Table 4. *Possible hydrogen bonds*

Donor (D)		Acceptor (A)	$D\cdots A$ (Å)	D—H$\cdots A$ (°)
N(1)	H(1)	O(5)	3·245 (5)	121·9 (2)
N(2)	H(2)	O(5)	3·105 (5)	118·3 (2)
O(5)	H(4)	O(4)	2·942 (8)	159·6 (4)
O(5)	H(3)	O(2^{i})	2·861 (10)	138·8 (3)

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

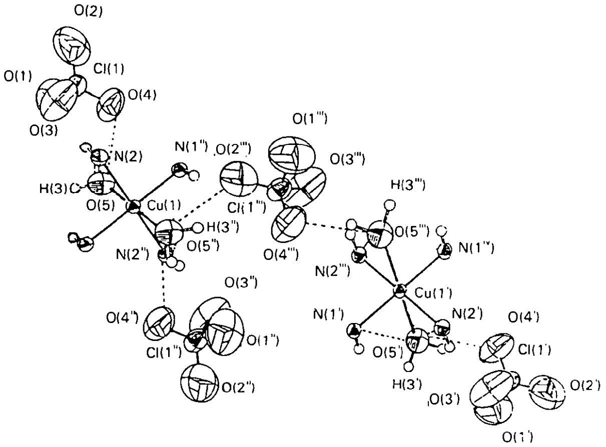


Fig. 2. *ORTEP* drawing (Johnson, 1976) of $[Cu(Me_8[14]aneN_4)(H_2O)_2](ClO_4)_2$ illustrating the intramolecular and intermolecular hydrogen bonds (broken lines, see Table 4) for the perchlorate ions, water molecules and macrocyclic ligands. Symmetry code: (i) $-x, -y, -z$; (ii) $-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iii) $-x, \frac{1}{2}-y, \frac{1}{2}+z$.

The coordination bond lengths in the equatorial plane, 2·035 (3) and 2·031 (4) Å, are longer than those of the Ni complex of the same ligand and consistent with those of $Cu(Et_4Me_2[14]aneN_4)(ClO_4)_2$ (Lee, Lee, Juang & Chung, 1985). The Cu—O(axial) distance, 2·815 (5) Å, is longer than the typical value for Cu^{II} complexes and is significantly longer than the Cu—N(equatorial) distances. Each of these water molecules forms intramolecular hydrogen bonds with one H of an amino group and one O of the perchlorate ion, as well as an intermolecular hydrogen bond with the perchlorate O of a neighboring molecule. The possible hydrogen-bond distances and angles are listed in Table 4 and shown in Fig. 2.

References

Curtis, N. F. (1974). *J. Chem. Soc. Dalton Trans.* pp. 347–350.

International Tables for X-ray Crystallography (1974). Vol. IV, p. 202. Birmingham: Kynoch Press. (Present distributor D. Reidel. Dordrecht.)

Ito, T., Ito, H. & Toriumi, K. (1981). *Acta Cryst.* B**37**, 1412–1415.

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

Juang, W. B. (1984). MS thesis, Institute of Chemistry, National Tsing Hua Univ.

Lee, T.-J., Lee, T.-Y., Juang, W.-B. & Chung, C.-S. (1985). *Acta Cryst.* C**41**, 000–000.

Lee, T.-J., Lu, T.-H., Chung, C.-S. & Lee, T.-Y. (1984). *Acta Cryst.* C**40**, 70–72.

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

Pavkovic, S. F. & Brown, J. N. (1982). *Acta Cryst.* B**38**, 274–276.

Acta Cryst. (1985). C**41**, 1598–1602

Structures of Monomethylcarbonato- and Hydrogencarbonato(1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane)cadmium(II) Perchlorate, $[Cd(O_2COCH_3)(Me_4[14]aneN_4)](ClO_4)$ (I) and $[Cd(O_2COH)(Me_4[14]aneN_4)](ClO_4)$ (II)

By Haruko Ito* and Tasuku Ito†

Department of Applied Molecular Science, Institute for Molecular Science, Okazaki National Research Institutes, Okazaki 444, *Japan*

(*Received* 27 *April* 1985; *accepted* 26 *June* 1985)

