carbonato 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.

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

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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, $\alpha = 105{\cdot}95\,(4)$, $\beta = 105{\cdot}59\,(5)$, $\gamma = 102{\cdot}73\,(5)^\circ$, $V = 618{\cdot}2\,(6)$ 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

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crystal structure of the new compound was determined and is reported here. It has not been possible yet to grow adequate crystals of $[Pt(Me_2SO)_4](ClO_4)_2$.

Experimental. $[Pt(Me_2SO)_4](ClO_4)_2$ was prepared according to the method already described (Price *et al.*, 1972). The compound was dissolved in water, filtered and slowly evaporated. Crystals of $[Pt(Me_2SO)_2(OH)]_2(ClO_4)_2$ were isolated. Elemental analysis: theor. %C: 10·26, %H: 2·80, %Cl: 7·58; exp. %C: 10·39, %H: 2·70, %Cl: 7·57.

A set of precession photographs indicated that the crystals of $[Pt(Me_2SO)_2(OH)]_2(ClO_4)_2$ belong to the triclinic system. Since there is one cation and two ClO_4^- ions per unit cell, the $P\bar{1}$ space group implied that there was a centre of symmetry in the dimeric cation. Cell parameters obtained by least-squares refinement from setting angles of 15 automatically centred reflections (2θ range 10–25°) on a Syntex $P\bar{1}$ diffractometer using graphite-monochromatized Mo $K\alpha$ radiation.

Intensity data collected from a hexagonal plate with approximate dimensions 0·314 mm ($\bar{2}01$; $20\bar{1}$), 0·392 mm ($11\bar{1}$; $\bar{1}\bar{1}1$), 0·206 mm ($1\bar{1}0$; $\bar{1}10$) and 0·040 mm (001; $00\bar{1}$). A total of 3636 independent reflections (h −10→10, k −12→12, l −15→14) measured in range $2\theta < 60°$, $2\theta/\theta$ scan technique, Mo $K\alpha$ radiation. Scan rate 1° min^{-1} for most reflections, but rates as high as 24° min^{-1} selected for strong reflections by the autocollection program. 2θ scan range 1° below $K\alpha_1$ and 1° above $K\alpha_2$ selected. Background time to scan time ratio 0·50. During data collection, three standard reflections, measured after every 47 reflections, showed intensity fluctuations within ±2% of their mean values.

2697 reflections with $I > 2{\cdot}5\sigma(I)$ considered observed; $\sigma(I)$ calculated as already described (Melanson & Rochon, 1975). Absorption correction based on equations of crystal faces applied to all reflections, transmission factors 0·059–0·470. Data then corrected for Lorentz and polarization effects. Scattering factors of Cromer & Waber (1965) used and anomalous-dispersion terms (Cromer, 1965) included in calculations.

Three-dimensional Patterson map clearly indicated space group $P\bar{1}$ and position of Pt atom. Positions of all other atoms, except those of H, obtained by structure-factor and Fourier-map calculations. Function minimized $\sum w(F_o - F_c)^2$. Isotropic secondary-extinction correction (Coppens & Hamilton, 1970) included in calculations. Individual weights $w = 1/\sigma^2(F)$ finally applied. H atoms could not be located. Refinement of the scale factor, coordinates and anisotropic temperature factors of all atoms converged to $R = 0{\cdot}051$, $wR = 0{\cdot}049$, $S = 1{\cdot}71$. A few residual peaks (<1·6 e Å^{-3}) found in close environment of Pt atom. Max. Δ/σ in final refinement cycle <0·3.

Calculations performed on a Cyber 171 computer with programs already described (Melanson & Rochon, 1975).*

Discussion. $[Pt(Me_2SO)_4](ClO_4)_2$ was suggested (Price *et al.*, 1972) to be a *cis*-isomer with two S-bonded and two O-bonded Me_2SO ligands similar to $[Pd(Me_2SO)_4](ClO_4)_2$ (Wayland & Schramm, 1969). A proton NMR study in CH_3NO_2 solution has shown that the O-bonded sulfoxides exchange rapidly with the free ligand while the S-bonded sulfoxides were kinetically stable. The kinetic instability of the O-coordinated sulfoxide may be used to prepare complexes of the form $[Pt(Me_2SO)_2L_2]$.

