length, passing from the $+2$ to the $+3$ oxidation state, would be counterbalanced by the decrease in the Ru—S bond order.

On the other hand, if the $Ru^{III}$—S bonding has a prevailing $\sigma$ character, this would induce a positive charge on the S atom and thereby would increase the $p\pi$–$d\pi$ overlap between oxygen and sulfur orbitals, with a consequent increase in the S=O bond order (Davies, 1981) and decrease of the S—O bond lengths. In fact, the S(2)—O(2) bond length of 1.467 (3) Å, comparable to those of 1.467 (5) Å in the $[(dmso)_2H]^+$ analogue and 1.465 (4) Å in the tmso derivative, appears to be shorter than the S—O bond lengths in $Ru^{II}$ S-bonded dmso complexes, which average 1.48 (1) Å (Alessio et al., 1988), as has already been indicated. The S(1)—O(1) bond distance of 1.472 (2) Å is slightly longer, owing to hydrogen-bonding effects, as also found in the tmso derivative [1.488 (2) Å] (Alessio et al., 1990).

The strengthening of the S—O bond in $Ru^{III}$ complexes is clearly shown by the higher $\nu$(S=O) stretching frequencies, e.g. 1129 cm$^{-1}$ in $[(dmso)_2H]$-$[Ru(dmso)_2Cl_4]$ versus 1089 cm$^{-1}$ in trans-$[RuCl_2(dmso)_4]$ (Alessio et al., 1988).

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# Structure of Dichloro(2-pyrimidinol-κN,O)mercury(II)

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**Abstract.** [HgCl$_2$(C$_4$H$_4$N$_2$O)], $M_r = 367.6$, monoclinic, $P2_1/c$, $a = 10.506$ (3), $b = 4.187$ (1), $c = 17.337$ (12) Å, $\beta = 92.97$ (7)°, $V = 761.6$ (6) Å$^3$, $Z = 4$, $D_x = 3.206$ Mg m$^{-3}$, $\lambda$(Mo $K\alpha$) = 0.71069 Å, $\mu = 20.848$ mm$^{-1}$, $F(000) = 656$, $T = 295$ K, final $R = 0.059$ for 1704 unique observed reflections. The Hg atom is coordinated by the two Cl and one N atom and the carbonyl O atom of 2-pyrimidinol, forming a four-membered chelate ring. A hydrogen bond N—H⋯O and the weak interaction of Cl atoms with neighbouring Hg atoms results in a ladder-like structure along the $b$ axis.

**Introduction.** Metal complexes of pyrimidine derivatives have, for a long time, been widely studied, especially pyrimidines that play an important role in biochemistry (Beauchamp & Simard, 1984). Surprisingly enough, we have found very few references to 2-pyrimidinol (Goodgame & Jeeves, 1979), despite the fact that it is one of the simplest of the family, the only crystal structure report being of a copper(II) complex (Cartwright, Reynolds & Skapski, 1977). As part of our work on the coordination chemistry of pyrimidines (Romero, Salas, Simard, Quirós & Beauchamp, 1990), we report here the synthesis and crystal structure of the compound obtained by the reaction of mercury oxide with 2-pyrimidinol hydrochloride.

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**Experimental.** Dichloro(2-pyrimidinol)mercury(II) was prepared by dissolving mercury(II) oxide in a boiling solution of 0.2 mmol of 2-pyrimidinol hydrochloride. After 30 min reflux, excess HgO was filtered off prior to cooling to room temperature, when white needles of the compound appeared.

A needle of dimensions 0.24 × 0.12 × 0.11 mm was mounted in a Siemens $R3m/V$ diffractometer. Unit cell and orientation matrix deduced from 25 centred reflections with $25 < \theta < 40°$. Space group uniquely identified by systematic absences. Graphite-monochromatized Mo $K\alpha$ radiation. 8572 reflections measured ($\omega$ scan) across the whole sphere ($-14 \le h \le 14$, $-5 \le k \le 5$, $-20 \le l \le 20$, $3 < 2\theta < 60°$), merged to 2130 independent reflections ($R_{int} = 0.033$). Orientation and stability checked every hour, with no significant change in the four standard reflections. 1704 reflections with $|F_o| > 4\sigma(|F_o|)$ used. Data were corrected for Lp effects and empirically for absorption (minimum and maximum transmission factors 0.0643 and 0.1302), using the *EMPIR* facility of the *SHELXTL-Plus* package, (Sheldrick, 1987), based on the $\psi$ scan of eight selected reflections (a numerical absorption correction was also run in parallel yielding virtually the same results).

