The BIS complex is exactly linear with staggered tricyclohexylphosphine groups, as required by the location of the cation on a center of symmetry. This contrasts with the analogous complexes with SCN^- (Muir, Muir & Lorca, 1980) and PF_6^- (Cooper, Dennis, Henrick & McPartlin, 1980), which have nearly eclipsed tricyclohexylphosphine groups, and for which the P—Au—P angles are 177·2 (4) and 178·0 (2)°, respectively. Au—P bond lengths and their deviations are 2·321 (2), 2·306 (15) and 2·325 (1) Å, respectively, for the BIS, SCN^- and PF_6^- complexes.

Both of the title compounds resulted from our attempt to prepare a higher-coordinate complex with Cy_3P, specifically, L'_3AuCl. We find, however, that although two-, three-, or four-coordinate complexes can be prepared with $L' = Ph_3P$, only linear two-coordinate complexes can be prepared with $L' = Cy_3P$. This difference between Cy_3P and Ph_3P could be attributed to either steric or electronic effects. Since the ligand cone angles are not that different (170 *vs* 145°: Tolman, 1977), the effect may well be largely electronic. The phenyl group, through resonance, may better maintain optimum electronic density on the P and Au, even when additional groups are added. The cyclohexyl group, however, has only inductive effects with which to adjust electronic density in the complex.

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Structure of a Binuclear Manganese(II) Complex: 1,1,1,1,1,2-Hexaaqua-μ-(*o*-phenylenediaminetetraacetato-O^1: N,N',O^2,O^3,O^4,O^5)-dimanganese(II), $[Mn_2(C_{14}H_{12}N_2O_8)(H_2O)_6]$

BY NORIYUKI NAKASUKA, SHIGEKI AZUMA, CHUJI KATAYAMA, MASAKO HONDA, JIRO TANAKA AND MOTOHARU TANAKA*

Department of Chemistry, Faculty of Science, Nagoya University, Chikusa, Nagoya 464, *Japan*

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Abstract. $M_r = 554·24$, triclinic, $P\bar{1}$, $a = 9·893$ (1), $b = 11·543$ (1), $c = 9·844$ (1) Å, $\alpha = 98·71$ (1), $\beta = 104·59$ (1), $\gamma = 97·70$ (1)°, $V = 1057·9$ (2) Å^3, $Z = 2$, $D_m = 1·744$, $D_x = 1·741$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5417 Å, $\mu = 102·23$ cm^{-1}, $F(000) = 568$, $T = 293$ K. Final $R = 0·048$ for 3335 observed reflections. The title compound is a binuclear manganese(II) complex bridged by a carboxylate oxygen of the aminopolycarboxylic acid. The chelated manganese(II) ion is coordinated to a water molecule and is heptacoordinate, whereas the other metal ion is octahedrally surrounded by six oxygen atoms.

Introduction. In an attempt to improve the complexing ability of aminopolycarboxylic acids such as ethylenediaminetetraacetic acid (H_4edta), substitution of the phenylene group for the ethylenic backbone has been proved to reduce the protonation constants of nitrogen donor atoms drastically, and to modify the formation constant for a series of transition-metal ions (Grimes, Huggard & Wilford, 1963; Nakasuka, Kunimatsu, Matsumura & Tanaka, 1985). The electron-withdrawing effect of the benzene ring apparently causes these changes in complexation of this type of new ligand, *o*-phenylenediamine-N,N,N',N'-tetraacetic acid (H_4phdta), and the planar configuration of the N—C—C—N moiety is expected to modify the mode of

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* To whom correspondence should be addressed.

