Moreover, this type of polymeric structure, although quite common among halogen metal complexes with monodentate organic ligands, has not previously been described for a lanthanoid chloride.

In the title compound Cl bridges are symmmetrical, as found in di-μ-chloro-bis[di-η-cyclopentadienyl-scandium(III)] (Atwood & Smith, 1973) and the Yb analogue (Baker, Brown & Raymond, 1975), whereas in a previously described dimeric Ce complex containing the cyclooctatetraene ligand (Hodgson & Raymond, 1972) the Cl bridges are definitely asymmetrical. The asymmetry in the Ce complex was attributed to the radius of Ce, large compared to that of Sc and Yb, and to the corresponding increase in metal—metal distance, which does not allow the Cl^- ion to span the gap. However, this explanation is not consistent with the symmetry of the Cl bridges in the title compound, with the La—La distance of 4·732 (3) Å still longer than Ce—Ce, 4·642 (3) Å.

The La—Cl(1) bond, with a terminal Cl, is shorter than the La—Cl(2) bonds with bridge Cl atoms, which is consistent with the usual lengthening of a bond with a bridge halide (Atwood & Smith, 1973). The La—O(carbonyl) distance is shorter than all the La—O distances found in $[La(dmp)_8](ClO_4)_3$ (Castellani Bisi, Della Giusta, Coda & Tazzoli, 1974); this could reflect the crowded environment about La in $[La(dmp)_8](ClO_4)_3$. Bond lengths and angles of dmp compare well with those found in the uncoordinated ligand (Brown, Norment & Levy, 1957) and in the lanthanoid complexes containing it.

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Structure of Bis(1,3-propanediamine)mercury(II) Sulphate Dihydrate, $[Hg(C_3H_{10}N_2)_2]SO_4.2H_2O$

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Abstract. $M_r = 480·90$, monoclinic, $P2$, $a = 13·830$ (2), $b = 6·023$ (1), $c = 8·250$ (1) Å, $\beta = 97·45$ (3)°, $V = 681·4$ (2) Å^3, $Z = 2$, $D_x = 2·343$, $D_m = 2·34$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 116·9$ cm^{-1}, $F(000) = 464$, room temperature, final $R = 0·033$ for 1914 independent observed reflections. The structure is built up of the polymeric $[Hg(1,3\text{-propanediamine})_2]_n^{2n+}$ cations with the Hg^{2+} ions bridged by the 1,3-propanediamine ligands and tetrahedrally coordinated by the N atoms. The sulphate ions do not belong to the mercury coordination sphere but are connected in chains with the water molecules through hydrogen bonds.

Introduction. The great majority of metal complexes with 1,3-propanediamine (tn) contain tn as the bidentate chelating ligand. A similar chelating property of tn was expected for mercury complexes, analogously to the mercury complexes with ethylenediamine (Duplančić, Grdenić, Kamenar, Matković & Sikirica, 1976; Grdenić, Sikirica & Vicković, 1977).

Experimental. Title compound prepared by the procedure described for the preparation of the analogous perchlorate complex $[Hg(tn)_2][ClO_4]_2$ (Pfeiffer, Schmitz & Böhm, 1952). Density measured by flotation in methylene iodide and benzene. Crystal 0·23 × 0·36 ×

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0·27 mm, Philips PW 1100 diffractometer, graphite monochromator, Mo $K\alpha$, ω-scan technique, 20 reflections used to determine cell parameters. No correction for absorption. Data collected within range $2 < \theta < 30°$, h −19→18, k 0→8, l 0→11; 1921 unique reflections of which 1914 with $I > 2\sigma(I)$ used in subsequent calculations. Three check reflections measured every two hours of exposure time showed no significant change with time. Structure solved from Patterson and Fourier syntheses and refined by full-matrix least squares assuming anisotropic thermal parameters for all non-H atoms. H atoms could not be located. Refinement converged with $R = 0{\cdot}033$ ($R_w = 0{\cdot}048$). Function minimized $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F_o)$. $(\Delta/\sigma)_{max} = 0{\cdot}49$. Max. and min. height in final difference Fourier map 0·77 and −3·04 e Å^{-3}. Atomic scattering factors and anomalous-dispersion corrections for all atoms from *International Tables for X-ray Crystallography* (1974). All calculations performed using the Univac 1110 of the SRCE, University Computing Centre, Zagreb, with programs written by Domenicano, Spagna & Vaciago (1969).

