# Synthesis and Solid-state Structural Characterization of N,N'-Dicyclohexyldithiooxamide Complexes of HgX<sub>2</sub> (X = SCN or Cl)<sup>†</sup>

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*N*,*N*'-Dicyclohexyldithiooxamide (H<sub>2</sub>L) reacted with HgX<sub>2</sub> (X = SCN or Cl) to form the novel mercury mixed-ligand complexes [Hg(H<sub>2</sub>L)(SCN)<sub>2</sub>] **1**, [HgCl<sub>2</sub>(H<sub>2</sub>L)] **2** and [{HgCl<sub>2</sub>(H<sub>2</sub>L)}<sub>2</sub>]•EtOH **3**. The crystal and molecular structures of **1** and **3** have been determined. Crystals of **1** are monoclinic, space group  $P2_1/n$  (no. 14), with a = 11.318(1), b = 17.727(2), c = 11.536(2) Å,  $\beta = 109.08(2)^{\circ}$  and Z = 4. Crystals of **3** are monoclinic, space group  $P2_1$  (no. 4), with a = 8.563(1), b = 21.414(3), c = 11.649(2) Å,  $\beta = 103.58(2)^{\circ}$  and Z = 2. The structures were each refined by a full-matrix least-squares procedure to R1 = 0.031 for 2218 reflections with  $F^2 \ge 2.0\sigma(F^2)$  for **1** and R1 = 0.047 (2374 reflections) for **3**. Complex **1** is mononuclear with HgS<sub>4</sub> units linked by short intermolecular S···S interactions. Complex **3** is a binuclear zwitterionic system with one S,S'-chelating H<sub>2</sub>L ligand bonded to a mercury atom and a second ligand acting in an unusual conformation as a S,S'-bidentate bridging group between the ionic species HgS<sub>2</sub>Cl<sup>+</sup> and HgCl<sub>3</sub><sup>-</sup>. The two mercury atoms are separated at a non-interacting distance. The infrared spectra of the complexes in the range 650–200 cm<sup>-1</sup> are discussed in the light of the known structures.

The co-ordination chemistry of mercury(II) with sulfur-donor ligands is a topic of current research largely because of the relevance of such complexes as structural and spectroscopic models in biological systems<sup>1-14</sup> and solid-state materials.<sup>15</sup>

Monofunctional alkene- and arene-thiolate ligands have played a major role as model compounds in these investigations. Also of interest are the chelating agents based on the S-C-C-S configuration which can mimic the polysulfhydryl metal-binding sites in metallothioneins, and are believed to be effective as mercury(II) antidotes.<sup>16</sup> Very recently, a mononuclear HgS<sub>4</sub> core with a 1,2-alkanedithiolate ligand has been reported for the [Hg(SC<sub>6</sub>H<sub>11</sub>)<sub>2</sub>]<sup>2-</sup> anion.<sup>11</sup> Among related Sdonor ligands, N,N'-disubstituted dithiooxamides of the general formula RNHC(S)C(S)NHR are a class of versatile ligands with low-lying  $\pi$  orbitals, that have found a wide range of interesting applications.<sup>17</sup> Although extensively reported the number of structurally characterized transition-metal complexes with dithiooxamides as co-ordinating agents is rather scarce, and mostly limited to complexes of the Group 10 elements. S,S'-Chelate co-ordination has been observed in most of these complexes whereas N,S-co-ordination has been found in copper and in certain polymeric nickel complexes.<sup>18-23</sup> The interaction of mercury(II) with RHNC(S)C(S)NHR ligands has been mentioned before in the literature, but without the characterization of any compound.<sup>24</sup> Herein we report the isolation of novel adduct complexes formed upon the reactions of HgX<sub>2</sub> (X = SCN or Cl) with the N,N'-dicyclohexyldithiooxamide (H<sub>2</sub>L) ligand.

