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

Os1–Br	2·559 (2)	Os1–Br2	2·544 (2)
Os1–O	2·07 (1)	OS1–C11	1·76 (3)
Os1–C12	1·89 (2)	Os1–C13	1·92 (2)
Os2–Br	2·569 (2)	Os2–Br1	2·552 (2)
Os2–C	2·09 (1)	Os2–C21	1·95 (2)
Os2–C22	1·92 (2)	Os2–C23	1·84 (2)
C–O	1·25 (2)	C–N	1·39 (2)
N–Cl	1·47 (2)	Cl–C2	1·51 (3)
C1–C3	1·45 (3)	C11–O11	1·22 (3)
C12–O12	1·12 (2)	C13–O13	1·13 (2)
C21–O21	1·17 (2)	C22–O22	1·09 (2)
C23–O23	1·14 (3)		
Br–Os1–Br2	88·1 (1)	Br–Os1–O	88·0 (3)
Br–Os1–C11	175·6 (7)	Br–Os1–C12	90·3 (6)
Br–Os1–C13	92·2 (6)	Br2–Os1–O	85·8 (3)
Br2–Os1–C11	87·4 (7)	Br2–Os1–C12	89·6 (6)
Br2–Os1–C13	178·9 (5)	O–Os1–C11	91·3 (8)
O–Os1–C12	175·1 (7)	O–Os1–C13	93·2 (7)
C11–Os1–C12	90·(1)	C11–Os1–C13	92·(1)
C12–Os1–C13	91·5 (8)	Br–Os2–Br1	89·0 (1)
Br–Os2–C	87·0 (5)	Br–Os2–C21	91·1 (7)
Br–Os2–C22	88·4 (6)	Br–Os2–C23	177·3 (6)
Br1–Os2–C	89·2 (4)	Br1–Os2–C21	87·5 (5)
Br1–Os2–C22	176·8 (6)	Br1–Os2–C23	88·3 (6)
C–Os2–C21	176·2 (7)	C–Os–C22	88·7 (7)
C–Os2–C23	92·4 (9)	C21–Os2–C22	94·5 (8)
C21–Os2–C23	89· (1)	C22–Os2–C23	94·2 (9)
Os1–Br–Os2	101·0 (1)	Os2–C–O	129· (1)
Os2–C–N	120· (1)	O–C–N	111· (1)
Os1–O–C	131· (1)	C–N–C1	128· (1)
N–C1–C2	108· (2)	N–C1–C3	106· (1)
C2–C1C3	113· (1)	Os1–C11–O11	178· (1)
OS1–C12–O12	179· (1)	Os1–C13–O13	174· (2)
Os2–C21–O21	174· (2)	Os2–C22–O22	178· (1)
Os2–C23–O23	176· (1)		

(Morrison, Geoffroy, Rheingold & Fultz, 1985). In our compound the Os1—Br—Os2 angle is 101·0(1)°. The Os—C(CO) distances are somewhat shorter for two CO ligands *trans* to the bridged Br ligand [Os2—C23, 1·84 (2), Os1—C11, 1·76 (3) Å]. Similar phenomena were observed previously (Churchill & Lashewycz, 1979). Since both Os metal atoms are in a formally divalent oxidation state, the corresponding C—O distances are normal, and the relatively shorter Os—C distance may be due to the stronger σ donor ability of the CO ligand affected by the unique *trans* influence of the bridged Br ligand. The carboxamido ligand shows partial double-bond character for both C=O [1·25 (2) Å] and CN [1·39 (2) Å] bonds, similar to many other complexes of the same type (Szostak, Strouse & Kaesz, 1980). The hindered rotation about the C—N bond was indicated by the nonequivalence of the two methyl groups in the NMR spectrum. The carboxamido group (OCN) is planar with the O—C—N angle smaller than for a normal sp^2 hybrid.

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References

Churchill, M. R. & Lashewycz, R. A. (1979). *Inorg. Chem.* **18**, 1926–1930.

Dombek, B. D. (1981). *J. Am. Chem. Soc.* **103**, 6508–6510.

Gabe, E. J. & Lee, F. L. (1981). *Acta Cryst.* A**37**, C339.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Lin, Y. C., Mayr, A., Knobler, C. B. & Kaesz, H. D. (1984). *J. Organomet. Chem.* **272**, 207–229.

Morrison, E. D., Geoffroy, G. L. & Rheingold, A. L. (1985). *J. Am. Chem. Soc.* **107**, 254–255.

Morrison, E. D., Geoffroy, G. L., Rheingold, A. L. & Fultz, W. C. (1985). *Organometallics*, **4**, 1413–1418.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Szostak, R., Strouse, C. E. & Kaesz, H. D. (1980). *J. Organomet. Chem.* **191**, 243–260.