$[Pt(Me_2SO)_4](ClO_4)_2$ was prepared in our laboratory. When dissolved in water, the solution was found to become acidic (pH ~2) with the formation of a hydroxo-bridged dimer:

$$2[Pt(Me_2SO)_4](ClO_4)_2 + 2H_2O \rightarrow [Pt(Me_2SO)_2(OH)]_2(ClO_4)_2 + 2H^+ + 2ClO_4^- + 4Me_2SO.$$

In aqueous solution, the O-bonded Me_2SO ligands are probably displaced by water molecules, which then dissociate forming a dimer. The latter was dissolved in Me_2SO in an attempt to reverse the above reaction, but $[Pt(Me_2SO)_4]^{2+}$ could not be obtained by this method.

As expected, the crystal-structure determination of the dimer has shown that the Me_2SO ligands are bonded to Pt through their S atoms. Platinum, being a soft metal, does not form strong Pt—O bonds with neutral O ligands.

The refined atomic parameters for the analysed crystal are listed in Table 1. A view of the molecular cation is shown in Fig. 1. The ion is a centrosymmetric dimer bridged by hydroxo groups. The $S_2PtO_2PtS_2$ moiety is essentially planar. The weighted best plane was calculated through five atoms. The deviations from this plane are: Pt, −0·0011 (4); S(1), 0·005 (3); S(2), 0·017 (3); O(1), 0·037 (9); and O(1′), 0·208 (9) Å. Therefore O(1′) lies 0·2 Å out of the best plane. This is similar to the structure of $[(NH_3)_2Pt(OH)_2Pt(NH_3)_2](NO_3)_2$ where the dimeric ion is also planar (Stanko, Hollis, Schreifels & Hoeschele, 1977; Faggiani, Lippert, Lock & Rosenberg, 1977). But it is different from the structure of $[\{P(Et)_3\}_2Pt(OH)_2Pt\{P(Et)_3\}_2](BF_4)_2$ (Bushnell, 1978), which contains a bent hydroxo bridge. The dihedral angle between the two planes in the phosphine structure is 36·4°. Therefore Me_2SO seems to have more similarities with amines than with phosphine compounds.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42380 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters with their e.s.d.'s and equivalent isotropic temperature factors* (Pt, Cl, S: ×10^4; C, O: ×10^3)

$$U_{eq} = \tfrac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	U_{eq}(Å^2)
Pt	1946·7 (6)	577·4 (5)	1285·6 (3)	281
Cl	−703 (5)	6913 (5)	2456 (4)	532
S(1)	4593 (4)	−298 (3)	1776 (2)	258
S(2)	3152 (4)	2793 (3)	3157 (2)	359
C(1)	394 (2)	−239 (1)	66 (1)	40
C(2)	521 (2)	−54 (2)	339 (1)	41
C(3)	349 (2)	450 (1)	261 (1)	56
C(4)	124 (2)	292 (2)	387 (1)	68
O(1)	−56 (1)	120 (1)	64 (1)	66
O(2)	640 (1)	74 (1)	168 (1)	36
O(3)	500 (1)	301 (1)	423 (1)	64
O(4)	84 (4)	719 (5)	350 (3)	222
O(5)	−217 (3)	587 (4)	250 (2)	214
O(6)	−11 (5)	648 (3)	149 (3)	245
O(7)	−89 (6)	836 (4)	283 (4)	258

Table 2. *Bond distances* (Å) *and angles* (°)

