure of a PhDTA complex of the large cadmium ion is of interest in this context, especially because this cation has a general tendency to give heptacoordinate EDTA complexes (Pozhidaev, Polinova & Porai-Koshits, 1972; Zhang, Shao & Jin, 1981; Solans, Gali, Font-Altaba, Oliva & Herrera, 1983; Solans, Font-Altaba, Oliva & Herrera, 1985).

Experimental. Crystal prepared similarly to a method described previously (Nakasuka, Kunimatsu, Matsumura & Tanaka, 1985). Elemental analysis: (calcd for $C_{14}H_{28}N_2O_{16}Cd_2$) C 23·84, N 3·97, H 4·00%, (found) C 23·74, N 3·99, H 3·06%. Colorless, slightly efflorescent crystal 0·15 × 0·08 × 0·23 mm. D_m by flotation in $C_6H_{12}/C_2H_2Br_4$. Rigaku AFC-5A automated four-circle diffractometer. Cell dimensions from 20 selected reflections with $29{\cdot}9 < \theta < 30{\cdot}2°$. Total of 3774 reflections measured, $2\theta_{\max} = 126°$, $-13 \leq h \leq 13$, $-14 \leq k \leq 14$, $0 \leq l \leq 12$, $R_{\rm int} = 0{\cdot}016$. 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 3365 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 0·032 to 0·30. Non-H atoms assigned ansiotropic temperature factors. H atoms located from difference synthesis and refined with isotropic temperature factors equivalent to those for bonded atoms. Attempts to locate all H atoms unsuccessful. $R = 0{\cdot}055$, $wR = 0{\cdot}063$, $S = 3{\cdot}77$, $w = 1/\sigma^2(F^2)$, $(\Delta/\sigma)_{\max} = 0{\cdot}12$ for B_{23} of O(1) atom, $\Delta\rho_{\max} = 0{\cdot}56$ e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). All calculations made on FACOM 382 computer at Nagoya University Computation Center.

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

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

	x	y	z	$B_{\rm eq}$(Å^2)
Cd(1)	0·27805 (5)	0·57655 (5)	0·67524 (6)	3·97 (2)
Cd(2)	0·34087 (5)	0·34542 (3)	0·94063 (6)	3·70 (2)
O(31)	0·3296 (6)	0·1954 (6)	0·6856 (7)	4·89 (20)
O(21)	0·2535 (5)	0·4263 (5)	0·7766 (8)	4·62 (19)
O(22)	0·0972 (5)	0·3889 (5)	0·5720 (7)	4·48 (18)
O(2)	0·1499 (5)	0·6105 (6)	0·4892 (7)	4·57 (19)
O(51)	0·5491 (7)	0·4320 (6)	0·8911 (8)	4·89 (20)
O(1)	0·1862 (6)	0·6861 (6)	0·8496 (8)	5·42 (22)
O(41)	0·2423 (6)	0·3888 (6)	1·1475 (7)	4·94 (20)
O(3)	0·3475 (8)	0·4713 (8)	0·4740 (9)	5·98 (26)
O(11)	0·5086 (4)	0·3367 (5)	1·1246 (7)	4·08 (17)
O(12)	0·5590 (6)	0·2335 (6)	1·2518 (8)	5·35 (22)
O(32)	0·3407 (10)	0·0057 (7)	0·5395 (9)	7·10 (20)
O(42)	0·0665 (6)	0·4193 (7)	1·1971 (8)	5·58 (23)
N(20)	0·1059 (6)	0·2463 (6)	0·8238 (8)	3·80 (20)
N(10)	0·2872 (6)	0·1308 (6)	0·9129 (8)	3·74 (20)
C(22)	0·1460 (7)	0·3613 (7)	0·6718 (10)	3·78 (23)
C(12)	0·4804 (7)	0·2444 (7)	1·1529 (10)	4·01 (24)
C(11)	0·3449 (8)	0·1460 (8)	1·0706 (11)	4·36 (27)
C(21)	0·0674 (7)	0·2402 (7)	0·6664 (10)	3·72 (23)
C(42)	0·1279 (8)	0·3833 (7)	1·1068 (10)	4·01 (25)
C(20)	0·0615 (7)	0·1193 (7)	0·8078 (9)	3·72 (23)
C(50)	−0·0266 (9)	−0·1249 (9)	0·7716 (12)	5·07 (30)
C(31)	0·3483 (8)	0·0614 (8)	0·8021 (11)	4·70 (29)
C(32)	0·3378 (9)	0·0887 (8)	0·6660 (12)	5·01 (30)
C(10)	0·1494 (7)	0·0644 (7)	0·8523 (10)	3·87 (24)
C(41)	0·0561 (8)	0·3355 (8)	0·9311 (10)	4·16 (27)
C(60)	0·1023 (9)	−0·0575 (8)	0·8326 (11)	4·77 (29)
C(30)	−0·0691 (8)	0·0511 (9)	0·7478 (12)	4·83 (29)
C(40)	−0·1144 (9)	−0·0700 (9)	0·7276 (12)	4·98 (30)
O(61)	0·5457 (8)	0·6788 (8)	0·4396 (12)	7·09 (32)
O(62)	0·3247 (9)	0·7517 (9)	0·1464 (10)	6·74 (29)
O(63)	0·3227 (10)	0·7618 (8)	0·4241 (11)	7·39 (33)
O(64)	0·4018 (8)	0·0151 (8)	0·2904 (11)	7·04 (30)

