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Bis(biuret)mercury(II) Dichloride

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(*Received* 17 *May* 1976; *acccepted* 7 *June* 1976)

Abstract. Hg(NH$_2$CONHCONH$_2$)$_2$Cl$_2$ was crystallized from aqueous solution. Space group $P2_1/c$, $Z=2$, $a=3\cdot840$ (2), $b=18\cdot394$ (4), $c=9\cdot010$ (3) Å, $\beta=110\cdot20$ (2)°, $V=597\cdot3$ Å^3, $D_c=2\cdot65$, $D_o=2\cdot56$ (6) g cm^{-3}. The Hg atom lies on a centre of symmetry and has a distorted octahedral coordination geometry. The donor atoms are two Cl$^-$ ions and amide O atoms of four biuret molecules. The biuret ligands are monodentate, but each coordinating amide O atom is bonded to two Hg atoms. The Hg atoms are joined by double oxygen bridges to form infinite coordination polymers.

Introduction. Very small single crystals of Hg(BiuH$_2$)$_2$Cl$_2$ [BiuH$_2$ = H$_2$N–CO–NH–CO–NH$_2$] were obtained by slow evaporation of an aqueous solution containing stoichiometric amounts of HgCl$_2$ and biuret. A needle-shaped crystal of dimensions $0\cdot14 \times 0\cdot04 \times 0\cdot04$ mm, elongated along **a**, was used to record the intensities of 1055 independent reflexions (Enraf–Nonius CAD-4/F automatic diffractometer, ω–2θ scans, graphite-monochromated Mo $K\alpha$ radiation, $\lambda = 0\cdot7107$ Å, $1\cdot5° < \theta < 25°$). Three reference reflexions were measured after every 6000 s of X-ray exposure. No decomposition was detected. The 712 reflexions with intensities $I > 1\cdot5\sigma(I)$, where the standard deviations $\sigma(I)$ were based on counting statistics, were used to solve and refine the structure. Lorentz, polarization and absorption corrections ($\mu = 133\cdot4$ cm^{-1}) were applied. The scattering factors for Hg^{2+}, Cl$^-$, C, N and O were taken from *International Tables for X-ray Crystallography* (1974). The Hg^{2+} and Cl$^-$ ions were treated as anomalous scatterers. The structure was solved by Patterson and Fourier methods. The H atoms were not located. The refinement was carried out by full-matrix least squares. The function minimized was $\Sigma\,\sigma^{-2}(F)(|F_o| - s\,|F_c|)^2$. The values of $\sigma(F)$ were given by the square root of a second-degree polynomial in $|F_o|$, with coefficients fitted to a curve of ΔF *versus* $|F_o|$ after each refinement cycle. A Fourier $(F_o - F_c)$ synthesis computed after the last refinement cycle contained no significant excursions above background. The final values of the residuals were $R = 0\cdot049$, $R_w = 0\cdot053$ for the 712 reflexions used in the refinement, and $R = 0\cdot079$, $R_w = 0\cdot099$ for all 1055 reflexions.* The atomic positional and vibrational parameters are listed in Table 1.

Discussion. The Hg atoms in the structure occupy centres of symmetry and have a distorted octahedral coordination geometry. Each Hg atom is surrounded by two Cl atoms and four biuret molecules. The biuret molecules act as monodentate ligands, but the single O(amide) donor atom in each ligand is bonded to two Hg atoms. The result is that each Hg atom is joined to its neighbours in the x and $\bar{x}$ directions by double O(amide) bridges, and that the structure contains infinite –HgCl$_2$–[O(amide)]$_2$–HgCl$_2$– chains parallel to the a axis (Fig. 1 and Table 2).

The configuration of the two NH$_2$–CO–NH groups in the biuret molecule with respect to the central

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31963 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1 NZ, England.

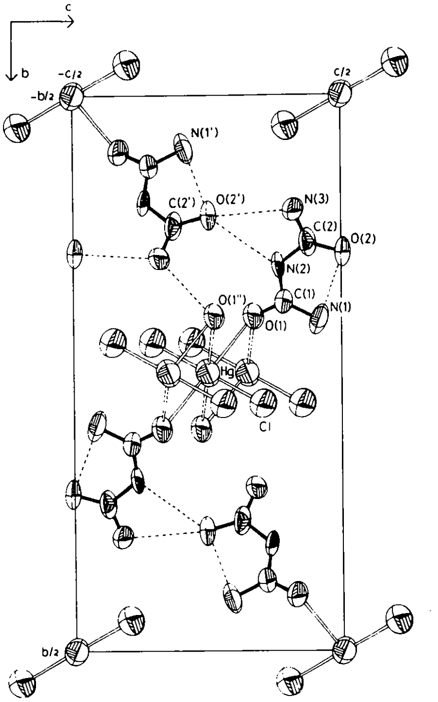

Fig. 1. Projection of the structure of $Hg(BiuH_2)_2Cl_2$ along **a***. Vibrational ellipsoids are shown at the 85% probability level. Dashed lines indicate hydrogen bonds. The superscripts used to identify symmetry-related atoms are explained in the caption to Table 2.