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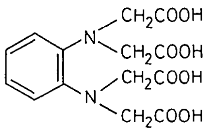
Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters*

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

	x	y	z	B_{eq}(Å^2)
Mn(1)	0·7520 (1)	0·6714 (1)	0·5652 (1)	2·01 (2)
Mn(2)	1·2844 (1)	0·6240 (1)	1·0237 (1)	2·26 (2)
O(12)	0·9980 (4)	0·6326 (4)	0·2648 (4)	3·64 (10)
O(11)	0·8499 (4)	0·5959 (3)	0·3963 (4)	2·79 (8)
O(31)	0·8677 (3)	0·6552 (3)	0·7818 (3)	2·67 (8)
O(32)	1·0764 (3)	0·6559 (3)	0·9308 (4)	2·98 (9)
O(21)	0·5588 (4)	0·6826 (3)	0·6384 (4)	3·34 (9)
O(22)	0·4556 (4)	0·7809 (3)	0·7831 (4)	3·89 (10)
O(41)	0·6353 (4)	0·7421 (3)	0·3874 (3)	3·68 (10)
O(42)	0·5038 (5)	0·8767 (4)	0·3249 (4)	3·56 (12)
O(4)	1·2042 (4)	0·4380 (3)	0·9989 (4)	3·39 (10)
O(2)	1·3784 (4)	0·8131 (4)	1·0361 (4)	3·53 (10)
O(6)	0·6730 (4)	0·4757 (3)	0·5384 (4)	3·58 (10)
O(1)	1·3334 (4)	0·5710 (3)	0·8202 (3)	2·59 (8)
O(3)	1·2586 (4)	0·6776 (4)	1·2391 (4)	3·56 (10)
O(5)	1·4932 (5)	0·6028 (5)	1·1353 (5)	5·51 (14)
N(10)	0·9913 (4)	0·7760 (3)	0·6144 (4)	1·98 (8)
N(20)	0·7593 (4)	0·8792 (3)	0·6624 (4)	2·04 (8)
C(10)	1·0164 (5)	0·8963 (4)	0·6971 (4)	2·08 (10)
C(20)	0·9029 (5)	0·9449 (4)	0·7271 (5)	2·06 (10)
C(30)	0·9287 (5)	1·0572 (4)	0·8142 (5)	2·63 (11)
C(40)	1·0653 (6)	1·1219 (4)	0·8678 (5)	3·02 (13)
C(50)	1·1776 (5)	1·0762 (4)	0·8336 (6)	3·04 (12)
C(60)	1·1542 (5)	0·9631 (5)	0·7506 (5)	2·82 (12)
C(31)	1·0711 (5)	0·6991 (4)	0·6996 (5)	2·34 (11)
C(32)	1·0017 (4)	0·6683 (4)	0·8137 (5)	2·11 (10)
C(11)	1·0262 (5)	0·7726 (4)	0·4770 (5)	2·49 (11)
C(12)	0·9523 (5)	0·6569 (4)	0·3710 (5)	2·41 (11)
C(21)	0·6779 (5)	0·8758 (4)	0·7700 (5)	2·95 (12)
C(22)	0·5539 (5)	0·7720 (4)	0·7258 (5)	2·55 (11)
C(41)	0·6859 (5)	0·9318 (4)	0·5423 (5)	2·86 (12)
C(42)	0·6008 (5)	0·8432 (4)	0·4085 (5)	2·82 (12)

binding in metal complexes. In fact it has been demonstrated that the coordination polyhedron in Co^{II}–phdta is trigonal-prismatic rather than anti-prismatic (O_h) (McCandlish, Michael, Neal, Lingafelter & Rose, 1978).



H$_4$phdta

In the course of our thermodynamic investigations, the manganese(II) ion has been found to complex this ligand much more exothermically than is expected from the ligand-field theory. This finding prompted us to elucidate the structure of an Mn^{II}–phdta complex.