Abstract. Compound (I), $[Cd(C_{14}H_{32}N_4)(C_2H_3O_3)]ClO_4$, $M_r = 543{\cdot}33$, monoclinic, Pa, $a = 15{\cdot}926$ (2), $b = 8{\cdot}414$ (1), $c = 8{\cdot}497$ (1) Å, $\beta = 98{\cdot}21$ (1)°, $V = 1126{\cdot}9$ (3) Å^3, $Z = 2$, $D_m = 1{\cdot}56$ (by flotation in CCl_4/hexane, at 293 K),‡ $D_x = 1{\cdot}60$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 1{\cdot}13$ mm^{-1}, $F(000) = 560$, $T = 184$ K, final $R = 0{\cdot}022$ and $wR = 0{\cdot}029$ for 2566 observed reflections; compound (II), $[Cd(C_{14}H_{32}N_4)(CHO_3)]$-

---

* Aichi Kyoiku University, Kariya 448, Japan.

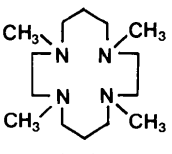
† To whom correspondence should be addressed.

‡ At 293 K, $a = 16{\cdot}049$ (2), $b = 8{\cdot}462$ (1), $c = 8{\cdot}549$ (1) Å, $D_x = 1{\cdot}57$ Mg m^{-3}.

0108-2701/85/111598-05$01.50

$\mathrm{ClO_4}$, $M_r = 529{\cdot}30$, monoclinic, $P2_1/a$, $a = 15{\cdot}378\,(1)$, $b = 16{\cdot}435\,(2)$, $c = 8{\cdot}587\,(1)$ Å, $\beta = 94{\cdot}05\,(1)°$, $V = 2165{\cdot}0\,(4)$ Å^3, $Z = 4$, $D_m = 1{\cdot}62$ (by flotation in $\mathrm{CCl_4/CHBr_3}$), $D_x = 1{\cdot}62$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 1{\cdot}17$ mm^{-1}, $F(000) = 1088$, $T = 293$ K, final $R = 0{\cdot}028$ and $wR = 0{\cdot}035$ for 4713 observed reflections. Each complex cation has a distorted octahedral geometry of *cis*-$\mathrm{CdO_2N_4}$ type with the macrocyclic ligand folded and the four methyl groups on the same side as the carbonate ligand. The monomethylcarbonate and hydrogencarbonate ions chelate the metal unsymmetrically with one short and one long Cd—O bond.

Introduction. Certain zinc(II) complexes of tetraazacycloalkanes have been shown to take up $\mathrm{CO_2}$ as monoalkylcarbonate ion in basic alcohol (Kato & Ito, 1985*a*). The efficiency of the $\mathrm{CO_2}$ uptake depends on the system, that is, the kind of macrocyclic ligand and metal ion. In order to investigate the role of the metal ion, we have investigated similar reactions undergone by cadmium(II) complexes of tetraazacycloalkanes. In this paper, the structures of $\mathrm{[Cd(O_2COCH_3)(Me_4[14]aneN_4)](ClO_4)}$ (I) and $\mathrm{[Cd(O_2COH)(Me_4[14]aneN_4)](ClO_4)}$ (II) obtained from such reactions are described in comparison with those of $\mathrm{[Zn(O_2COCH_3)(Me_4[14]aneN_4)](ClO_4)}$ (III) (Kato & Ito, 1985*b*) and $\mathrm{[Cd(O_2CH)(Me_4[14]aneN_4)](ClO_4)}$ (IV) (Ito & Ito, 1985).



$\mathrm{Me_4[14]aneN_4}$

Experimental. (I) and (II) prepared by bubbling $\mathrm{CO_2}$ through a methanolic solution or an aqueous solution, respectively, of $\mathrm{[Cd(Me_4[14]aneN_4)](ClO_4)_2}$ containing an equivalent amount of triethylamine. The starting compound, $\mathrm{[Cd(Me_4[14]aneN_4)](ClO_4)_2}$, was obtained by mixing an equivalent amount of $\mathrm{Cd(H_2O)_6(ClO_4)_2}$ and $\mathrm{Me_4[14]aneN_4}$ in methanol.