The results of this study include the X-ray structural determinations of  $[Hg(H_2L)(SCN)_2]$  and  $[{HgCl_2(H_2L)}_2]$ . EtOH. It was of interest to examine the co-ordinative be-

haviour of the  $H_2L$  ligand towards the 'soft'  $Hg^{2+}$  metal ion and its dependence on the anions associated with the metal centre.

# **Experimental**

All commercially available reagents and chemicals were of analytical or reagent-grade purity and used without further purification. The C, H, N and S analyses were determined at the Instituto de Quimica de Materiales, Medio Ambiente y Energia with a Carlo Erba EA 1108 elemental microanalyser. Infrared spectra were recorded in the range 200–4800 cm<sup>-1</sup> on a Nicolet 510P FTIR spectrophotometer. The samples were Nujol or halogenocarbon mulls supported between CsI discs; CsI pellets were also run and no significant differences were observed.

Syntheses.—[Hg(H<sub>2</sub>L)(SCN)<sub>2</sub>] 1. N,N'-Dicyclohexyldithiooxamide (0.71 g, 2.50 mmol) was dissolved in dry acetone (100 cm<sup>3</sup>) to which Hg(SCN)<sub>2</sub> (0.40 g, 1.25 mmol) was added in small portions. The reaction mixture was stirred at 35 °C for 4 h. The yellow precipitate that immediately formed was collected by filtration, washed with acetone and dried *in vacuo*. The solid was sparingly soluble in most solvents including acetone. The product was recrystallized by dissolving a very small portion in warm acetone and allowing the solution to cool slowly. The yellow needle crystals of 1 were isolated by filtration and dried *in vacuo*. Yield: 0.61 g (80%) (Found: C, 32.35; H, 4.15; N, 9.3; S, 20.15. C<sub>16</sub>H<sub>24</sub>HgN<sub>4</sub>S<sub>4</sub> requires C, 31.95; H, 4.0; N, 9.3; S, 21.3%). IR(KBr): 3154m, 2124vs (HgSC≡N), 1563vs and 1508m cm<sup>-1</sup>.

[HgCl<sub>2</sub>(H<sub>2</sub>L)] 2. N,N'-Dicyclohexyldithiooxamide (0.71 g, 2.50 mmol) was dissolved in dry acetone (100 cm<sup>3</sup>) to which HgCl<sub>2</sub> (0.34 g, 1.25 mmol) was added with stirring in small portions. The deep yellow reaction mixture was stirred at 25 °C

<sup>†</sup> Supplementary data available: see Instructions for Authors, J. Chem. Soc., Dalton Trans., 1995, Issue 1, pp. xxv-xxx.

for 4 h. It was then filtered and the filtrate was stored in a refrigerator for a few days whereupon the major product deposited as bright yellow needles which were collected by filtration. The crystals cracked within a few hours presumably due to loss of acetone molecules of crystallization, as evidenced by the gradual disappearance of the IR band at *ca.* 1695 cm<sup>-1</sup> [v(CO)]. Total removal of acetone under vacuum yielded the powdery yellow solid **2**. Yield: 0.49 g (70%) (Found: C, 30.0; H, 4.6; N, 5.5; S, 11.85. C<sub>14</sub>H<sub>24</sub>Cl<sub>2</sub>HgN<sub>2</sub>S<sub>2</sub> requires C, 30.2; H, 4.35; N, 5.0; S, 11.5%). IR (KBr): 3156m, 1553s and 1508s cm<sup>-1</sup>.