Experimental. Crystal prepared by neutralizing aqueous H$_4$phdta (1·31 mmol) with KOH (2·50 mmol), followed by addition of manganese(II) acetate (1·25 mmol) and then of ethanol. Absence of K$^+$ confirmed by flame photometry. Elemental analysis: (calcd for $C_{14}H_{24}Mn_2N_2O_{14}$) C 30·34, N 5·05, H 4·36%; (found) C 30·58, N 4·94, H 4·25%. Well formed, almost colorless and transparent crystal 0·20 × 0·20 × 0·08 mm. D_m by flotation in $C_6H_5CH_3/C_2H_4Br_2$. Rigaku AFC-5 automated four-circle diffractometer. Cell dimensions from 20 selected reflections with $28 < \theta < 31°$. Total of 3768 reflections measured, $2\theta_{max} = 126°$, $-11 \leq h \leq 11$, $-13 \leq k \leq 13$, $0 \leq l \leq 11$, $R_{int} = 0{\cdot}022$. Three standard reflections after every 100 reflections (fluctuation less than 3·5%). Structure solved by the Monte Carlo direct method (Furusaki, 1979) with *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) using 3335 non-zero unique reflections, refined on F^2 by full-matrix least-squares program with absorption correction by analytical method (Katayama, Sakabe & Sakabe, 1972), transmission factors 0·13 to 0·44. Non-H atoms: anisotropic temperature factors. All H atoms located from difference Fourier map and refined with isotropic temperature factors equivalent to those for bonded atoms. $R = 0{\cdot}048$, $wR = 0{\cdot}051$, $S = 2{\cdot}38$, $w = 1/\sigma^2(F^2)$, $(\Delta/\sigma)_{max} = 0{\cdot}061$ for y of H(5B) atom, $\sigma_{max} = 0{\cdot}52$ e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). *ORTEP* (Johnson, 1965) employed for drawing molecular structure and *PLUTO*78 (Motherwell, 1978) for crystal-structure projection. All calculations made on a FACOM 382 computer at the Computation Center, Nagoya University.

Discussion. Final fractional coordinates are given in Table 1.* The numbering system appears in Fig. 1, while bond lengths and bond angles may be found in Tables 2 and 3 respectively. Fig. 2 shows the crystal structure viewed along **c**. The ligand is hexadentate and the Mn^{II}(1) ion is further coordinated to one water molecule. This type of heptacoordinate complex has been found for Mn^{II}–edta (Richards, Pedersen, Silverton & Hoard, 1964), Fe^{III}–(cyclohexane)dta (Cohen & Hoard, 1966), *etc.* On the other hand the

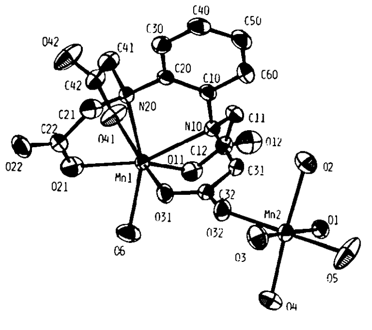


Fig. 1. An *ORTEP* plot of [Mn(H$_2$O)(phdta)Mn(H$_2$O)$_5$] showing the atom-numbering scheme. The thermal ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity.

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* Lists of structure factors, anisotropic thermal parameters, normal intermolecular distances, non-essential bond lengths, non-essential bond angles, H-atom parameters and a stereoview of the molecule have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42198 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