Acta Cryst. (1988). C**44**, 981–986

Polydentate Chelates. 3. Structures of egta^{4-} Chelates of Manganese(II) and Copper(II): $\mathrm{Sr[Mn(egta)].7H_2O}$ and $\mathrm{[Cu_2(egta)(OH_2)_2].2H_2O}$

By Cynthia K. Schauer and Oren P. Anderson*

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523, *USA*

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Abstract. Compound (1): $\mathrm{Sr[Mn(C_{14}H_{20}N_2O_{10})].7H_2O}$, $M_r = 645{\cdot}0$, monoclinic, $P2_1/n$, $a = 16{\cdot}535\,(4)$, $b = 8{\cdot}415\,(2)$, $c = 17{\cdot}457\,(4)$ Å, $\beta = 97{\cdot}11\,(2)°$, $V = 2410{\cdot}3\,(5)$ Å^3, $Z = 4$, $D_x = 1{\cdot}78$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 28{\cdot}97$ cm^{-1}, $F(000) = 1324$, $T = 143$ K. Compound (2): $\mathrm{[Cu_2(C_{14}H_{20}N_2O_{10})(H_2O)_2].2H_2O}$, $M_r = 575{\cdot}5$, monoclinic, $C2/c$, $a = 20{\cdot}962\,(5)$, $b = 7{\cdot}513\,(2)$, $c = 13{\cdot}545\,(2)$ Å, $\beta = 90{\cdot}85\,(2)°$, $V = 2132{\cdot}9\,(4)$ Å^3, $Z = 4$, $D_x = 1{\cdot}79$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 20{\cdot}71$ cm^{-1}, $F(000) = 1184$, $T = 143$ K. For (1), $R = 0{\cdot}036$ for 3421 unique observed reflections; for (2), $R = 0{\cdot}031$ for 1670 unique observed reflections.

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* To whom all correspondence should be addressed.

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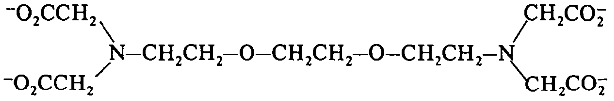
In (1) the octadentate $egta^{4-}$ ligand ($egta^{4-}$ = the anion of 3,12-bis(carboxymethyl)-6,9-dioxa-3,12-diazatetradecanedioic acid) forms a complex anion $\{[Mn(egta)]^{2-}\}$ with a distorted dodecahedral coordination sphere. The carboxylate O atoms of $egta^{4-}$ are bound to Mn^{II} at shorter distances [Mn—O(carb,ave.) = 2·25 (3) Å] than are the N atoms [Mn—N(ave.) = 2·426 (1) Å] and the ether O atoms [Mn—O(ether,ave.) = 2·51 (3) Å]; the Mn—N distances in (1) are exceptionally long. The compound $[Cu_2(egta)(OH_2)_2].2H_2O$ (2) contains neutral centrosymmetric dinuclear $[Cu_2(egta)(OH_2)_2]$ units. The coordination of Cu^{II} is square pyramidal; the basal plane contains an amino N atom [Cu—N = 1·992 (2) Å], two carboxylate oxygen atoms [Cu—O(carb,ave.) = 1·934 (8) Å], and a water molecule [Cu—O_w = 1·938 (2) Å], while an ether O atom is bound at a long distance [Cu—O(ether) = 2·408 (2) Å] in the apical site.

Introduction. The structural aspects of metal ion chelation by 'highly polydentate' ligands (*i.e.* ligands possessing six or more metal-binding sites) have been the subject of recent studies in this laboratory. The octadentate ligand $egta^{4-}$ has been of particular interest as a model for the binding sites of calcium-binding proteins, and the structures of the calcium and cadmium complexes of this ligand have been recently reported (Schauer & Anderson, 1987). Both Ca^{2+} and Cd^{2+} utilize the octadentate chelating capability of the $egta^{4-}$ ligand to form eight-coordinate complex ions.



$egta^{4-}$

Eight-coordination is not common for metals of the first transition series, however. In order to explore the structural variations that occur on formation of complexes between $egta^{4-}$ and metal ions smaller than calcium, the structures of manganese(II) and copper(II) complexes of $egta^{4-}$ have been determined. The high-spin manganese(II) ion, with an eight-coordinate ionic radius of 0·96 Å (Shannon, 1976), is the largest of the dipositive first-row transition-metal ions, yet is much smaller than the calcium ion ($r_{\rm ion}$ = 1·12 Å for eight-coordination). If eight-coordination is possible for any first-series transition-metal ion, it is most likely to be for this case.

The much smaller copper(II) ion ($r_{\rm ion}$ = 0·73 Å for six-coordination) is not likely to form an eight-coordinate complex ion. Indeed, in $[Cu(H_3dtpa)]$[H_5dtpa = 3,6,9-tris(carboxymethyl)-3,6,9-triazaundecanedioic acid, potentially octadentate] Cu^{II} was bound in a distorted octahedron, and two of the carboxylic acid groups were not coordinated to the metal (Seccombe, Lee & Henry, 1975). The manner in which Cu^{II} would achieve a coordination number less than eight with $egta^{4-}$ was of interest, especially given the weak coordinating ability of the two ether O atoms in that ligand.

Experimental. All chemicals used as purchased: H_4egta (J. T. Baker), $Sr(OH)_2.8H_2O$ (Alfa), $MnCO_3$ (J. T. Baker), $CuCO_3$ (Mallinckrodt).