Crystal size $0{\cdot}65 \times 0{\cdot}50 \times 0{\cdot}45$ (I), $0{\cdot}28 \times 0{\cdot}28 \times 0{\cdot}28$ mm (II). Rigaku AFC-5 four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. Cell dimensions from least-squares refinement of 50 reflections in 2θ range 25–30°, θ–2θ scan mode, scan rate 3° min^{-1} for both crystals. Scan range (°) = $1{\cdot}2 + 0{\cdot}5\tan\theta$ for (I) and $1{\cdot}1 + 0{\cdot}5\tan\theta$ for (II). For (I), 2948 reflections measured, $2\theta_{\max} = 55°$, $-20 \le h \le 20$, $0 \le k \le 10$, $0 \le l \le 10$, $R_{\mathrm{int}} = 0{\cdot}013$; for (II), 6917 reflections measured, $2\theta_{\max} = 60°$, $-21 \le h \le 21$, $0 \le k \le 23$, $0 \le l \le 12$, $R_{\mathrm{int}} = 0{\cdot}009$. Three standard reflections after every 100 reflections (fluctuations of F_o values $<2\%$). Intensity data for (I) collected at 184 K using cold nitrogen gas stream. Temperature measured before and after data collection. Lorentz–polarization correction, no absorption correction. Structures solved by conventional heavy-atom method and refined by block-diagonal least-squares method on F using data with $|F_o| > 3\sigma(|F_o|)$. Parameters refined: 405 for (I) and 386 for (II). $w = [\{\sigma(F_o)_{\mathrm{count}}\}^2 + (0{\cdot}015|F_o|)^2]^{-1}$. Non-H atoms refined anisotropically. All H atoms located by difference Fourier maps refined with isotropic temperature factor. Atomic scattering factors and anomalous scattering corrections for non-H atoms from *International Tables for X-ray Crystallography* (1974). For H atoms, scattering factors given by Stewart, Davidson & Simpson (1965). $(\Delta/\sigma)_{\max} = 0{\cdot}25$ and $0{\cdot}11$, $(\Delta\rho)_{\max} = 0{\cdot}9$ and $0{\cdot}6$ e Å^{-3}, $(\Delta\rho)_{\min} = -1{\cdot}2$ and $-0{\cdot}5$ e Å^{-3}, for (I) and (II), respectively. Atomic parameters are listed in Tables 1 and 2.* Calculations were carried out on the HITAC M-200H computer at the Computer Center of the Institute for Molecular Science with the *Universal Crystallographic Computation Program System, UNICS* III (Sakurai & Kobayashi, 1979).

Discussion. Fig. 1 shows perspective views of the complex cations of (I) and (II) along with the atom numbering scheme. Relevant bond lengths and angles are listed in Table 3. Each complex cation has a distorted octahedral geometry of *cis*-$\mathrm{CdO_2N_4}$ type. The $\mathrm{CH_3OCO_2^-}$ or $\mathrm{HOCO_2^-}$ ligand chelates the $\mathrm{Cd^{2+}}$ ion and the tetraazamacrocycle is folded. All four methyl groups of the $\mathrm{Me_4[14]aneN_4}$ ligand are disposed toward the same side as the $\mathrm{CH_3OCO_2^-}$ or $\mathrm{HOCO_2^-}$ ligand.

In the chelate of $\mathrm{CH_3OCO_2^-}$ or $\mathrm{HOCO_2^-}$, the Cd—O(1) bond is shorter than that of Cd—O(2). The difference is larger in (I) (0·226 Å) than in (II) (0·152 Å), because of steric constraint between the methyl group of $\mathrm{CH_3OCO_2^-}$ and the *N*-methyl groups of $\mathrm{Me_4[14]aneN_4}$. In (II), such a steric effect is less important, although there may be an intermolecular hydrogen bond between O(2) and O(3) (see below). In fact, the two Cd—O bonds are equivalent in $\mathrm{[Cd(O_2CH)(Me_4[14]aneN_4)](ClO_4)}$ (IV) where there are no such interactions and the complex cation has a twofold axis. The average Cd—O distances of 2·40 (I) and 2·41 Å (II) are almost the same as that found for (IV) (2·40 Å). There is a trend in these complexes that the longer Cd—O(2) is, the shorter Cd—O(1) is. The observed Cd—O distances are in the range of those reported for a four-membered chelate ring of type $\mathrm{Cd{<}^{O}_{O}{>}C}$, but are longer than those of unidentate

---

* Lists of structure factors, anisotropic thermal parameters for non-H atoms and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42337 (40 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Cd—O bonds (West, 1935; Griffith, Charles & Amma, 1982; Alcock, Curzon, Moore & Pierpoint, 1984; Rodesiler, Turner, Charles, Griffith & Amma, 1984).