N(imide) atom is the same as in biuret hydrate (Hughes, Yakel & Freeman, 1961). The NH_2–CO–NH groups are planar within the limits of precision. The deviations of the atoms from the plane fitted by least squares to the whole biuret molecule are: O(1) –0·05, O(2) –0·07, N(1) 0·11, N(2) 0·03, N(3) 0·04, C(1) 0·03, C(2) 0·00 Å (e.s.d.'s of the atomic positions are 0·02 Å). There is an intramolecular N–H · · · O hydrogen bond between the N(amide) atom of the coordinating amide group and the O(amide) atom O(2) in the other half of the molecule. The atom O(2) is involved, in addition, in two hydrogen bonds with the amide and imide N atoms N(3) and N(2) of a neighbouring biuret molecule (Fig. 1 and Table 2).

Biuret can form metal complexes in three different ways. (i) Anionic bis(biuretato) complexes are formed with several transition-metal ions at *p*H's sufficiently high to permit biuret to coordinate as a bidentate dinegative ligand *via* deprotonated amide N atoms. This type of coordination has been shown by X-ray crystal-structure determinations for Cu^{II} (Freeman, Smith & Taylor, 1961; Birker & Beurskens, 1974*a*) and Co^{III} (Bour, Beurskens & Steggerda, 1972; Birker, Smits, Bour & Beurskens, 1973; Birker & Beurskens, 1974*b*), and from spectroscopic evidence for Ni^{II} (McLellan & Melson, 1967), Co^{II} (Kedzia, Armendarez & Nakamoto, 1968), Cu^{III} and Ni^{III} (Bour, Birker & Steggerda, 1971). (ii) Cationic bis(biuret) complexes in

Table 1. *Atomic fractional positional parameters and thermal parameters* (Å^2)

Estimated standard deviations are in given parentheses. The temperature factors are $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$.

	10^3x	10^4y	10^3z	10^3U_{11}	10^3U_{22}	10^3U_{33}	10^3U_{12}	10^3U_{13}	10^3U_{23}
Hg	0	0	0	40·7 (5)	38·4 (5)	31·5 (4)	–1·9 (7)	14·2 (3)	3·1 (7)
Cl	254 (1)	553 (2)	243·1 (5)	50 (2)	42 (2)	36 (2)	0 (2)	13 (2)	–3 (2)
O(1)	–367 (3)	–1010 (6)	118 (1)	49 (6)	34 (5)	18 (5)	–4 (5)	6 (4)	1 (6)
O(2)	144 (3)	–2163 (6)	527 (1)	64 (7)	44 (6)	15 (5)	1 (5)	17 (5)	–1 (4)
N(1)	–205 (4)	–949 (8)	385 (1)	59 (9)	46 (8)	22 (8)	7 (7)	18 (6)	–8 (6)
N(2)	–20 (4)	–1923 (7)	262 (1)	44 (7)	34 (6)	9 (5)	–2 (6)	8 (6)	3 (5)
N(3)	314 (4)	–2940 (7)	368 (1)	61 (9)	26 (6)	19 (6)	7 (6)	9 (6)	–0 (5)
C(1)	–204 (4)	–1270 (8)	255 (2)	43 (8)	29 (7)	19 (7)	–3 (6)	13 (6)	–3 (6)
C(2)	151 (4)	–2343 (8)	397 (2)	38 (8)	42 (9)	12 (6)	–10 (7)	4 (6)	–1 (6)

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

Standard deviations in parentheses. Superscripts indicate atoms whose coordinates are related to those shown in Table 1 by the following transformations: none x,y,z; (i) $x, -\frac{1}{2}-y, -\frac{1}{2}+z$; (ii) $1+x,y,z$; (iii) $1+x, -\frac{1}{2}-y, \frac{1}{2}+z$.