The Hg atom was located from a Patterson synthesis, the others from $\Delta F$ map. Structure refined anisotropically on $|F_o|$ by full-matrix least-squares method. Weight for the reflections given by $w^{-1} = \sigma^2(F) + 0.001F^2$. An extinction parameter was refined to a final value of 3.0 (8) × $10^{-4}$. The four H atoms were readily located from the subsequent $\Delta F$ map, nevertheless their positions were idealized and a fixed $B_{iso} = 4.2$ Å$^2$ was assigned to them. Final $R = 0.059$, $wR = 0.068$, $S = 1.40$, mean and maximum shift/$\sigma$ in the last cycle 0.001 and 0.004 for 92 refined parameters. Residual peaks and holes near the Hg atom of 2.1 and $-1.9$ e Å$^{-3}$. All calculations and drawings made with the *SHELXTL-Plus* package on a MicroVAX II computer. Scattering factors and anomalous-dispersion contributions included in the package. Final atomic coordinates are listed in Table 1.* H-atom coordinates, anisotropic thermal parameters and observed and calculated structure factors are included in the supplementary material.

**Discussion.** The structure consists of HgCl$_2$(2-pyrimidinol) units in which the Hg atom is coordinated by the two Cl atoms and an organic bidentate ligand that coordinates *via* N(3) and the carbonyl O atom,

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55574 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

**Table 1.** *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic displacement coefficients* (Å$^2 \times 10^3$)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

|       | $x$       | $y$        | $z$      | $U_{eq}$ |
|-------|-----------|------------|----------|----------|
| Hg    | 1822 (1)  | 2845 (1)   | 3303 (1) | 44 (1)   |
| Cl(1) | 179 (3)   | 6449 (9)   | 3466 (2) | 49 (1)   |
| Cl(2) | 3348 (3)  | −413 (9)   | 2781 (2) | 53 (1)   |
| N(1)  | 4005 (10) | 2001 (25)  | 5564 (6) | 40 (3)   |
| C(2)  | 3326 (12) | 2620 (30)  | 4871 (7) | 38 (4)   |
| O(2)  | 3752 (8)  | 4498 (24)  | 4375 (5) | 48 (3)   |
| N(3)  | 2191 (10) | 1091 (29)  | 4733 (6) | 44 (3)   |
| C(4)  | 1755 (11) | −736 (32)  | 5284 (8) | 41 (4)   |
| C(5)  | 2414 (12) | −1240 (33) | 5979 (7) | 42 (4)   |
| C(6)  | 3559 (12) | 147 (31)   | 6106 (7) | 40 (4)   |

**Table 2.** *Interatomic distances* (Å) *and bond angles* (°)

| | | | |
|---|---|---|---|
| Hg—Cl(1) | 2.321 (4) | C(1)—Hg—Cl(2) | 164.1 (1) |
| Hg—Cl(2) | 2.324 (4) | Cl(1)—Hg—O(2) | 106.0 (2) |
| Hg—O(2) | 2.767 (9) | Cl(2)—Hg—O(2) | 85.1 (2) |
| Hg—N(3) | 2.60 (1) | Cl(1)—Hg—N(3) | 98.2 (3) |
| N(1)—C(2) | 1.39 (2) | Cl(2)—Hg—N(3) | 97.7 (3) |
| N(1)—C(6) | 1.32 (2) | O(2)—Hg—N(3) | 50.0 (3) |
| C(2)—O(2) | 1.26 (2) | C(2)—N(1)—C(6) | 123 (1) |
| C(2)—N(3) | 1.36 (2) | N(1)—C(2)—O(2) | 121 (1) |
| N(3)—C(4) | 1.32 (2) | N(1)—C(2)—N(3) | 118 (1) |
| C(4)—C(5) | 1.37 (2) | O(2)—C(2)—N(3) | 121 (1) |
| C(5)—C(6) | 1.34 (2) | Hg—O(2)—C(2) | 91.9 (7) |
| Hg···Cl(1ⁱ) | 3.209 (4) | Hg—N(3)—C(2) | 96.9 (8) |
| Hg···Cl(2ⁱⁱ) | 3.395 (5) | Hg—N(3)—C(4) | 144.3 (8) |
| N(1)···O(2ⁱⁱⁱ) | 2.78 (1) | C(2)—N(3)—C(4) | 118 (1) |
| H(1)···O(2ⁱⁱⁱ) | 1.83 | N(3)—C(4)—C(5) | 123 (1) |
| | | C(4)—C(5)—C(6) | 119 (1) |
| | | N(1)—C(6)—C(5) | 119 (1) |

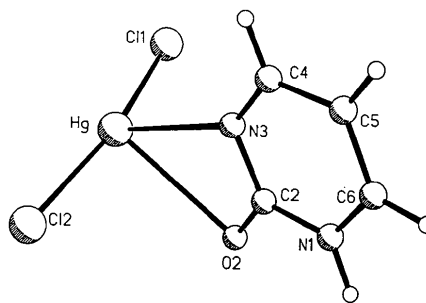Symmetry code: (i) $x$, $y - 1$, $z$; (ii) $x$, $y + 1$, $z$; (iii) $1 - x$, $1 - y$, $1 - z$.