The overall structures of (I) and (II) are quite similar except for the effect brought about by the steric interaction between the methyl groups. The averaged Cd—N distance of 2·36 (1) Å for both (I) and (II) is comparable to the value reported for the Cd—N(bipyridine) bond in [CdX_2(bpy)$_2$] (X = NO_3^-, NCS$^-$) (Rodesiler, Turner, Charles, Griffith & Amma, 1984), and is a little shorter than that reported for [Cd(Me$_4$[16]aneN$_4$)(NO$_3$)]$_2$[Cd(NO$_3$)$_4$] (Me$_4$[16]aneN$_4$ = 1,5,9,13-tetramethyl-1,5,9,13-tetraazacyclohexadecane) (Alcock, Curzon, Moore & Pierpoint, 1984).

Table 1. *Fractional atomic coordinates* (Cd, Cl ×10^5; O, C, N ×10^4) *and equivalent isotropic thermal parameters for* [Cd(O$_2$COCH$_3$)(*Me*$_4$[14]*ane*N$_4$)]-(ClO$_4$) (I)

	x	*y*	*z*	B_{eq}(Å^2)†
Cd	0 (4)	20355 (2)	0 (7)	1·5
Cl	18494 (6)	60907 (11)	45284 (13)	3·2
O*P*(1)*	2129 (4)	7665 (6)	4652 (10)	7·8
O*P*(2)	2390 (3)	5065 (7)	5517 (7)	7·7
O*P*(3)	1003 (3)	5849 (6)	4789 (6)	6·3
O*P*(4)	1845 (5)	5646 (11)	2901 (8)	11·0
O(1)	−817 (2)	−216 (3)	−383 (3)	2·7
O(2)	−613 (2)	868 (3)	−2648 (4)	3·1
O(3)	−1389 (2)	−1357 (3)	−2591 (3)	2·6
C	−913 (2)	−155 (4)	−1881 (4)	2·1
C(*M*)	−1516 (3)	−1355 (6)	−4286 (5)	3·9
N(1)	478 (2)	1129 (3)	2631 (3)	1·8
N(4)	−1049 (2)	3165 (3)	1398 (4)	1·9
N(8)	188 (2)	4513 (3)	−1139 (3)	2·0
N(11)	1352 (2)	1653 (4)	−731 (3)	1·9
C(2)	−39 (3)	2046 (4)	3649 (5)	2·2
C(3)	−958 (3)	2225 (4)	2889 (5)	2·3
C(5)	−963 (2)	4885 (4)	1780 (4)	2·4
C(6)	−859 (3)	5935 (4)	379 (5)	2·6
C(7)	20 (3)	5897 (4)	−149 (6)	2·4
C(9)	1100 (2)	4519 (4)	−1345 (4)	2·6
C(10)	1402 (3)	2941 (4)	−1910 (5)	2·5
C(12)	2066 (2)	1798 (5)	597 (5)	2·4
C(13)	1991 (2)	793 (5)	2051 (4)	2·6
C(14)	1393 (2)	1432 (5)	3159 (4)	2·4
C(*M*1)	294 (3)	−597 (5)	2798 (4)	2·7
C(*M*2)	−1888 (3)	2849 (4)	454 (6)	2·6
C(*M*3)	−343 (3)	4634 (5)	−2730 (4)	2·7
C(*M*4)	1415 (2)	108 (5)	−1539 (4)	2·7

* O*P*(*i*) denotes perchlorate oxygen, C(*M*) methyl carbon.

† $B_{eq} = \frac{4}{3}\sum_i\sum_j a_i a_j \beta_{ij}$, where the a_i's are the unit-cell edges in direct space.