Pt–S(1)	2·223 (3)	S(1)–C(2)	1·78 (1)
Pt–S(2)	2·203 (2)	S(2)–C(3)	1·76 (1)
Pt–O(1)	2·031 (9)	S(2)–C(4)	1·79 (1)
Pt–O(1′)	2·064 (8)	Cl–O(4)	1·30 (3)
S(1)–O(2)	1·476 (9)	Cl–O(5)	1·27 (3)
S(2)–O(3)	1·462 (9)	Cl–O(6)	1·25 (4)
S(1)–C(1)	1·78 (1)	Cl–O(7)	1·29 (4)
S(1)–Pt–S(2)	95·0 (1)	O(2)–S(1)–C(1)	109·7 (5)
S(1)–Pt–O(1)	174·1 (3)	O(2)–S(1)–C(2)	109·4 (5)
S(1)–Pt–O(1′)	94·5 (2)	O(3)–S(2)–C(3)	109·2 (6)
S(2)–Pt–O(1)	90·8 (3)	O(3)–S(2)–C(4)	108·9 (6)
S(2)–Pt–O(1′)	168·6 (3)	C(1)–S(1)–C(2)	101·1 (6)
O(1)–Pt–O(1′)	79·6 (4)	C(3)–S(2)–C(4)	104·1 (7)
Pt–O(1)–Pt′	100·4 (4)	O(4)–Cl–O(5)	108 (2)
Pt–S(1)–O(2)	113·9 (3)	O(4)–Cl–O(6)	103 (2)
Pt–S(1)–C(1)	108·6 (4)	O(4)–Cl–O(7)	97 (2)
Pt–S(1)–C(2)	113·4 (4)	O(5)–Cl–O(6)	118 (2)
Pt–S(2)–O(3)	119·6 (4)	O(5)–Cl–O(7)	109 (2)
Pt–S(2)–C(3)	105·1 (5)	O(6)–Cl–O(7)	119 (2)
Pt–S(2)–C(4)	108·9 (5)		

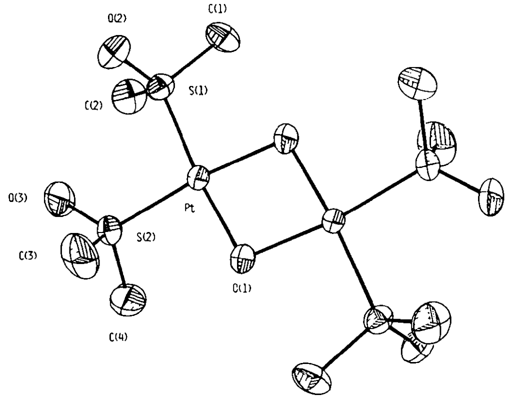

Fig. 1. Labelled diagram of the $[Pt(Me_2SO)_2OH]_2^{2+}$ cation. The ellipsoids correspond to 50% probability.

Bond lengths and angles are given in Table 2. The angles around the Pt atom show considerable strain inside the four-membered ring. The O(1)–Pt–O(1′) angle is reduced to 79·6 (4)° while the Pt–O(1)–Pt angle is 100·4 (4)°. These values are very close to those found in $[Pt(NH_3)_2OH]_2^{2+}$ but are slightly different from those found in a Cl-bridged dimer where Cl–Pt–Cl′ = 84·7 (1) and Pt–Cl–Pt′ = 95·3 (1)° (Rochon & Melanson, 1981). The Pt–O distances (2·03–2·06 Å) agree well with the values (2·02–2·05 Å) found in the ammine hydroxo dimer but are shorter than the values [2·09–2·17 (1) Å] found in the bent phosphine dimer.

The Pt–S bonds [2·203 (2), 2·223 (3) Å] are normal and agree with values found in other Pt–Me_2SO compounds (Melanson & Rochon, 1975, 1977, 1978*a,b*, 1984; Melanson, Hubert & Rochon, 1976). The S atoms in the Me_2SO molecules are in an approximate tetrahedral environment with angles ranging from 105·1 to 119·6°. The Pt–S–O angles are slightly larger than the Pt–S–C angles as observed in other Pt–Me_2SO complexes mentioned above.

The Cl–O bond distances in the ClO_4^- ions vary from 1·25 (4) to 1·30 (3) Å. The thermal factors of the O atoms are very high resulting in very large standard deviations. The bond angles vary from 97 (2) to 118 (2)°.

The packing of molecules is shown in Fig. 2. The hydroxo-bridged group O(1) is hydrogen-bonded to an O atom O(2) in one Me_2SO ligand. The distance O(1)···O(2) is 2·76 (1) Å and the angles Pt–O(1)··· O(2) are favourable. There are also several short contacts between the methyl groups of the Me_2SO molecules and the perchlorate O atoms. These distances with favourable angles (Table 3) might indicate that hydrogen bonding of the type C–H···O is important in stabilizing this crystal.