$Sr[Mn(egta)].7H_2O$ (1). $MnCO_3$ (0·230 g, 1·00 mmol), H_4egta (0·380 g, 1·00 mmol) dissolved in 10 mL of boiling water. $Sr(OH)_2.8H_2O$ (0·530 g, 1·00 mmol) added, resulting solution filtered. Colorless crystal (0·32 × 0·36 × 0·50 mm) obtained after addition of 10 mL hot water, 30 mL acetone, slow cooling. Nicolet *R*3*m* diffractometer, cell constants from least-squares fitting of setting angles for 25 reflections ($2\theta_{\rm ave}$ = 20·65°). Data collected for $3·5 \le 2\theta \le 50·0°$, $\pm h$, $-k$, $-l$, $\theta/2\theta$ scans. Three reflections ($\bar{1}\bar{1}8$, $0\bar{4}0$, $80\bar{2}$) monitored every 97 data points showed rapid degradation at room temperature, no variation in intensity at 143 K. Lorentz and polarization corrections applied, also empirical absorption correction (ψ-scan data, transmission factors ±25% of mean value); of 4087 unique reflections, 3421 observed [$I \ge 2\sigma(I)$] and used in further calculations. Structure isomorphous with $Sr[Cd(egta)].7H_2O$ (Schauer & Anderson, 1987), coordinates from that structure used as starting point for refinement (Sheldrick, 1983); all non-H atoms refined anisotropically; C-bound H atoms included in calculated positions. Block weighted $\{w = [\sigma^2(F) + gF^2]^{-1}$, $g = 6·2 \times 10^{-4}\}$ least-squares refinement on *F* yielded R = 0·036, wR = 0·049, S = 1·40 at convergence (mean shift/e.s.d. < 0·01, max. shift/e.s.d. < 0·05, over last three cycles), with largest peak in final Fourier synthesis of ±0·7 e $Å^{-3}$ (H atom of water molecule), minimum of −0·3 e $Å^{-3}$. Neutral-atom scattering factors and anomalous-dispersion correction terms used (*International Tables for X-ray Crystallography,* 1974); software for diffractometer provided with Nicolet *R*3*m*; *SHELXTL* programs (Sheldrick, 1983) used for structure refinement and plotting.[*]

Solid-state magnetic susceptibility measured at room temperature {Cahn-Ventron 7600 Faraday magnetic susceptibility system, $Hg[Co(SCN)_4]$ calibrant, corrected using Pascal's constants}. Room-temperature magnetic moment (μ = 5·90 BM) confirms high-spin nature of Mn^{II} in (1).

$[Cu_2(egta)(OH_2)_2].2H_2O$ (2). $CuCO_3$ (0·248 g, 2·00 mmol), H_4egta (0·380 g, 1·00 mmol) dissolved in 15 mL of water. Blue crystal [0·37 ($010 \rightarrow 0\bar{1}0$) × 0·18 ($001 \rightarrow 00\bar{1}$) × 0·11 ($100 \rightarrow \bar{1}00$) mm] obtained on slow

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[*] Lists of H-atom coordinates, anisotropic thermal parameters, and observed and calculated structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44749 (41 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

evaporation. Nicolet $R3m$ diffractometer, cell constants from least-squares fitting of setting angles for 25 reflections ($2\theta_{\rm ave} = 22{\cdot}04°$). Crystals of (2) commonly twinned, single crystal obtained by appropriate cleavage. Data collected for $3{\cdot}5 \leq 2\theta \leq 50{\cdot}0°$, $-h$, $-k$, $\pm l$, $\theta/2\theta$ scans. Three reflections ($\bar{8}00$, $\bar{1}\bar{3}5$, $\bar{1}\bar{3}2$) monitored every 97 data points showed no significant variation. Lorentz and polarization corrections applied, also analytical absorption correction (transmission factors ±8% of mean value); of 1866 unique reflections, 1670 observed [$I \geq 2\sigma(I)$] and used in further calculations. Crystallographically unique copper(II) atom located by Patterson map interpretation, other atoms of unique half of molecule located in subsequent Fourier syntheses (Sheldrick, 1983); all non-H atoms refined anisotropically; C-bound H atoms included in calculated positions. Block weighted $\{w = [\sigma^2(F) + gF^2]^{-1}, g = 4{\cdot}7 \times 10^{-4}\}$ least-squares refinement on F yielded $R = 0{\cdot}031$, $wR = 0{\cdot}046$, and $S = 1{\cdot}61$ at convergence (mean shift/e.s.d. $< 0{\cdot}001$, max. shift/e.s.d. $< 0{\cdot}005$, over last three cycles), with highest peak in final Fourier synthesis of $+0{\cdot}7$ e Å^{-3} (H atom of water molecule), minimum of $-0{\cdot}3$ e Å^{-3}. Neutral-atom scattering factors and anomalous-dispersion correction terms used (*International Tables for X-ray Crystallography,* 1974); software for diffractometer provided with Nicolet $R3m$; *SHELXTL* programs (Sheldrick, 1983) used for structure solution, refinement and plotting.

Discussion. The structure of the $[\mathrm{Mn(egta)}]^{2-}$ complex ion in (1) is depicted in Fig. 1, and that of the neutral dinuclear $[\mathrm{Cu_2(egta)(OH_2)_2}]$ complex in (2) is depicted in Fig. 2. Final atomic coordinates and equivalent isotropic thermal parameters for refined atoms are given in Table 1 for (1) and in Table 2 for (2); selected bond lengths and angles for (1) and (2) are given in Tables 3 and 4, respectively.

$\mathrm{Sr[Mn(egta)].7H_2O}$ (1)

Both the Ca ion ($r_{\rm ion} = 1{\cdot}12$ Å) and the Cd ion ($r_{\rm ion} = 1{\cdot}10$ Å) (Shannon, 1976) form eight-coordinate chelates with egta^{4-} (Schauer & Anderson, 1987). The ionic radius of an eight-coordinate high-spin Mn$^{\rm II}$ ion is 0·14 Å less than that of a Cd$^{\rm II}$ ion. If the ligand atoms of egta^{4-} bind to Mn$^{\rm II}$ at distances consistent with the metal's smaller radius, a coordination number lower than eight might be expected in the $[\mathrm{Mn(egta)}]^{2-}$ complex ion.