Table 2. *Fractional atomic coordinates* (×10^5) *and equivalent isotropic thermal parameters for* [Cd-(O$_2$COH)(Me$_4$[14]aneN$_4$)](ClO$_4$) (II)

	x	*y*	*z*	B_{eq}(Å^2)*
Cd	23576 (1)	6883 (1)	21158 (2)	2·4
Cl	−6258 (5)	25097 (5)	−36499 (8)	4·2
O(1)	20734 (13)	−124 (15)	−2188 (23)	4·6
O(2)	8988 (13)	2684 (14)	9876 (21)	4·1
O(3)	7894 (13)	−3520 (15)	−13315 (22)	4·6
C	12692 (18)	−264 (17)	−1508 (30)	3·5
N(1)	37508 (13)	10729 (14)	13294 (25)	3·1
N(4)	32248 (16)	−3967 (14)	31588 (27)	3·6
N(8)	17704 (14)	8797 (14)	45290 (24)	3·1
N(11)	18916 (14)	20523 (14)	18210 (25)	3·3
C(2)	43695 (18)	5246 (21)	22084 (38)	4·3
C(3)	40274 (21)	−3437 (21)	22895 (38)	4·6
C(5)	34631 (22)	−3670 (20)	48667 (36)	4·5
C(6)	26970 (23)	−2290 (21)	58614 (33)	4·6
C(7)	23693 (20)	6279 (19)	58876 (30)	3·8
C(9)	16209 (18)	17751 (19)	46187 (32)	3·8
C(10)	12684 (19)	21274 (19)	30634 (35)	4·1
C(12)	25840 (21)	26750 (19)	20708 (36)	4·4
C(13)	33672 (22)	25697 (19)	11053 (38)	4·6
C(14)	40098 (19)	19294 (20)	16662 (36)	4·2
C(*M*1)	37840 (21)	9250 (21)	−3701 (35)	4·3
C(*M*2)	27869 (25)	−11792 (20)	27614 (41)	5·3
C(*M*3)	9266 (20)	4500 (23)	46094 (37)	4·6
C(*M*4)	14060 (22)	21710 (20)	2829 (36)	4·6
O*P*(1)	−6785 (20)	19039 (18)	−48330 (34)	7·4
O*P*(2)	−14457 (19)	26084 (20)	−30548 (39)	8·3
O*P*(3)	−4255 (31)	32729 (24)	−43192 (41)	12·0
O*P*(4)	−110 (25)	23521 (30)	−24832 (40)	13·6

* See footnotes to Table 1.

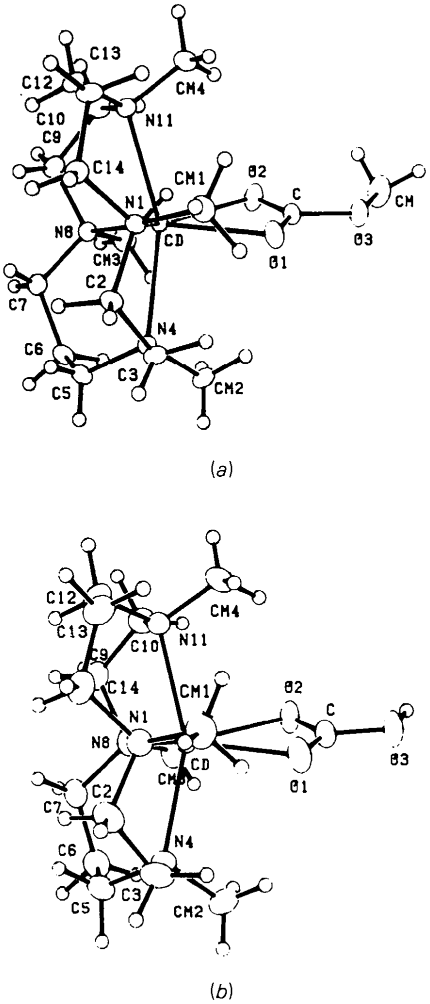
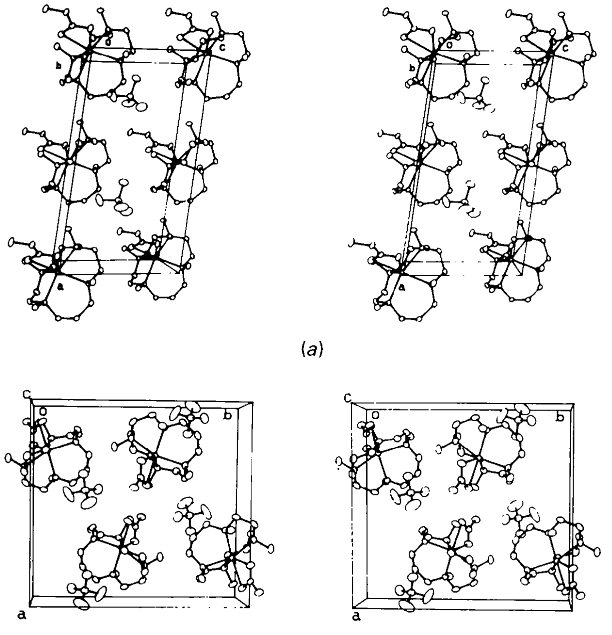