Discussion. Final fractional coordinates are given in Table 1.* The numbering system and a molecular structure appear in Fig. 1, while bond lengths and bond angles are listed in Table 2. Cd(2) is chelated by hexadentate phdta and further coordinated to two waters, O(51) and O(51$^{\rm i}$) [symmetry code: (i) $1-x$, $1-y$, $2-z$], giving rise to an octacoordinate structure. On the other hand, the Cd(1) ion is bonded to two bidentate carboxylates and to three water molecules, giving heptacoordination (Fig. 1). Cd(2) is linked to

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* Lists of structure factors, fractional atomic coordinates of H atoms, anisotropic thermal parameters, selected bond lengths and bond angles, non-essential bond lengths and bond angles, and normal intermolecular distances have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43236 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Cd(1) through a carboxylate group, O(21) of which is directly bonded to both cadmium ions. The dinuclear complexes are further dimerized, with a centre of symmetry located at the midpoint of Cd(2) and Cd(2$^{\rm i}$). Each dinuclear entity is linked together through O(51), O(51$^{\rm i}$) and other carboxylate groups, O(11), O(12), O(11$^{\rm i}$) and O(12$^{\rm i}$) of which act as bridging atoms between Cd(1$^{\rm i}$) and Cd(2) as well as between Cd(1) and Cd(2$^{\rm i}$), respectively. Thus the Cd–PhDTA complex forms a discrete tetranuclear entity, differing from the infinite chain structure of Cd–EDTA (Solans *et al.*, 1985). As heptacoordination has been commonly observed in the EDTA complexes so far studied (Pozhidaev *et al.*, 1972; Zhang *et al.*, 1981; Solans, Gali, Font-Altaba, Oliva & Herrera, 1983; Solans *et al.*, 1985), octacoordination is a special feature of the present complex. This may be attributed to the large ionic radius of the cadmium ion and particularly to the rigid configuration of phdta, of which the phenylenediamine chelate ring is quite planar. This point is well illustrated by the sum of the interior angles for a diamine chelate ring. It amounts to 539·9 (1·3)° for $\mathrm{Cd_2}$(phdta), but to 508·1° in the case of Mg[Cd(edta)] (Solans, Gali, Font-Altaba, Oliva & Herrera, 1983), which is considerably reduced from 540° for the ideally planar configuration. The phdta anion is too rigid to encircle the whole large cation, and a vacant part is occupied by two water molecules, resulting in octacoordination.