That expectation is not realized. As may be seen in Fig. 1, the egta^{4-} ligand utilizes all eight of its binding sites in coordinating the Mn$^{\rm II}$ atom. Just as in $[\mathrm{Ca(egta)}]^{2-}$ and $[\mathrm{Cd(egta)}]^{2-}$, the polyhedron formed by the ligand atoms about the Mn$^{\rm II}$ ion is best described as dodecahedral. A dodecahedron is commonly described as resulting from the orthogonal intersection of two trapezoids (with vertices *BAAB*) – in (1) the trapezoids are formed by O(1) (*B*), N(1) (*A*), O(3) (*A*) and O(9) (*B*), as well as by O(7) (*B*), N(2) (*A*), O(6) (*A*) and O(5) (*B*). Constraints associated with the chelating nature of the ligand distort the trapezoids from planarity to a small degree [deviations from least-squares planes: O(1) 0·16 (1), N(1) −0·26 (1), O(3) 0·26 (1), O(9) −0·16 (1); O(7) −0·13 (1), N(2) 0·22 (1), O(6) −0·22 (1), O(5) 0·13 (1) Å]. The dihedral angle between the trapezoidal least-squares planes [90·5 (1)°] is very close to the expected value of 90°.

As might be expected from the isomorphous character of crystals of (1) and of $\mathrm{Sr[Cd(egta)].7H_2O}$, the complex anions and the partially aquated Sr counterions in these two compounds engage in very similar patterns of bridging interactions involving carboxylate groups and occluded water molecules. Differences in details of interionic bonding do exist between these two structures, of course, and the largest such disparity occurs in the bidentate bridge to the Sr atom involving O(7) [Sr—O(7) = 3·162 (3) Å in (1); Sr—O(7) = 2·995 (3) Å in the Cd compound].

The Mn$^{\rm II}$ and Cd$^{\rm II}$ atoms exhibit similar ligand-atom preferences in binding egta^{4-}. In (1), the carboxylate O

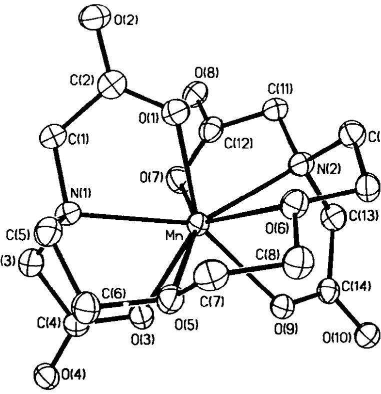

Fig. 1. A thermal-ellipsoid plot (50% probability) of the $[\mathrm{Mn(egta)}]^{2-}$ complex anion in (1). H atoms have been omitted for clarity.

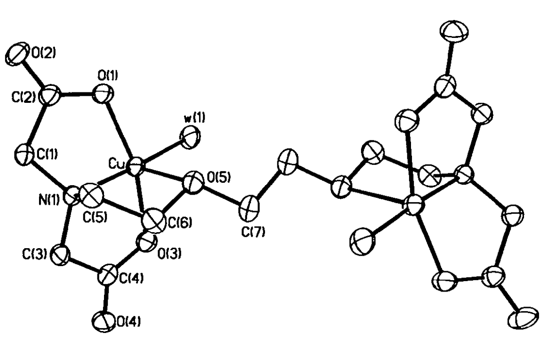

Fig. 2. A thermal-ellipsoid plot (50% probability) of the dinuclear unit in (2). A center of inversion relates the unlabeled half of the molecule to the labeled half. H atoms have been omitted for clarity.

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($\text{Å}^2 \times 10^3$) *for* (1)

E.s.d.'s in the least-significant digits are given in parentheses.