Fig. 1. Structures of (*a*) [Cd(O$_2$COCH$_3$)(Me$_4$[14]aneN$_4$)]$^+$ (I) and (*b*) [Cd(O$_2$COH)(Me$_4$[14]aneN$_4$)]$^+$ (II) with numbering scheme. Thermal ellipsoids are drawn at the 30% probability level except for H, for which B = 1·0 Å^2 is used.

Table 3. *Relevant bond distances* (Å) *and angles* (°)

	(I)	(II)
Cd–O(1)	2·295 (3)	2·326 (2)
Cd–O(2)	2·521 (3)	2·478 (2)
Cd–N(1)	2·382 (3)	2·377 (2)
Cd–N(4)	2·381 (3)	2·365 (2)
Cd–N(8)	2·336 (3)	2·339 (2)
Cd–N(11)	2·347 (3)	2·362 (2)
O(1)–C	1·262 (4)	1·242 (3)
O(2)–C	1·218 (5)	1·262 (3)
O(3)–C	1·353 (4)	1·324 (4)
O(3)–C(*M*)	1·426 (5)	–
O(1)–Cd–O(2)	54·0 (1)	54·2 (1)
O(1)–Cd–N(1)	88·1 (1)	90·3 (1)
O(1)–Cd–N(4)	88·7 (1)	91·1 (1)
O(1)–Cd–N(8)	141·4 (1)	140·3 (1)
O(1)–Cd–N(11)	111·9 (1)	109·9 (1)
O(2)–Cd–N(1)	138·1 (1)	140·6 (1)
O(2)–Cd–N(4)	113·0 (1)	114·1 (1)
O(2)–Cd–N(8)	92·0 (1)	89·3 (1)
O(2)–Cd–N(11)	87·9 (1)	87·9 (1)
N(1)–Cd–N(4)	79·2 (1)	79·2 (1)
N(1)–Cd–N(8)	129·2 (1)	128·9 (1)
N(1)–Cd–N(11)	91·3 (1)	89·4 (1)
N(4)–Cd–N(8)	89·5 (1)	90·5 (1)
N(4)–Cd–N(11)	157·2 (1)	156·2 (1)
N(8)–Cd–N(11)	80·5 (1)	80·5 (1)
Cd–O(1)–C	95·5 (2)	95·4 (2)
Cd–O(2)–C	86·0 (2)	87·9 (2)
O(1)–C–O(2)	124·6 (3)	122·3 (3)
O(1)–C–O(3)	113·5 (3)	118·3 (3)
O(2)–C–O(3)	121·9 (3)	119·4 (3)
C–O(3)–C(*M*)	116·0 (3)	–



(*a*)

(*b*)

Fig. 2. Views of the crystal packing in (*a*) $[Cd(O_2COCH_3)(Me_4[14]aneN_4)](ClO_4)$ (I) and (*b*) $[Cd(O_2COH)(Me_4[14]aneN_4)](ClO_4)$ (II).

In both compounds, the bite angle O(1)—Cd—O(2) is very sharp at about 54°. This value is similar to those reported for cadmium(II) complexes containing bidentate nitrate (Alcock, Curzon, Moore & Pierpoint, 1984; Rodesiler, Turner, Charles, Griffith & Amma, 1984) or a bidentate benzoate ligand (Charles, Griffith, Rodesiler & Amma, 1983).