Hg–Cl	2·30 (4)	Cl–Hg–O(1)	92·0 (2)	C(1)–N(2) · · · O(2^{i})	134·1 (9)
Hg–O(1)	2·76 (1)	Cl–Hg–O(1^{ii})	84·8 (2)	C(2)–N(2) · · O(2^{i})	99·1 (9)
Hg–O(1^{ii})	2·95 (2)	O(1)–Hg–O(1^{ii})	84·4 (2)	C(2)–N(3) · · · O(2^{i})	101·8 (9)
C(1)–O(1)	1·27 (2)	Hg–O(1)–C(1)	118·8 (9)	C(2)–N(3) · · · O(1^{iii})	119·6 (9)
C(2)–O(2)	1·23 (2)	Hg–O(1^{ii})–C(1^{ii})	131·1 (9)	O(2^{i})–N(3) · · · O(1^{iii})	138·1 (6)
C(1)–N(1)	1·32 (2)	O(1)–C(1)–N(1)	123 (2)	Hg^{iii}–O(1^{iii}) · · N(3)	106·4 (4)
C(1)–N(2)	1·38 (2)	O(1)–C(1)–N(2)	116 (1)	C(2)–O(2) · · N(1)	87 (1)
C(2)–N(2)	1·40 (2)	N(1)–C(1)–N(2)	120 (1)	C(2^{i})–O(2^{i}) · · · N(2)	128 (1)
C(2)–N(3)	1·34 (2)	C(1)–N(2)–C(2)	127 (1)	C(2^{i})–O(2^{i}) · · · N(3)	162 (1)
N(1) · · · O(2)	2·69 (2)	O(2)–C(2)–N(2)	122 (2)	N(1^{i}) · · · O(2^{i}) · · · N(3)	109·9 (5)
N(2) · · · O(2^{i})	2·93 (2)	O(2)–C(2)–N(3)	125 (1)	N(1^{i}) · · · O(2^{i}) · · · N(2)	128·5 (6)
N(3) · · · O(1^{iii})	2·90 (2)	N(2)–C(2)–N(3)	113 (1)		
N(3) · · · O(2^{i})	2·91 (2)	C(1)–N(1) · · · O(2)	84 (1)		

which biuret is bound to the metal as a bidentate neutral ligand *via* two O atoms are formed with Cu^{II} (Freeman & Smith, 1966), Zn^{II} (Nardelli, Fava & Giraldi, 1963) and Sr^{II} (Salim Haddad & Gentile, 1975), as shown by structure analyses. The same type of coordination has been inferred from IR spectroscopic data for Co^{II}, Ni^{II} and Mn^{II} complexes (Nuttall & Melson, 1969). (iii) Finally, Cavalca, Nardelli & Fava (1960) have shown that biuret acts as a monodentate neutral ligand in Cd(BiuH$_2$)$_2$Cl$_2$. The structure consists of infinite chains in which pairs of Cl atoms form double bridges between Cd atoms. The biuret molecules are anchored to the —Cd—Cl$_2$—Cd—Cl$_2$— chains by Cd—O(amide) bonds.

Nardelli & Chierici (1960) have characterized a Hg^{II} complex which they describe as isostructural with Cd(BiuH$_2$)$_2$Cl$_2$ on the basis of a similarity between the unit-cell parameters of the crystals of the two complexes. The unit-cell parameters reported by Nardelli & Chierici (1960) are significantly different from those now found by us* (Table 3). It is therefore not surprising that the present Hg complex is not isostructural with the Cd(BiuH$_2$)$_2$Cl$_2$ complex of Cavalca, Nardelli & Fava (1960). Both complexes contain monodentate biuret ligands. However, the double chloride bridges of the Cd complex are replaced by double O(amide) bridges in the Hg complex. The Hg—O—Hg bridges are less symmetrical (Hg—O = 2·76, 2·95 Å) than the Cd—Cl—Cd bridges (Cd—Cl = 2·55, 2·62 Å). These structural differences between Cd(BiuH$_2$)$_2$Cl$_2$ and the form of Hg(BiuH$_2$)$_2$Cl$_2$ prepared by us provide an explanation for the observation by Nuttall & Melson (1969) that the far-IR spectra of the two complexes are significantly different. In the spectrum of Cd(BiuH$_2$)$_2$Cl$_2$, Nuttall & Melson assign two low-frequency bands at 212 and 178 cm^{-1} to ν(M—Cl), and a single band at 308 cm^{-1} to ν(M—O). This assignment is consistent with the existence in this complex of two types of Cd—Cl bonds with different bond lengths, and only a single type of Cd—O bond. In the spectrum of Hg(BiuH$_2$)$_2$Cl$_2$ there is only *one* low-frequency band ascribable to ν(M—Cl) at 175 cm^{-1}, but there are *two* bands in the ν(M—O) region at 302 and 324 cm^{-1} (plus a shoulder at 288 cm^{-1}). This is just as expected for the spectrum of a complex with a single type of Hg—Cl bond but with two crystallographically distinct types of Hg—O bonds.

Table 3. *Comparison of the unit-cell parameters with those of Nardelli & Chierici* (1960)

	Nardelli & Chierici (1960)	Present work
a	3·768 ± 4 Å	3·840 (2) Å
b	20·56 ± 2	18·394 (4)
c	8·16 ± 1	9·010 (3)
β	109·1 ± 3°	110·20 (2)°
Space group	$P2_1/c$	$P2_1/c$

We gratefully acknowledge financial support from the Australian Research Grants Committee (Grant 65/15552), and the award of a University of Sydney Post-Doctoral Fellowship to PJMWLB.

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* New X-ray diffraction photographs have recently been recorded with crystals taken from the original preparation of Nardelli & Chierici (1960). The results confirm that the unit-cell parameters and space group were correctly reported, and show that the crystals prepared in Parma in 1960 and those used in the present work belong to different crystalline modifications of Hg(BiuH$_2$)$_2$Cl$_2$ (Professor M. Nardelli, Parma, personal communication).