	x	*y*	*z*	U_{eq}*
Mn	7564 (1)	608 (1)	105 (1)	20 (1)
Sr	9228 (1)	5210 (1)	821 (1)	24 (1)
C(1)	6361 (2)	−2013 (5)	532 (2)	25 (1)
C(2)	6189 (2)	−1729 (5)	−337 (2)	25 (1)
C(3)	7085 (2)	−869 (5)	1710 (2)	29 (1)
C(4)	7817 (2)	192 (4)	1901 (2)	23 (1)
C(5)	5961 (2)	548 (5)	977 (2)	28 (1)
C(6)	6249 (2)	2202 (5)	1154 (2)	27 (1)
C(7)	6181 (2)	3610 (5)	−49 (2)	28 (1)
C(8)	6703 (2)	4022 (5)	−663 (2)	27 (1)
C(9)	7509 (2)	2766 (5)	−1519 (2)	24 (1)
C(10)	7792 (2)	1135 (5)	−1721 (2)	26 (1)
C(11)	8264 (2)	−1409 (5)	−1200 (2)	26 (1)
C(12)	8395 (2)	−2383 (5)	−459 (2)	25 (1)
C(13)	9054 (2)	936 (5)	−834 (2)	26 (1)
C(14)	9084 (2)	2323 (5)	−278 (2)	22 (1)
N(1)	6653 (2)	−562 (4)	937 (2)	23 (1)
N(2)	8232 (2)	290 (4)	−1047 (2)	23 (1)
O(1)	6550 (2)	−588 (3)	−617 (2)	27 (1)
O(2)	5712 (2)	−2675 (4)	−714 (2)	30 (1)
O(3)	8140 (2)	746 (4)	1344 (2)	29 (1)
O(4)	8090 (2)	386 (3)	2600 (2)	26 (1)
O(5)	6698 (2)	2767 (3)	548 (2)	25 (1)
O(6)	6998 (2)	2559 (3)	−926 (2)	25 (1)
O(7)	8289 (2)	−1710 (3)	164 (2)	28 (1)
O(8)	8579 (2)	−3822 (3)	−528 (2)	29 (1)
O(9)	8494 (2)	2532 (3)	106 (1)	23 (1)
O(10)	9707 (2)	3191 (3)	−205 (2)	26 (1)
w(1)†	9435 (2)	2685 (4)	1627 (2)	53 (1)
w(2)	10680 (2)	5233 (3)	1715 (2)	29 (1)
w(3)	9104 (2)	7554 (4)	1727 (2)	36 (1)
w(4)	7814 (2)	4937 (4)	1222 (2)	32 (1)
w(5)	5249 (2)	5970 (4)	1931 (2)	36 (1)
w(6)	4480 (2)	2963 (4)	2222 (2)	34 (1)
w(7)	10596 (2)	3914 (4)	3121 (2)	35 (1)

* Equivalent isotropic *U* is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

† *w*(*n*) refers to the O atom of water molecule *n*.

Table 2. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($\text{Å}^2 \times 10^3$) *for* (2)

E.s.d.'s in the least-significant digits are given in parentheses.

	x	*y*	*z*	U_{eq}*
Cu	3712 (1)	2799 (1)	4361 (1)	23 (1)
C(1)	3441 (2)	6276 (4)	4875 (2)	27 (1)
C(2)	3746 (2)	6266 (4)	3851 (2)	28 (1)
C(3)	3111 (2)	3979 (4)	6092 (2)	25 (1)
C(4)	2969 (2)	2014 (4)	5928 (2)	27 (1)
C(5)	4238 (1)	4833 (4)	5944 (2)	28 (1)
C(6)	4532 (2)	3070 (5)	6196 (2)	31 (1)
C(7)	4849 (2)	336 (5)	5464 (3)	36 (1)
N(1)	3610 (1)	4625 (3)	5413 (2)	21 (1)
O(1)	3953 (1)	4772 (3)	3536 (2)	31 (1)
O(2)	3768 (1)	7641 (3)	3377 (2)	44 (1)
O(3)	3241 (1)	1224 (3)	5219 (2)	28 (1)
O(4)	2584 (1)	1293 (3)	6487 (2)	37 (1)
O(5)	4671 (1)	2158 (3)	5295 (2)	30 (1)
w(1)	3810 (1)	1115 (3)	3290 (2)	34 (1)
w(2)	2976 (1)	2114 (3)	1893 (2)	40 (1)

* Equivalent isotropic *U* is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3. *Selected bond lengths* (Å) *and angles* (°) *for* (1)

E.s.d.'s in the least-significant digits are given in parentheses.