Discussion. Final atomic coordinates and equivalent isotropic thermal parameters are given in Table 1.* A view of the structure and atom-numbering scheme are shown in Fig. 1. Interatomic distances and angles are given in Table 2. Though $Z = 2$ in the space group $P2$ the unit cell contains two crystallographically independent Hg and S atoms. Both Hg as well as both S atoms are in the special positions so that the $[Hg(tn)_2]_n^{2n+}$ cations and SO_4^{2-} anions lie on crystallographically different twofold axes.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39592 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

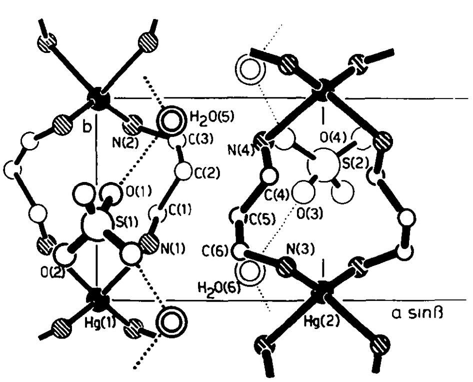

Fig. 1. The crystal structure of bis(1,3-propanediamine)mercury(II) sulphate dihydrate seen along the z axis. Hydrogen bonds between sulphate and water O atoms are shown by dotted lines.

The cations have an open-chain structure with tn as the bridging ligands. Both Hg(1) and Hg(2) are effectively coordinated by four tn N atoms in a considerably distorted tetrahedron (Grdenić, 1965).

Table 1. *Fractional atomic coordinates* (×10^4) *and equivalent isotropic temperature factors with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
Hg(1)	0	0	0	1·94 (1)
Hg(2)	5000	395 (1)	5000	1·64 (2)
N(1)	1143 (5)	2759 (12)	989 (8)	1·1 (1)
N(2)	778 (6)	8603 (14)	−1995 (10)	2·1 (2)
N(3)	4208 (7)	1686 (16)	6914 (11)	0·8 (2)
N(4)	3711 (8)	7825 (20)	4038 (12)	1·5 (3)
S(1)	0	3731 (7)	5000	1·02 (8)
S(2)	5000	6659 (4)	0	1·17 (6)
O(1)	313 (6)	5213 (14)	3688 (9)	1·1 (2)
O(2)	−758 (7)	2264 (16)	4243 (11)	1·5 (2)
O(3)	4565 (7)	5323 (13)	1203 (10)	2·9 (2)
O(4)	5872 (5)	7974 (12)	762 (8)	2·0 (2)
O(5)	1590 (9)	8838 (29)	4065 (14)	2·9 (3)
O(6)	3431 (8)	1386 (30)	1147 (13)	2·2 (2)
C(1)	1333 (6)	4222 (15)	−426 (10)	1·5 (2)
C(2)	1903 (7)	6413 (17)	−39 (12)	2·1 (2)
C(3)	1784 (7)	7876 (17)	−1526 (12)	2·1 (2)
C(4)	3783 (9)	6129 (21)	5342 (14)	1·4 (3)
C(5)	3142 (9)	4127 (21)	4861 (14)	1·2 (2)
C(6)	3167 (8)	2445 (20)	6294 (13)	1·1 (2)

Table 2. *Interatomic distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

(*a*) Bond lengths

Hg(1)–N(1)	2·365 (7)	Hg(2)–N(3)	2·179 (10)
Hg(1)–N(2^{i})	2·244 (9)	Hg(2)–N(4^{i})	2·416 (11)
S(1)–O(1)	1·509 (9)	S(2)–O(3)	1·466 (9)
S(1)–O(2)	1·450 (9)	S(2)–O(4)	1·510 (7)
N(1)–C(1)	1·512 (11)	N(3)–C(6)	1·534 (14)
C(1)–C(2)	1·549 (13)	C(6)–C(5)	1·554 (16)
C(2)–C(3)	1·503 (14)	C(5)–C(4)	1·518 (17)
C(3)–N(2)	1·462 (13)	C(4)–N(4)	1·478 (16)

(*b*) Bond angles

N(1)–Hg(1)–N(2^{i})	98·9 (3)	N(3)–Hg(2)–N(4^{i})	92·7 (4)
N(1)–Hg(1)–N(1^{ii})	90·7 (2)	N(3)–Hg(2)–N(3^{iv})	138·2 (4)
N(1^{ii})–Hg(1)–N(2^{i})	111·9 (3)	N(3)–Hg(2)–N(4^{v})	114·2 (3)
N(2^{i})–Hg(1)–N(2^{iii})	135·9 (3)	N(4^{i})–Hg(2)–N(4^{v})	100·3 (4)
N(1)–C(1)–C(2)	118·1 (7)	N(4)–C(4)–C(5)	112·1 (9)
C(1)–C(2)–C(3)	109·4 (8)	C(4)–C(5)–C(6)	111·3 (9)
C(2)–C(3)–N(2)	113·1 (8)	C(5)–C(6)–N(3)	112·0 (9)
O(3)–S(2)–O(4)	112·4 (4)	O(1)–S(1)–O(1^{vii})	107·5 (5)
O(3)–S(2)–O(3^{vi})	113·4 (5)	O(1)–S(1)–O(2^{vii})	114·3 (5)
O(3)–S(2)–O(4^{vi})	101·2 (4)	O(1)–S(1)–O(2)	108·1 (5)
O(4)–S(2)–O(4^{vi})	116·7 (4)	O(2)–S(1)–O(2^{vii})	104·9 (5)