It is interesting to note that the angle N(1)—Cd—N(8), which is *trans* to the narrow O(1)—Cd—O(2), is expanded to 129·2 (1)° for (I) and 128·9 (1)° for (II). They are close to the 120° of the trigonal bipyramidal structure. On the other hand, other *cis* N—Cd—N angles are in the range 79–92°, which is normal because the rigidity of the macrocycles causes more or less narrow bite angles for the five-membered chelate rings. In view of the angles subtended at Cd by donor atoms, coordination geometries of (I) and (II) may be taken as trigonal bipyramidal type with the two donor oxygen atoms occupying an apex of the in-plane triangle. A very similar trigonal bipyramidal structure has been found for a complex with four nitrogen and two oxygen donors, $[Cd(NO_3)(Me_4[16]aneN_4)]_2[Cd(NO_3)_4]$ (Alcock, Curzon, Moore & Pierpoint, 1984).

Stereoscopic views of the crystal structures of (I) and (II) are shown in Fig. 2. In the crystal structure of (II), the O(3)—H group is involved in an intermolecular hydrogen bond with an O(2)···O(3) distance of 2·629 (3) Å. Other intermolecular contacts are normal in both (I) and (II).

The most striking difference in the structure between the present Cd complexes and the analogous Zn complex (III) is that the $CH_3OCO_2^-$ or $HOCO_2^-$ ligand in the Cd complexes chelates the metal to yield six-coordinate complexes, while the $CH_3OCO_2^-$ ion in $[Zn(O_2COCH_3)(Me_4[14]aneN_4)](ClO_4)$ (III) acts as a unidentate ligand to give a five-coordinate complex of the trigonal bipyramidal type (Kato & Ito, 1985*b*). To our knowledge, the present $CH_3OCO_2^-$ complex (I) is the first example in which the $CH_3OCO_2^-$ ligand acts as a chelating agent. The $CH_3OCO_2^-$ ligand in other structurally known compounds, $[Zn(O_2COCH_3)$(1,4,8,11-tetraazacyclotetradecane)](ClO_4) and $[Zn(O_2COCH_3)$(1,4,8,12-tetraazacyclopentadecane)](ClO_4) (Kato & Ito, 1985*b*), and $[Ni(O_2COCH_3)(Me_4[14]aneN_4)](ClO_4)$, $[Ni(O_2COCH_3)_2(Me_4[14]aneN_4)]$, and $[Cu(O_2COCH_3)$(1,4,8,11-tetraazacyclotetradecane)](ClO_4) (Kato & Ito, 1985*c*), is either unidentate or bridging bidentate.

Such structural differences among (I), (II) and (III) are noted in their IR spectral data. The asymmetric and symmetric CO stretching frequencies (ν^a_{CO} and ν^s_{CO}) are observed at 1605 and 1342 cm^{-1} in (I), 1590 and 1352 cm^{-1} in (II) and 1676 and 1310 cm^{-1} in (III). The differences, $\Delta\nu = \nu^a_{CO} - \nu^s_{CO}$, are 263 and 238 cm^{-1} for (I) and (II), respectively, whereas it is 366 cm^{-1} for (III). The relation between the value of $\Delta\nu$ and the coordination type of monoalkylcarbonato or hydrogencarbonato complexes has been well documented (*e.g.* Kato & Ito, 1985*a*).

The structural difference between the present Cd complexes and the Zn homolog of (I) arises from the difference in ionic radii and weak chelating ability of the $ROCO_2^-$ ligand. In fact, coordination bond lengths are definitely longer for both M—O and M—N bonds for the Cd complexes. The short Zn–donor bonds may prevent $CH_3OCO_2^-$ from chelation owing to the steric requirements. Although the coordination number differs between the Cd and Zn complexes, the geometry about the metal is alike in the sense that both can be regarded as trigonal bipyramidal, as described previously. So far as the $Me_4[14]aneN_4$ complexes of Cd^{II} and Zn^{II} are concerned, no distinct difference in the efficiency of CO_2 uptake has been found, although Zn^{II} is generally superior to Cd^{II} in complexes with tetraazacycloalkane.

References

ALCOCK, N. W., CURZON, E. H., MOORE, P. & PIERPOINT, C. (1984). *J. Chem. Soc. Dalton Trans.* pp. 605–610.

CHARLES, N. G., GRIFFITH, E. A. H., RODESILER, P. F. & AMMA, E. L. (1983). *Inorg. Chem.* **22**, 2717–2723.