(*a*) Complex ion		(*b*) Counterion	
Mn—N(1)	2·426 (3)	Sr—O(9)	2·781 (3)
Mn—N(2)	2·427 (3)	Sr—O(10)	2·660 (3)
Mn—O(1)	2·211 (3)	Sr—*w*(1)	2·547 (4)
Mn—O(3)	2·256 (3)	Sr—*w*(2)	2·697 (3)
Mn—O(5)	2·493 (3)	Sr—*w*(3)	2·552 (3)
Mn—O(6)	2·529 (3)	Sr—*w*(4)	2·531 (3)
Mn—O(7)	2·285 (3)	Sr—O(7*a*)	3·163 (3)
Mn—O(9)	2·233 (3)	Sr—O(8*a*)	2·596 (3)
		Sr—O(10*a*)	2·558 (3)
N(1)—Mn—N(2)	146·2 (1)	O(9)—Sr—O(10)	47·9 (1)
N(1)—Mn—O(1)	71·0 (1)	O(9)—Sr—*w*(1)	66·0 (1)
N(2)—Mn—O(1)	82·4 (1)	O(10)—Sr—*w*(1)	78·9 (1)
N(1)—Mn—O(3)	70·6 (1)	O(9)—Sr—*w*(2)	125·0 (1)
N(2)—Mn—O(3)	128·3 (1)	O(10)—Sr—*w*(2)	94·3 (1)
O(1)—Mn—O(3)	140·4 (1)	*w*(1)—Sr—*w*(2)	68·7 (1)
N(1)—Mn—O(5)	71·8 (1)	O(9)—Sr—*w*(3)	147·2 (1)
N(2)—Mn—O(5)	132·4 (1)	O(10)—Sr—*w*(3)	164·6 (1)
O(1)—Mn—O(5)	94·9 (1)	*w*(1)—Sr—*w*(3)	108·6 (1)
O(3)—Mn—O(5)	81·7 (1)	*w*(2)—Sr—*w*(3)	76·7 (1)
N(1)—Mn—O(6)	119·1 (1)	O(9)—Sr—*w*(4)	71·6 (1)
N(2)—Mn—O(6)	69·4 (1)	O(10)—Sr—*w*(4)	119·4 (1)
O(1)—Mn—O(6)	72·7 (1)	*w*(1)—Sr—*w*(4)	80·7 (1)
O(3)—Mn—O(6)	136·4 (1)	*w*(2)—Sr—*w*(4)	128·8 (1)
O(5)—Mn—O(6)	64·7 (1)	*w*(3)—Sr—*w*(4)	75·6 (1)
N(1)—Mn—O(7)	89·3 (1)	O(9)—Sr—O(7*a*)	109·5 (1)
N(2)—Mn—O(7)	69·7 (1)	O(10)—Sr—O(7*a*)	116·9 (1)
O(1)—Mn—O(7)	89·6 (1)	*w*(1)—Sr—O(7*a*)	155·5 (1)
O(3)—Mn—O(7)	81·0 (1)	*w*(2)—Sr—O(7*a*)	124·5 (1)
O(5)—Mn—O(7)	157·8 (1)	*w*(3)—Sr—O(7*a*)	61·2 (1)
O(6)—Mn—O(7)	137·0 (1)	*w*(4)—Sr—O(7*a*)	75·3 (1)
N(1)—Mn—O(9)	140·6 (1)	O(9)—Sr—O(8*a*)	74·8 (1)
N(2)—Mn—O(9)	72·3 (1)	O(10)—Sr—O(8*a*)	73·4 (1)
O(1)—Mn—O(9)	143·5 (1)	*w*(1)—Sr—O(8*a*)	140·8 (1)
O(3)—Mn—O(9)	75·7 (1)	*w*(2)—Sr—O(8*a*)	139·6 (1)
O(5)—Mn—O(9)	83·9 (1)	*w*(3)—Sr—O(8*a*)	105·3 (1)
O(6)—Mn—O(9)	74·0 (1)	*w*(4)—Sr—O(8*a*)	89·3 (1)
O(7)—Mn—O(9)	105·2 (1)	O(7*a*)—Sr—O(8*a*)	44·3 (1)
		O(9)—Sr—O(10*a*)	121·5 (1)
		O(10)—Sr—O(10*a*)	76·9 (1)
		w(1)—Sr—O(10*a*)	128·2 (1)
		w(2)—Sr—O(10*a*)	68·3 (1)
		w(3)—Sr—O(10*a*)	88·1 (1)
		w(4)—Sr—O(10*a*)	150·6 (1)
		O(7*a*)—Sr—O(10*a*)	75·4 (1)
		O(8*a*)—Sr—O(10*a*)	71·4 (1)

Table 4. *Selected bond lengths* (Å) *and angles* (°) *for* (2)

E.s.d.'s in the least-significant digits are given in parentheses.

Cu—N(1)	1·992 (2)	Cu—O(5)	2·408 (2)
Cu—O(1)	1·928 (2)	Cu—*w*(1)	1·938 (2)
Cu—O(3)	1·939 (2)		
N(1)—Cu—O(1)	85·2 (1)	O(3)—Cu—O(5)	89·5 (1)
N(1)—Cu—O(3)	86·0 (1)	N(1)—Cu—*w*(1)	177·2 (1)
O(1)—Cu—O(3)	163·1 (1)	O(1)—Cu—*w*(1)	92·1 (1)
N(1)—Cu—O(5)	81·9 (1)	O(3)—Cu—*w*(1)	96·4 (1)
O(1)—Cu—O(5)	103·5 (1)	O(5)—Cu—*w*(1)	99·5 (1)

atoms are bound to Mn^{2+} at the shortest distances [Mn—O(carb,ave.) = 2·25 (3) Å], followed by the amine N atoms [Mn—N(ave.) = 2·426 (1) Å] and the ether O atoms [Mn—O(ether,ave.) = 2·51 (3) Å]. In $\mathrm{Mn[Mn(Hedta)]_2.10H_2O}$ (Richards, Pederson, Silverton & Hoard, 1964), the mean Mn—O(carb) distance [2·24 (2) Å] is nearly identical with that found in (1), while the mean Mn—N distance [2·38 (3) Å] is shorter by 0·05 Å. Unfortunately, good comparison data do not exist for $\mathrm{Mn^{II}}$—O(ether) bond lengths.

The differences in the mean metal–ligand bonding parameters exhibited for $\mathrm{[Mn(egta)]^{2-}}$ and $\mathrm{[Cd(egta)]^{2-}}$ differ among the ligand atom types. The amine N atoms are bound at the same distance in the two complexes, while the carboxylate O atoms and ether O atoms in (1) are bound at average distances 0·10 and 0·09 Å shorter, respectively, than in the Cd^{II} complex. Since the carboxylate oxygen atoms are bound at a 'normal' distance (based on the $Hedta^{3-}$ structure), the strain associated with achieving eight-coordination about high-spin Mn^{II} is accommodated in the N—O—O—N belt of the chelate, mainly by forming very long (and presumably very weak) Mn—N bonds.

Conformational parameters associated with the chelate rings in (1) are very similar to the corresponding parameters in the cadmium complex. Thus, the observed differences in the metal–ligand bond lengths must result in differences in the bond angles characterizing the chelate. If one compares the $[Mn(egta)]^{2-}$ and $[Cd(egta)]^{2-}$ chelates, Mn—O(carb)—C > Cd—O(carb)—C, and Mn—O(ether)—C > Cd—O(ether)—C. These results are as expected, given the shorter bond lengths between the ether O atoms and carboxylate O atoms and the Mn^{II} ion. The corresponding angles involving the N atoms are nearly identical for the two complexes.