$Mn^{II}(2)$ ion is nearly octahedrally coordinated by oxygen donor atoms. The manganese(II) ion is also surrounded octahedrally by four water molecules and two bridging carboxylate oxygen atoms in $[Cu^{II}(edta)Mn^{II}(H_2O)_4].2H_2O$ (Solans, Font-Altaba, Oliva & Herrera, 1983). In the case of the Mn–edta complex, a pseudo twofold axis passes through the midpoint of the two nitrogen atoms, the metal ion and the oxygen of the water molecule, but this is not so for Mn–phdta. The oxygen atom O(6) in a hydrated water molecule is appreciably deviated from a line bisecting the nitrogen atoms and passing through the central metal ion. Mn(1) and the four oxygen donor atoms from carboxylate groups are in close proximity to a plane normal to the bisecting line. Hence it may be pointless to distinguish a *G* ring from an *R* one (Weakliem & Hoard, 1959). There is still, however, a small difference in the deviation from the plane. Thus O(11) and O(21) are located nearer to the N–Mn–N plane as to be classified as *G*. The two manganese ions are linked together by a bidentate carboxylate group. An intermolecular hydrogen-bond network results from all the water molecules of hydration. All carboxylate oxygen atoms are receptors in hydrogen bonds from a water molecule, except O(32) which serves as a bridging atom. The carboxylate oxygen atoms not bound to Mn(1) form two hydrogen bonds. O(1) and O(3) of hydrated water are also receptors. The O···O distances range from 2·64 to 2·85 Å, except for O(3)···O(6) 3·020 (6) Å and O(3)···O(42) 2·960 (6) Å. The O···H···O bond angles range from 151 to 178°. The Mn–N distances are longer in the H_4phdta complex than in the H_4edta complex, apparently due to reduced electron density on the nitrogen atoms of the former. However, an averaged Mn(1)–O distance is shorter in the H_4phdta complex. The mean distance of Mn(2)–O(water) is 2·183 Å, and this is longer than that of the corresponding H_4edta complex by 0·028 Å. The sum of the interior angles in the diamine chelate ring is 537·5 (1·4)°, only slightly deviated from planarity (540°).

Table 2. *Pertinent lengths* (Å) *for the binuclear complex*

(*a*) Mn(1)			
Mn(1)–N(10)	2·403 (3)	Mn(1)–N(20)	2·428 (4)
Mn(1)–O(11)	2·250 (4)	Mn(1)–O(21)	2·219 (4)
Mn(1)–O(31)	2·200 (3)	Mn(1)–O(41)	2·174 (4)
Mn(1)–O(6)	2·242 (4)		
(*b*) Mn(2)			
Mn(2)–O(1)	2·195 (4)	Mn(2)–O(2)	2·228 (4)
Mn(2)–O(3)	2·205 (4)	Mn(2)–O(4)	2·142 (4)
Mn(2)–O(5)	2·146 (5)	Mn(2)–O(32)	2·137 (3)
(*c*) Others			
C(10)–C(20)	1·396 (7)	C(20)–C(30)	1·395 (6)
C(30)–C(40)	1·384 (7)	C(40)–C(50)	1·385 (8)
C(50)–C(60)	1·387 (7)	C(60)–C(10)	1·402 (6)
C(10)–N(10)	1·454 (5)	C(20)–N(20)	1·452 (5)
N(10)–C(11)	1·474 (7)	N(20)–C(21)	1·485 (7)
N(10)–C(31)	1·482 (6)	N(20)–C(41)	1·481 (6)
C(11)–C(12)	1·530 (6)	C(21)–C(22)	1·519 (6)
C(31)–C(32)	1·518 (7)	C(41)–C(42)	1·514 (6)
C(12)–O(11)	1·254 (6)	C(12)–O(12)	1·249 (7)
C(22)–O(21)	1·254 (6)	C(22)–O(22)	1·250 (7)
C(32)–O(31)	1·266 (5)	C(32)–O(32)	1·242 (5)
C(42)–O(41)	1·262 (7)	C(42)–O(42)	1·243 (7)