[{HgCl<sub>2</sub>(H<sub>2</sub>L)}<sub>2</sub>]•EtOH **3**. This complex was synthesized in a manner analogous to that described above from N,N'-dicyclohexyldithiooxamide (0.71 g, 2.5 mmol) and HgCl<sub>2</sub> (0.34 g, 1.25 mmol) in acetone–ethanol (1:1, 100 cm<sup>3</sup>) at room temperature. The reaction mixture was stirred for 24 h at 25 °C and then filtered. The filtrate was kept at 10 °C for 3 d. Light green-yellow prismatic crystals of complex **3** were collected and dried under vacuum. Yield: 0.45 g (60%) (Found: C, 32.25; H, 4.9; N, 4.9; S, 11.2. C<sub>16</sub>H<sub>30</sub>Cl<sub>2</sub>HgN<sub>2</sub>OS<sub>2</sub> requires C, 32.0; H, 5.0; N, 4.7; S, 10.7%). IR (KBr): 3154m, 1550s and 1508s cm<sup>-1</sup>. Suitable crystals of **3** for X-ray diffraction analysis were also obtained by slow diffusion of ethanol in a diluted acetone solution of complex **3**.

X-Ray Crystallography.—The crystal data and details of data collection and refinement are summarized for the crystal structures of complexes 1 and 3 in Table 1. Diffraction intensities were collected at 298 K on a Siemens R3m automated diffractometer, with graphite-monochromatized Mo-Ka radiation ( $\lambda = 0.710$  73 Å). The  $\omega$ -2 $\theta$  scan mode was used in the 20 range 3-45°, with a variable scan speed  $4.10-29.30^{\circ}$ min<sup>-1</sup>. Two standard reflections checked every 98 showed no significant crystal decay. Intensities were corrected for Lorentz, polarization and absorption effects through a semi-empirical psi-scan correction (XEMP in the SHELXTL PLUS package<sup>25</sup>). The structures were solved by direct methods and Fourier-difference synthesis (XS in the SHELXTL PLUS package<sup>25</sup>) and refined by full-matrix least-squares on  $F^2$  (SHELXL 93).<sup>26</sup> All calculations were performed on a PC 486/33. A soft metric similarity restraint was applied to the cyclic groups to help refinement. All the hydrogen atoms except for C[H(1S)] in complex 3 were included at calculated positions with fixed isotropic thermal parameters ( $U = 0.08 \text{ Å}^2$ ). The two rather strong intermolecular hydrogen bonds in 3 formed by the EtOH molecule via the hydroxyl group, N(1)-H(1') $\cdots$  O(1S) and O(1S)-H(1S)  $\cdots$  Cl(3), restrain the allowed positions of C[H(1S)] in accordance with the short O(1S) ... Cl(3) distance found. In the latest stages of refinement, all non-hydrogen atoms were treated anisotropically. Only C(2S)in the EtOH molecule showed an abnormally large anisotropic thermal parameter, reflecting some degree of disorder. Tables 2 and 3 list the atomic coordinates and Tables 4 and 5 relevant selected interatomic distances and angles for complexes 1 and 3, respectively. ORTEP-type drawings (XP in the SHELXTL PLUS<sup>25</sup> package) for both structures are shown with 40% probability ellipsoids in Figs. 1 and 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

## **Results and Discussion**

Reactions between covalent  $HgX_2$  (X = SCN or Cl) and N,N'dicyclohexyldithiooxamide in a 1:2 molar ratio in dry acetone led to the isolation of mononuclear [Hg(H<sub>2</sub>L)(SCN)<sub>2</sub>] 1 and [HgCl<sub>2</sub>(H<sub>2</sub>L)] 2. When the medium of synthesis is acetoneethanol (1:1), the reaction of HgCl<sub>2</sub> and H<sub>2</sub>L under similar conditions yields the binuclear [{HgCl<sub>2</sub>(H<sub>2</sub>L)}<sub>2</sub>] EtOH 3 as the principal product. The solid compounds are stable when kept in the dark in a dry atmosphere at room temperature. The very low solubility of complex 1 and the decomplexation reactions of 2 Table 1 Details of data collection and refinement for complexes 1 and 3