The lack of ^{17}O line broadening for the water resonance in NMR experiments on aqueous solutions of $[Mn(egta)]^{2-}$ led earlier investigators to conclude that the $egta^{4-}$ ligand was octahedrally coordinated to Mn^{II}, and that no water molecules were bound to the metal ion (Zetter, Grant, Wood, Dodgen & Hunt, 1972). The structure of the $[Mn(egta)]^{2-}$ anion lends credence to the latter conclusion, but suggests that the complex anion is eight-coordinate in solution, rather than octahedral.

$[Cu_2(egta)(OH_2)_2].2H_2O$ (2)

Only half of this dinuclear species is crystallographically unique (see Fig. 2), the other half being generated by a center of inversion at the midpoint of the C(7)—C(7′) bond. Each Cu^{II} atom exhibits square-pyramidal coordination, with ligand atoms including the O atom of a water molecule as well as the ether O atom, amine N atom, and the O atoms of two carboxylate groups at one end of $egta^{4-}$. The structure of this dinuclear Cu^{II} complex is quite different from that of the dinuclear magnesium complex of $egta^{4-}$ (Schauer, 1985), in which the ether O atoms are not utilized in coordination to the metal ion. In addition, the O atoms of the carboxylate groups occupy *cis* coordination sites in the Mg^{2+} complex, whereas they occupy *trans* sites in (2).

A dinuclear Cu^{II} complex of $edta^{4-}$ has been structurally characterized (Filippova, Polynova, Porai-Koshits, Novozhilova & Martynenko, 1973); in that complex each end of the $edta^{4-}$ acts as a tridentate ligand, and the coordination of the aminodiacetate portions of the ligand is similar to that in (2). In that $edta^{4-}$ complex, the Cu^{II} ions achieve square-pyramidal coordination through the binding of two water molecules.

In (2), $w(1)$ binds to Cu^{II} at the same distance [1·938 (2) Å] as do the carboxylate oxygen atoms [Cu—O(carb,ave.) = 1·934 (8) Å]. These distances are slightly shorter than those seen for comparable bonds in the six-coordinate H_3dtpa^{2-} (Seccombe, Lee & Henry, 1975), nta^{3-} (Whitlow, 1973; Fomenko, Kopaneva, Porai-Koshits & Polynova, 1974), ida^{2-} (Podder, Dattagupta, Saha & Saenger, 1979), and oda^{2-} (Whitlow & Davey, 1975) copper(II) complexes [Cu—O = 1·941 (3)–1·991 (3) Å].

The amine N atom is bound at a slightly longer distance than are the O atom donors [1·992 (2) Å]. This distance is also shorter than the corresponding distances in the nta^{3-}, ida^{2-}, and H_3dtpa^{2-} complexes [Cu—N = 2·014 (3)–2·086 (5) Å]. While the structures of the six-coordinate $[Cu(edta)]^{2-}$ complex ion (Novozhilova, Polynova, Porai-Koshits & Martynenko, 1967; Nesterova, Porai-Koshits & Logvinenko, 1979) and of $[Cu_2(edta)(OH_2)_4]$ (Filippova, Polynova, Porai-Koshits, Novozhilova & Martynenko, 1973) have been determined, the low precision of those results makes them of little value for comparison purposes. The ether O atom occupies the weakly bound apical site of the square pyramid. As expected, the Cu—O(ether) bond is long [2·408 (2) Å], although it is shorter than the bond between Cu^{II} and the ether O atom of oda^{2-} [2·488 (7) Å].

In six-coordinate $Cu(ida)(OH_2)_2$ and $Cu(oda)(OH_2)_3$, carboxylate O atoms of the ida^{2-} and oda^{2-} ligands occupy *cis* coordination sites. The adoption of a *trans* geometry in (2) must occur to maintain the N and the carboxylate O atoms in the basal coordination plane, where bonds to the metal are strong, and to restrict the weakly coordinating ether O atom to the apical site of the square pyramid. The Cu^{II} atom is 0·13 (1) Å above the least-squares plane through the basal ligand atoms, and the distance of closest approach of a ligand to the potential sixth coordination site [Cu—O(4′) = 3·012 (2) Å] does not suggest any significant bonding interaction.

Relationship of solid-state structure to solution structure. The relative ease of protonation of metal chelates has been used as an indication of whether ligand amine N atoms are bound (Kula, Sawyer, Chan & Finley, 1963). For a dinuclear Mg ion complex of $egta^{4-}$, $[Mg_2(egta)(OH_2)_6].5H_2O$, this criterion suggests that Mg^{2+} binds to only one end of the $egta^{4-}$ ligand in solution (Schauer, 1985). The equilibrium constants for protonation of $[Mg(egta)]^{2-}$ and $[Mg(edta)]^{2-}$ differ by nearly four orders of magnitude. Since $edta^{4-}$ is known to form a sexadentate chelate with Mg^{2+} (Stezowski, Countryman & Hoard, 1973), this large difference in protonation constants must be attributed to a structural difference between the two chelates.