Table 3. *Pertinent angles* (°) *for the binuclear complex*

(*a*) Mn(1)			
N(10)–Mn(1)–N(20)	71·8 (1)	N(10)–Mn(1)–O(11)	70·6 (1)
N(10)–Mn(1)–O(21)	140·1 (1)	N(10)–Mn(1)–O(31)	72·4 (1)
N(10)–Mn(1)–O(41)	103·6 (1)	N(10)–Mn(1)–O(6)	129·1 (2)
N(20)–Mn(1)–O(11)	128·3 (1)	N(20)–Mn(1)–O(21)	72·3 (1)
N(20)–Mn(1)–O(31)	87·4 (1)	N(20)–Mn(1)–O(41)	74·8 (1)
N(20)–Mn(1)–O(6)	152·7 (2)	O(11)–Mn(1)–O(21)	148·4 (1)
O(11)–Mn(1)–O(31)	112·8 (1)	O(11)–Mn(1)–O(41)	81·1 (2)
O(11)–Mn(1)–O(6)	78·7 (2)	O(21)–Mn(1)–O(31)	89·4 (1)
O(21)–Mn(1)–O(41)	83·0 (2)	O(21)–Mn(1)–O(6)	81·8 (2)
O(31)–Mn(1)–O(41)	162·0 (1)	O(31)–Mn(1)–O(6)	84·0 (1)
O(41)–Mn(1)–O(6)	110·8 (1)		
(*b*) Mn(2)			
O(1)–Mn(2)–O(2)	90·8 (2)	O(1)–Mn(2)–O(3)	174·1 (1)
O(1)–Mn(2)–O(4)	84·5 (2)	O(1)–Mn(2)–O(5)	89·2 (2)
O(1)–Mn(2)–O(32)	95·9 (1)	O(2)–Mn(2)–O(3)	88·0 (2)
O(2)–Mn(2)–O(4)	175·1 (2)	O(2)–Mn(2)–O(5)	86·8 (2)
O(2)–Mn(2)–O(32)	91·1 (2)	O(3)–Mn(2)–O(4)	96·4 (2)
O(3)–Mn(2)–O(5)	85·0 (2)	O(3)–Mn(2)–O(32)	89·9 (2)
O(4)–Mn(2)–O(5)	91·5 (2)	O(4)–Mn(2)–O(32)	91·0 (2)
O(5)–Mn(2)–O(32)	174·6 (2)		
(*c*) Chelate rings			
Mn(1)–N(10)–C(10)	113·8 (3)	N(10)–C(10)–C(20)	119·9 (4)
C(10)–C(20)–N(20)	119·2 (4)	C(20)–N(20)–Mn(1)	112·9 (3)
Mn(1)–N(10)–C(11)	107·8 (2)	N(10)–C(11)–C(12)	111·6 (4)
C(11)–C(12)–O(11)	117·6 (4)	C(12)–O(11)–Mn(1)	120·6 (3)
Mn(1)–N(10)–C(31)	100·9 (3)	N(10)–C(31)–C(32)	110·5 (4)
C(31)–C(32)–O(31)	116·7 (4)	C(32)–O(31)–Mn(1)	118·5 (3)
Mn(1)–N(20)–C(21)	104·7 (3)	N(20)–C(21)–C(22)	112·6 (4)
C(21)–C(22)–O(21)	118·4 (5)	C(22)–O(21)–Mn(1)	120·3 (3)
Mn(1)–N(20)–C(41)	106·8 (3)	N(20)–C(41)–C(42)	115·4 (4)
C(41)–C(42)–O(41)	118·1 (4)	C(42)–O(41)–Mn(1)	120·5 (3)
(*d*) Others			
C(10)–N(10)–C(11)	112·8 (4)	C(10)–N(10)–C(31)	110·5 (3)
C(20)–N(20)–C(21)	111·1 (3)	C(20)–N(20)–C(41)	110·4 (4)
O(11)–C(12)–O(12)	125·6 (4)	O(21)–C(22)–O(22)	124·6 (4)
O(31)–C(32)–O(32)	123·5 (5)	O(41)–C(42)–O(42)	124·5 (4)
Mn(2)–O(32)–C(32)	139·5 (4)		