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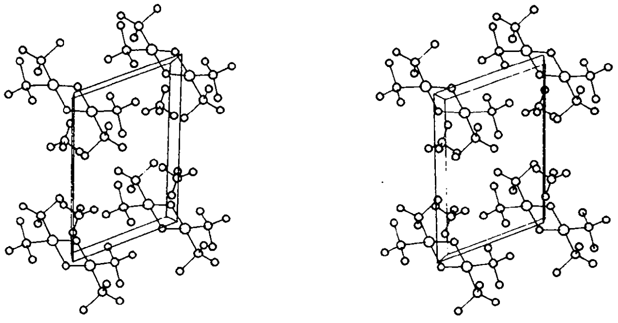

Fig. 2. Stereoscopic diagram of the packing in the $[Pt(Me_2SO)_2OH]_2(ClO_4)_2$ crystal (*a** axis horizontal and *c* axis vertical).

Table 3. *Distances* (Å) *and angles* (°) *of atoms possibly involved in hydrogen bonds*

O(1)···O(2^{i})	2·76 (1)	Pt–O(1)···O(2)	122·8 (4)
		Pt′–O(1)···O(2)	100·8 (4)
C(1)···O(6^{ii})	3·35 (4)	S(1)–C(1)···O(6)	91·1 (8)
C(2)···O(4^{ii})	3·42 (4)	S(1)–C(2)···O(4)	106·4 (8)
C(2)···O(7^{iii})	3·36 (5)	S(1)–C(2)···O(7)	88·1 (8)
C(3)···O(4^{iv})	3·46 (4)	S(2)–C(3)···O(4)	115·4 (9)
C(3)···O(3^{v})	3·27 (2)	S(2)–C(3)···O(3)	88·9 (6)
C(3)···O(5^{vi})	3·17 (3)	S(2)–C(3)···O(5)	114·7 (8)
C(4)···O(2^{i})	3·44 (2)	S(2)–C(4)···O(2)	115·8 (7)

Symmetry code: (i) $x-1, y, z$; (ii) $x, y-1, z$; (iii) $x+1, y-1, z$; (iv) x, y, z; (v) $1-x, 1-y, 1-z$; (vi) $x+1, y, z$.

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Bis[amino(methyl)glyoximato]nickel(II) Dihydrate: an Extended Interstack H-Bonding Network

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Abstract. Bis[2-(hydroxyimino)propionamide oximato]-nickel(II) dihydrate, $[Ni(C_3H_6N_3O_2)_2].2H_2O$, $M_r = 326·95$, monoclinic, $P2_1/c$, $a = 3·915$ (1), $b = 15·559$ (3), $c = 9·862$ (2) Å, $\beta = 96·47$ (2)°, $V = 597$ Å^3, $Z = 2$, $D_x = 1·82$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0·7107$ Å, $\mu = 15·8$ cm^{-1}, $F(000) = 340$, room temperature, final $R = 0·059$ for 1254 observed reflections. Planar complex molecules are stacked in columns along **a**; the interplanar separation is 3·34 (2) Å with the molecular planes inclined at 31·5 (5)° to the *a* axis. Each stack of molecules is linked with its four neighbouring stacks by H bridges involving the water molecules.

Introduction. Neutral bis(dioximato)metal complexes of Ni^{II}, Pd^{II} and Pt^{II} usually crystallize without the inclusion of solvent, with regular stacks of either the '*M*–*M*' or the '*M*–*L*' type (Endres, Keller, Lehmann, Poveda, Rupp & van de Sand, 1977). Owing to their pronounced capability of forming intermolecular H bridges, however, the bis(oxamide oximato)metal complexes [bis(diaminoglyoximato)metal complexes] always include H-bonded solvent or other molecules in the crystals. This leads to different structural patterns (Endres, 1978, 1979) and allows the synthesis of molecular metals by the inclusion of organic radicals (Endres, Bongart, Nöthe, Hennig, Schweitzer, Schäfer, Helberg & Flandrois, 1985). We have determined the structure of the title compound to compare it, especially with respect to H bonding, with the diaminoglyoxime and dimethylglyoxime (Godycki & Rundle, 1953) complexes.

Experimental. Powdery orange-red complex obtained by dropping ethanolic ligand solution containing aqueous ammonia into a boiling ethanolic solution of $NiCl_2.6H_2O$. Precipitate filtered off, washed with water, dried; suspended in water, diluted HCl added until

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