Equilibrium constants for protonation of Cu^{II} and Mn^{II} ML^{2-} complexes are very similar (Table 5; Martell & Smith, 1974). Thus, it seems likely that the

Table 5. *Selected stability constants*

The number to the left in each case is log K for the complexation of M^{2+} by L^{4-}, while the number to the right is log K for protonation of the complex ion ML^{2-}. Values are taken from Martell & Smith (1974).

Metal	egta^{4-}	edta^{4-}
Cu^{2+}	17·6/4·3	18·8/3·0
Mn^{2+}	12·2/4·1	13·9/3·1
Mg^{2+}	5·2/7·6	8·8/3·9

egta^{4-} ligand utilizes both amine N atoms in coordinating to Cu^{II} in solution. Preferential crystallization of (2) must be attributed to the low solubility of the neutral dinuclear species, and to the adoption of an especially favorable coordination environment about the Cu^{II} ion. The equilibrium constant for the formation of the dinuclear Cu^{II} complex has been measured [$Cu^{2+} + Cu(egta)^{2-} \rightleftarrows Cu_2(egta)$, log K = 4·31 (Ohzeki, Saruhashi & Kambara, 1980)].

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References

Filippova, T. V., Polynova, T. N., Porai-Koshits, M. A., Novozhilova, N. V. & Martynenko, L. I. (1973). *Zh. Strukt. Khim.* **14**, 280–285.

Fomenko, V. V., Kopaneva, L. I., Porai-Koshits, M. A. & Polynova, T. N. (1974). *Zh. Strukt. Khim.* **15**, 268–274.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 55, 99, 149. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Kula, R. J., Sawyer, D. T., Chan, S. I. & Finley, C. M. (1963). *J. Am. Chem. Soc.* **85**, 2930–2936.

Martell, A. E. & Smith, R. M. (1974). *Critical Stability Constants*. Vol. I. New York: Plenum.

Nesterova, Ya. M., Porai-Koshits, M. A. & Logvinenko, V. A. (1979). *Zh. Neorg. Khim.* **24**, 2273–2274.

Novozhilova, N. V., Polynova, T. N., Porai-Koshits, M. A. & Martynenko, L. I. (1967). *Zh. Strukt. Khim.* **8**, 553–554.

Ohzeki, K., Saruhashi, M. & Kambara, T. (1980). *Bull. Chem. Soc. Jpn*, **53**, 2548–2551.

Podder, A., Dattagupta, J. K., Saha, N. N. & Saenger, W. (1979). *Acta Cryst.* B**35**, 53–56.

Richards, S., Pedersen, B., Silverton, J. V. & Hoard, J. L. (1964). *Inorg. Chem.* **3**, 27–33.

Schauer, C. K. (1985). *Structural Variations in Metal Ion Complexes of the Ligand egta⁴⁻*. PhD Thesis, Colorado State Univ.

Schauer, C. K. & Anderson, O. P. (1987). *J. Am. Chem. Soc.* **109**, 3646–3656.

Seccombe, R. C., Lee, B. & Henry, G. M. (1975). *Inorg. Chem.* **14**, 1147–1154.

Shannon, R. D. (1976). *Acta Cryst.* A**32**, 751–767.

Sheldrick, G. M. (1983). *SHELXTL Users Manual*, revision 4. Nicolet XRD Corporation, Madison, Wisconsin, USA.

Stezowski, J. J., Countryman, R. & Hoard, J. L. (1973). *Inorg. Chem.* **12**, 1749–1754.

Whitlow, S. H. (1973). *Inorg. Chem.* **12**, 2286–2289.

Whitlow, S. H. & Davey, G. (1975). *J. Chem. Soc. Dalton Trans.* pp. 1228–1232.

Zetter, M. S., Grant, M. W., Wood, E. J., Dodgen, H. W. & Hunt, J. P. (1972). *Inorg. Chem.* **11**, 2701–2706.

Acta Cryst. (1988). C**44**, 986–990

Structure of Monoaquabis(isocyanato)(2,2′:6′,2″-terpyridyl)nickel(II)

By R. Cortés, M. I. Arriortua,* T. Rojo and J. L. Mesa

Departamentos de Química Inorgánica y Cristalografía-Mineralogía, Universidad del País Vasco,
Apartado 644, 48080 *Bilbao, Spain*

X. Solans

Departamento de Cristalografía, Universidad de Barcelona, Gran Vía 585, 08007 *Barcelona, Spain*

and D. Beltran

Departamento de Química Inorgánica, Universidad de Valencia, Burjasot, 46100 *Valencia, Spain*

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Abstract. [Ni($C_{15}H_{11}N_3$)(H_2O)(NCO)$_2$], $M_r = 394{\cdot}0$, monoclinic, $P2_1/n$, $a = 9{\cdot}488\ (7)$, $b = 13{\cdot}735\ (4)$, $c = 13{\cdot}985\ (17)$ Å, $\beta = 107{\cdot}82\ (5)^\circ$, $V = 1735\ (5)$ Å^3, $Z = 4$, $D_m = 1{\cdot}60\ (3)$, $D_x = 1{\cdot}51$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 1{\cdot}22$ mm^{-1}, $F(000) = 808$, room temperature, $R = 0{\cdot}047$ ($wR = 0{\cdot}053$) for 3211 reflections with $I \geq 2{\cdot}5\sigma(I)$. The Ni ion displays distorted octahedral coordination, with the three N atoms of 2,2′:6′,2″-terpyridine and the N atom of one NCO

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* Author to whom correspondence should be addressed at Departamento de Cristalografía-Mineralogía.

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