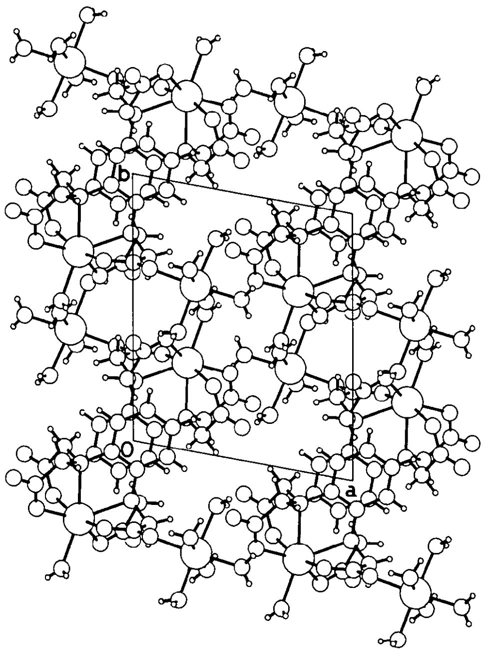

Fig. 2. A projection of the crystal structure along **c**.

Coordination of a water molecule is a common feature of H_4phdta and H_4edta complexes of the manganese(II) ion, which has a large radius (0·80 Å). Hydration in a chelated compound should result in greater exothermicity and in a smaller change in entropy (Anderegg, 1971), and this is just the case for both complexes. Hence these thermochemical data are satisfactorily interpretable in terms of $Mn(OH_2)L^{2-}$, which may be present in an aqueous solution.

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Acta Cryst. (1985). C**41**, 1179–1181

Structure of Iodotris(trimethylphosphine)cobalt(I), $[CoI(C_3H_9P)_3]$

BY J. A. BANDY

Chemical Crystallography Laboratory, 9 Parks Road, Oxford OX1 3PD, England

AND J. C. GREEN AND O. N. KIRCHNER

Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, England

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Abstract. $M_r = 414{\cdot}07$, monoclinic, $P2_1/m$, $a = 7{\cdot}702\,(1)$, $b = 13{\cdot}747\,(2)$, $c = 9{\cdot}304\,(1)$ Å, $\beta = 107{\cdot}92\,(1)°$, $U = 937{\cdot}3$ Å^3, $Z = 2$, $D_x = 1{\cdot}47$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ(Mo $K\alpha$) = 2·848 mm^{-1}, $F(000) = 412$, room temperature, $R = 0{\cdot}032$ for 1466 unique reflections. Each molecule possesses *m* symmetry and the central Co is found in a distorted tetrahedral coordination environment [Co—I 2·5495 (8), Co—P 2·232 (2), 2·237 (1) (×2) Å] agreeing well with predictions based on magnetic measurements.

Introduction. The four-coordinate d^8 complexes of the second- and third-row transition metals Rh and Ir adopt a square-planar geometry. This leads to a low-spin diamagnetic $e_g(4)a_{1g}(2)b_{2g}(2)$ molecule in which the strongly antibonding b_{1g} $(d_{x^2-y^2})$ orbital remains unfilled at the expense of spin-pairing of two electrons. Many examples of such compounds are known. In contrast the d^8 Co^I complexes adopt a high-spin $e(4)t_2(4)$ electronic configuration. A tetrahedral coordination geometry has been predicted but hitherto unproved as such complexes are easily oxidized to Co^{II} or react with neutral σ donors to give 18-electron five-coordinate species, generally of trigonal-bipyramidal geometry. We now report the crystal structure of $Co(PMe_3)_3I$, a tetrahedral four-coordinate Co^I d^8 complex. The complex was formed as a byproduct of the sodium-amalgam reduction of the half-sandwich complex $Co(\eta\text{-}C_5Me_5)(PMe_3)I_2$ and was isolated owing to the ease with which it crystallized from solution in petroleum ether as deep-blue, tabular, air-sensitive crystals. The complexes $Co(PMe_3)_3X$ (X = Cl, Br, I) are most conveniently synthesized by alternative literature preparations (Klein & Karsch, 1975*a*,*b*).

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