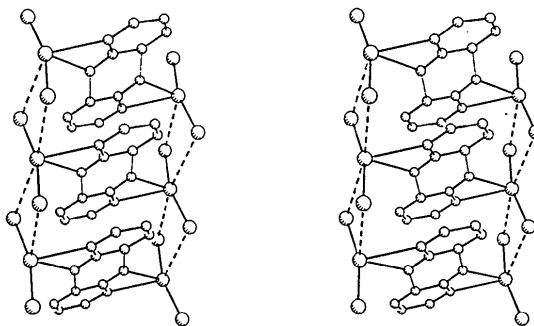Fig. 1. View of the molecule of [Hg(2-pyrimidinol)Cl$_2$].



Fig. 2. Stereoscopic view of the ladder-like structure that the compound forms along the $b$ axis.

forming a four-membered chelate ring (Fig. 1). We have not found any previous reference to a structure including an analogous Hg—N—C—O chelate. In the copper complex referenced above (Cartwright, Reynolds & Skapski, 1977), the interaction is fundamentally monodentate through the N atom, as happens with the mercury complex of 1-methyl-cytosine (Authier-Martin & Beauchamp, 1977). Interatomic distances and bond angles appear in Table 2.

The geometry around the metal atom is very irregular, as expected from the constraints imposed by chelation, but may be described as intermediate between a linear Cl—Hg—Cl and a planar trigonal N(3)—Hg—Cl$_2$ with the more weakly coordinated O atom out of the HgNCl$_2$ plane. The Hg—Cl distances are similar to those in analogous compounds (Authier-Martin & Beauchamp, 1977; Authier-Martin, Hubert, Rivest & Beauchamp, 1978), whereas the Hg—N(3) and Hg—O(2) bonds are longer than in complexes where the ligand is mono-dentate (Kosturko, Folzer & Stewart, 1974), which is also a logical consequence of bidentate union.

Distances and angles within the ligand are very similar to those in free 2-pyrimidinol (Furberg & Solbakk, 1970), the appreciable distortions in bond angles that appear in its hydrochloride (Furberg & Aas, 1975) not taking place in our compound. The pyrimidine ring is planar within 0.03 Å, with the Hg atom displaced 0.371 Å out of the plane.

A hydrogen bond is formed between the only possible donor, N(1), and the carbonyl O atom of a neighbouring molecule, giving pairs related by the symmetry centre at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. The Hg atom interacts weakly with Cl atoms of neighbouring unit cells at $y + 1$ and $y - 1$ ($b$ parameter is only 4.187 Å). This interaction together with the previous hydrogen bond generates a ladder-like structure along the $b$ axis (Fig. 2).

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# The First Zwitterionic and Bent-Sandwiched Hafnacarborane 4',5,5',6-Li(THF)-1,1'-commo-Hf(THF)Cl[2-(SiMe$_3$)-3-(Me)-2,3-C$_2$B$_4$H$_4$]$_2$

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**Abstract.** 4',5,5',6-(Tetrahydrofuranlithium)-1-chloro-3,3'-dimethyl-1-(tetrahydrofuran-O)-2,2'-bis(trimethylsilyl)dodecahydro-1,1'-commo-bis(2,3-dicarba-1-hafna-closo-heptaborate), C$_{20}$H$_{48}$B$_8$ClHfLiO$_2$Si$_2$, $M_r = 684.1$, monoclinic, $P2_1/c$, $a = 16.821$ (5), $b = 16.277$ (5), $c = 12.131$ (5) Å, $\beta = 90.41$ (3)°, $V = 3321$ (2) Å$^3$, $Z = 4$, $D_x = 1.368$ Mg m$^{-3}$, $\lambda$(Mo $K\alpha$) = 0.71073 Å, $\mu = 3.474$ mm$^{-1}$, $F(000) = 1376$, $T = 230$ K, final $R = 0.049$ for 2482 observed reflections. The structure shows that the title compound (2) is a zwitterion consisting of an anionic {1,1'-commo-Hf(Cl)(THF)[$\eta^5$-2-(SiMe$_3$)-3-(Me)-2,3-C$_2$B$_4$H$_4$]$_2$}$^-$ sandwich that is complexed with an exo-polyhedral [Li(THF)]$^+$ cation for charge compensation. Bond distances in the cage structure are Hf—C 2.50 (1)–2.55 (1), Hf—B 2.52 (2)–2.56 (2), Hf—C$_2$B$_3$ centroid 2.15 and 2.16, Hf—O(THF) 2.199 (8) and Hf—Cl 2.437 (3) Å. The Hf—centroid and Hf—Cl distances, the Cl—Hf—O(THF) angle of 89.7 (2)°, and the centroid—Hf—centroid angle of 134.1° of (2) resemble those of a hafnocene derivative despite the presence of a 2 − charge on each carborane ligand. As in

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