GRIFFITH, E. A. H., CHARLES, N. G. & AMMA, E. L. (1982). *Acta Cryst.* B**38**, 262–264.

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

ITO, H. & ITO, T. (1985). To be published elsewhere.

KATO, M. & ITO, T. (1985*a*). *Inorg. Chem.* **24**, 504–508.

KATO, M. & ITO, T. (1985*b*). *Inorg. Chem.* **24**, 509–514.

KATO, M. & ITO, T. (1985*c*). Unpublished results.

RODESILER, P. F., TURNER, R. W., CHARLES, N. G., GRIFFITH, E. A. H. & AMMA, E. L. (1984). *Inorg. Chem.* **23**, 999–1004.

SAKURAI, T. & KOBAYASHI, K. (1979). *Rikagaku Kenkyusho Hokoku*, **55**, 69–77 (in Japanese).

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

WEST, C. D. (1935). *Z. Kristallogr.* **89**, 480–493.

Acta Cryst. (1985). C**41**, 1602–1605

Synthesis and Structure of Di-μ-hydroxo-bis[bis(dimethyl sulfoxide)platinum(II)] Perchlorate

BY F. D. ROCHON, P. C. KONG AND R. MELANSON

Département de Chimie, Université du Québec à Montréal, CP 8888, *succ. A, Montréal, Canada H*3*C* 3*P*8

(*Received* 4 *June* 1985; *accepted* 24 *July* 1985)

Abstract. $[Pt_2(OH)_2(C_2H_6OS)_4](ClO_4)_2$, $M_r = 935{\cdot}62$, triclinic, $P\bar{1}$, $a = 7{\cdot}305\ (5)$, $b = 8{\cdot}804\ (6)$, $c = 10{\cdot}946\ (5)$ Å, $\alpha = 105{\cdot}95\ (4)$, $\beta = 105{\cdot}59\ (5)$, $\gamma = 102{\cdot}73\ (5)°$, $V = 618{\cdot}2\ (6)$ Å^3, $Z = 1$, $D_x = 2{\cdot}513$, $D_m = 2{\cdot}51\ (2)$ g cm^{-3} (flotation), $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 124{\cdot}86$ cm^{-1}, $F(000) = 440$, $T = 295$ K, $R = 0{\cdot}051$ for 2697 observed reflections. The hydroxo-bridged dimer $[(Me_2SO)_2Pt(OH)_2Pt(Me_2SO)_2](ClO_4)_2$ was isolated from an aqueous solution of *cis*-$[Pt(Me_2SO)_4](ClO_4)_2$ (two O-bonded and two S-bonded Me_2SO). The cation is a centrosymmetric dimer, each Pt atom having square-planar coordination, with the Me_2SO molecules bonded to Pt through their S atoms, Pt—S = 2·203 (2) and 2·223 (3) Å, bridged Pt—O = 2·031 (9) and 2·064 (8) Å. The crystal is stabilized by hydrogen bonding between the hydroxo ligand and the O atom of one Me_2SO. The perchlorate ions seem also to be hydrogen-bonded to the methyl groups of the Me_2SO ligands.

Introduction. Price, Williamson, Schramm & Wayland (1972) prepared a tetrasubstituted Me_2SO platinum(II) compound from the reactions of *cis*-$[Pt(Me_2SO)_2Cl_2]$ with a silver salt in Me_2SO:

$$cis\text{-}[Pt(Me_2SO)_2Cl_2] \xrightarrow[2Ag^+]{Me_2SO} [Pt(Me_2SO)_4]^{2+} + 2\,AgCl.$$

Using infrared spectroscopy the authors suggested that the compound was the *cis*-isomer with two S-bonded and two O-bonded Me_2SO ligands. We have synthesized this compound with a view to determining its crystal structure by X-ray diffraction methods. AgCl is slightly soluble in Me_2SO, therefore the platinum complex $[Pt(Me_2SO)_4]^{2+}$ was found to be contaminated with a small quantity of AgCl. In order to purify the complex, it was dissolved in water, filtered and crystals were grown upon slow evaporation. The analytical results indicated a different compound with an experimental formula $[Pt(Me_2SO)_2(OH)]_2(ClO_4)_2$. The

0108-2701/85/111602-04$01.50