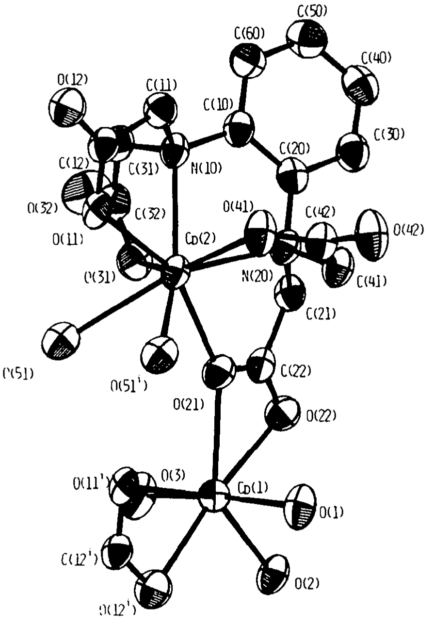

Fig. 1. *ORTEP* plots (Johnson, 1965) of $\mathrm{Cd_2(phdta)(H_2O)_4}$ showing the atom-numbering scheme. The thermal ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity [symmetry code: (i) $1-x$, $1-y$, $2-z$].

Table 2. *Important bond lengths* (Å) *and angles* (°)

Cd(1)—O(1)	2·302 (8)	Cd(1)—O(2)	2·327 (8)
Cd(1)—O(3)	2·284 (9)	Cd(1)—O(11)	2·452 (5)
Cd(1)—O(12)	2·365 (7)	Cd(1)—O(21)	2·436 (8)
Cd(1)—O(22)	2·391 (5)	Cd(2)—N(20)	2·464 (6)
Cd(2)—N(10)	2·455 (8)	Cd(2)—O(21)	2·380 (8)
Cd(2)—O(11)	2·387 (6)	Cd(2)—O(41)	2·463 (8)
Cd(2)—O(31)	2·377 (6)	Cd(2)—O(51$^{\rm i}$)	2·379 (5)
Cd(2)—O(51)	2·619 (8)		
O(1)—Cd(1)—O(2)	87·3 (3)	O(2)—Cd(1)—O(3)	83·9 (3)
O(2)—Cd(1)—O(22)	83·2 (8)	O(3)—Cd(1)—O(11$^{\rm i}$)	92·8 (2)
O(3)—Cd(1)—O(22)	89·7 (3)	O(11$^{\rm i}$)—Cd(1)—O(12$^{\rm i}$)	54·3 (3)
O(11$^{\rm i}$)—Cd(1)—O(21)	80·2 (2)	O(21)—Cd(1)—O(22)	53·9 (2)
N(10)—Cd(2)—N(20)	72·7 (2)	N(10)—Cd(2)—O(11)	70·1 (2)
N(10)—Cd(2)—O(21)	132·2 (2)	N(10)—Cd(2)—O(31)	70·2 (3)
N(10)—Cd(2)—O(41)	83·4 (3)	N(10)—Cd(2)—O(51)	118·0 (2)
N(20)—Cd(2)—O(21)	69·2 (3)	N(20)—Cd(2)—O(31)	82·4 (2)
N(20)—Cd(2)—O(41)	68·9 (2)	N(20)—Cd(2)—O(51)	144·8 (3)
O(11)—Cd(2)—O(31)	105·7 (2)	O(11)—Cd(2)—O(41)	84·3 (2)
O(11)—Cd(2)—O(51)	75·5 (2)	O(11)—Cd(2)—O(51$^{\rm i}$)	81·1 (2)
O(21)—Cd(2)—O(31)	77·1 (3)	O(21)—Cd(2)—O(41)	107·8 (3)
O(21)—Cd(2)—O(51)	81·8 (3)	O(21)—Cd(2)—O(51$^{\rm i}$)	79·6 (2)
O(31)—Cd(2)—O(41)	145·8 (2)	O(31)—Cd(2)—O(51)	71·8 (2)
O(41)—Cd(2)—O(51$^{\rm i}$)	79·1 (3)	O(51)—Cd(2)—O(51$^{\rm i}$)	66·2 (3)

Symmetry code: (i) $1-x$, $1-y$, $2-z$.