(*c*) Hydrogen bonds or intermolecular contacts

O(1)···O(5)	2·80 (2)	N(2)···O(1^{ii})	2·80 (1)
O(2)···O(5^{viii})	2·82 (2)	N(2)···O(2^{x})	2·88 (1)
O(3)···O(6)	2·84 (2)	N(3)···O(4^{v})	2·96 (2)
O(4)···O(6^{ix})	2·83 (2)	N(3)···O(3^{iv})	3·07 (1)
N(1)···O(1)	3·02 (1)	N(4)···O(5)	3·00 (2)
N(1)···O(6)	3·26 (1)	N(4)···O(3)	3·14 (1)

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

The planes defined by Hg(1), N(1), N(1[ii]) and Hg(1), N(2[i]), N(2[iii]) in the Hg(1) tetrahedron, and by Hg(2), N(4[i]), N(4[v]) and Hg(2), N(3), N(3[iv]) in the Hg(2) tetrahedron are not normal to each other but make angles of 80·4 (2) and 75·4 (2)° respectively. The N—Hg—N angles within the tetrahedron around Hg(1) vary from 90·7 (2) to 135·9 (3)°, those around Hg(2) from 92·7 (4) to 138·2 (4)°. The Hg—N bond lengths are significantly different, being 2·244 (9) (×2) and 2·365 (7) Å (×2) for Hg(1)—N, and 2·179 (10) (×2) and 2·416 (11) Å (×2) for Hg(2)—N, respectively. Whereas the shorter Hg—N bonds are close, the longer bonds are significantly larger than the sum of the corresponding covalent radii (1·48 Å for tetra-coordinated mercury, Grdenić, 1969). The angles between the shorter Hg—N bonds are larger [135·9 (3) and 138·2 (4)°] than the angles between the longer bonds [90·7 (2) and 100·3 (4)°].

The sulphate anions, located at the alternative diads, are bridged by the water molecules through hydrogen bonds O(1)···O(5), O(2)···O(5), O(3)···O(6) and O(4)···O(6) of 2·80 (2), 2·82 (2), 2·84 (2) and 2·83 (2) Å, respectively. The interatomic N···O distances (Table 2) of 2·80 (1) to 3·26 (1) Å indicate hydrogen bondings between the NH_2 groups and the SO_4 and H_2O O atoms, so that the structure consists of a three-dimensional network. The bond distances and angles in the sulphate ions and in the tn ligands are within expected values.

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Structure of Bis[*N*,*N*-bis(2-hydroxyethyl)dithiocarbamato]nickel(II), $C_{10}H_{20}N_2NiO_4S_4$

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Abstract. $M_r = 419{\cdot}25$, $P2_1/c$, $a = 6{\cdot}372\,(1)$, $b = 11{\cdot}844\,(1)$, $c = 11{\cdot}474\,(2)$ Å, $\beta = 93{\cdot}56\,(2)°$, $V = 864{\cdot}3$ Å^3, $Z = 2$, $D_x = 1{\cdot}611$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 1{\cdot}529$ mm^{-1}, $F(000) = 436$, $T = 293$ K, $R = 0{\cdot}046$, $R_w = 0{\cdot}047$ for 1551 unique reflections. The Ni atom is at $\bar{1}$ and is planar-coordinated to four sulphur atoms, with Ni—S(1) = 2·209 (1) and Ni—S(2) = 2·193 (1) Å, which agree with those in other (dithocarbamato)nickel compounds. The molecules are held together through O—H···O hydrogen bonds.

Introduction. Crystal structures of dithiocarbamates of nickel(II) $[Ni(S_2CNR_1R_2)_2]$ with various substituents (R_1 and R_2) have been reported (Raston & White, 1976). In all these cases the substituents were not hydrophilic in nature. We have observed that the presence of hydrophilic substituents such as C_2H_4OH causes high reactivity in nickel dithiocarbamates towards substitution reactions. To see whether this is reflected in the bond parameters of the compound, we undertook the crystal structure analysis of the title compound.

Experimental. Bis[*N*,*N*-bis(2-hydroxyethyl)dithiocarbamato]nickel(II) prepared using an earlier method (Sejekan & Aravamudan, 1978). Single crystals obtained by dissolving compound in acetone–water and evaporating solution. Needle-shaped green crystal

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