The failure in encircling and the increase in coordination number should lead to lengthening of metal–ligand bonds. This is just the case, and all the average values of Cd—N, Cd—O(carboxylate) and Cd—O(water) are greater for the present complex than for the EDTA complexes cited above. Metal–N bonds of PhDTA complexes are normally longer than those of the corresponding EDTA ones, owing to the lower electron density on the PhDTA nitrogen atoms. The mean value of M—O(carboxylate) bonds for PhDTA (Cu 2·031; Zn 2·083 Å), however, has been found to be shorter than or nearly equal to that for EDTA (Cu 2·121; Zn 2·08 Å) in the case of hexacoordinate copper(II) or zinc(II) complexes (Nakasuka *et al.*, 1986; Azuma *et al.*, 1986; Solans, Gali, Font-Altaba, Oliva & Herrera, 1983; Solans, Font-Altaba, Oliva & Herrera, 1983). The crowding around the central metal ion is thus partly relieved in the Cd–PhDTA complex to give an octacoordinate structure.

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Neutron and X-ray Diffraction Study of a Macrocyclic Nickel(II) Complex with Ni^{II} in a Pseudoaromatic Chelate Ring

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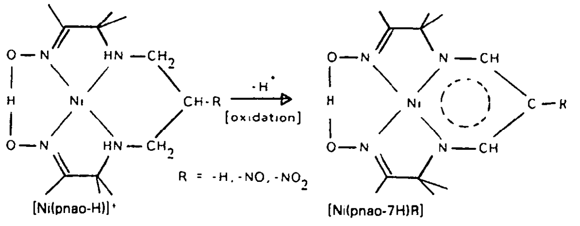
Abstract. [3,3′-Dimethyl-3,3′-(2-nitrosopropanediylidenediamino)bis(2-butanone oximato)-*N,N′,N″,N‴*]-nickel(II), [Ni(pnao−7H)NO], $[Ni(C_{13}H_{21}N_5O_3)]$, $M_r = 354\cdot1$, monoclinic, $P2_1/c$, $a = 10\cdot160\,(3)$, $b = 11\cdot305\,(3)$, $c = 14\cdot053\,(3)$ Å, $\beta = 107\cdot9\,(2)°$, $V = 1536\cdot3\,(3)$ Å^3, $Z = 4$, $D_m = 1\cdot530\,(6)$, $D_x = 1\cdot539$ g cm^{-3}, $\lambda(\text{Mo}\,K\alpha) = 0\cdot7107$, $\lambda(\text{neutron}) = 1\cdot058$ Å, $\mu = 12\cdot86$ (X-ray), $0\cdot084$ cm^{-1} (neutron), $F(000) = 744$, room temperature, $R = 0\cdot039$ (X-ray), $0\cdot074$ (neutron), unique reflections: 2004 (X-ray), 2315 (neutron). A combined X-ray/neutron diffraction study was carried out to investigate the aromatic behaviour of the six-membered heterocyclic chelate ring and the intramolecular hydrogen bonding. The H atoms were located precisely from the neutron data. The aromaticity of the six-membered chelate ring is suggested by its planarity and the relative shortness of the C—N and C—C bond distances in the ring. The short intramolecular O···O hydrogen bond [2·411 (3) Å] is symmetric.

Introduction. Oxidation of the [Ni(pnao−H)]$^+$ ion (structure *A*†) in basic solution easily yields a quasi-aromatic system [Ni(pnao−7H)*R*] (structure *B*) in which the central carbon atom in the six-membered heterocyclic ring exhibits a relatively high electron density (Urban & Vassian, 1979). Thus, this ring behaves like a phenol or aromatic amine with respect to the attachment of various functional groups while the rest of the molecule remains unreactive. This reactivity of the heterocyclic ring in these pseudoaromatic metal complexes has been utilized to connect two parent molecules having structure (*B*) through a $(\text{—CH—})_3$ or a $[\text{—CH—C(CH}_3\text{)—CH—}]$ linkage at the central carbon to form a highly conjugated dinuclear species with considerable kinetic stability (Ghiron, Murmann & Schlemper, 1986). The benzene-like behaviour of the six-membered chelate ring is reflected in the planar nature of complex (*B*) and the short bond length in the ring. We reported the first structure determination of the monoclinic and orthorhombic forms of the planar $C(12)\text{—}NO_2$ derivative of complex (*B*) at low temperature by X-ray diffraction and at room temperature by neutron diffraction (Hussain, Murmann & Schlemper, 1980; Hussain, Schlemper & Yelon, 1981).



(*A*) (*B*)

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† pnao = 3,3′-dimethyl-3,3′-(1,3-propanediylamino)bis(2-butanone oxime).