| Compound                                    | 1                              | 3                              |
|---|--------------------------------|--------------------------------|
| Formula                                     | C., H., HgN, S.                | CaoHerCLHgaN.OS.               |
| M   | 601.22                         | 1157.99                        |
| Crystal system                              | Monoclinic                     | Monoclinic                     |
| Space group                                 | $P2_1/n$ (no. 14)              | $P2_1$ (no. 4)                 |
| Crystal size/mm                             | $0.25 \times 0.08 \times 0.08$ | $0.40 \times 0.32 \times 0.20$ |
| a/Å   | 11.318(1)                      | 8.563(1)                       |
| b/Å   | 17.727(2)                      | 21.414(3)                      |
| c/Å   | 11.536(2)                      | 11.649(2)                      |
| β/°   | 109.08(2)                      | 103.58(2)                      |
| $U/Å^3$                                     | 2187.4(5)                      | 2076.3(5)                      |
| Ź   | 4                              | 2                              |
| $D_c/\mathrm{g}\mathrm{cm}^{-3}$            | 1.83                           | 1.85                           |
| F(000)                                      | 1168                           | 1124                           |
| $\mu/mm^{-1}$                               | 7.43                           | 7.87                           |
| θ Range/°                                   | 2.19-22.55                     | 1.80-22.55                     |
| Index ranges                                | $0 \leq h \leq 12$ ,           | $0 \leq h \leq 9$              |
| c   | $0 \leq k \leq 19$ ,           | $-1 \leq k \leq 23$            |
|   | $-12 \leq l \leq 11$           | $-12 \leq I \leq 12$           |
| Reflections collected                       | 3047                           | 3185                           |
| Independent reflections $(R_{int})$         | 2877 (0.021)                   | 2958 (0.049)                   |
| Observed reflections $[F^2 > 2\sigma(F^2)]$ | 2218                           | 2374                           |
| Maximum, minimum<br>transmission            | 0.496, 0.345                   | 0.154, 0.094                   |
| Data $(n)$ , parameters $(p)$               | 2874, 231                      | 2957, 246                      |
| $R1, wR2 [F^2 > 2\sigma(F^2)]^a$            | 0.031, 0.055                   | 0.047, 0.100                   |
| R1, wR2 (all data)                          | 0.054, 0.063                   | 0.070, 0.118                   |
| Goodness-of-fit on $F^{2b}$                 | 1.058                          | 1.042                          |
| Maximum peak,<br>hole/e Å <sup>-3</sup>     | 0.46, -0.46                    | 1.17, -1.44                    |

 $<sup>{}^{</sup>a}R1 = \Sigma ||F_{o}| - |F_{c}||/\Sigma F_{o}, wR2 = \{\Sigma [w(F_{o}^{2} - F_{c}^{2})^{2}]/\Sigma w(F_{o}^{2})^{2}\}^{\frac{1}{2}} \text{ where } w = 1/[\sigma^{2}(F_{o}^{2}) + (AP)^{2} + BP], P = (F_{o}^{2} + 2F_{c}^{2})/3, A = 0.027, 0; B = 0.059, 4.10 \text{ for } 1 \text{ and } 3. {}^{b}\text{Goodness of fit } S = \{\Sigma [w(F_{o}^{2} - F_{c}^{2})^{2}/(n - p)]^{\frac{1}{2}}.$ 

**Table 2** Atomic coordinates  $(\times 10^4)$  for  $[Hg(H_2L)(SCN)_2]$  1

| Atom  | x        | у         | Z       |
|-------|----------|-----------|---------|
| Hg    | 306(1)   | 460(1)    | 2657(1) |
| S(1)  | 522(2)   | -601(1)   | 4131(2) |
| S(2)  | -1587(2) | 221(1)    | 832(2)  |
| S(3)  | 258(2)   | 1791(1)   | 3541(2) |
| S(4)  | 2213(2)  | 911(1)    | 2136(2) |
| N(1)  | 2640(7)  | - 1290(4) | 3882(6) |
| N(2)  | -1486(7) | 1491(5)   | -532(8) |
| N(3)  | 937(5)   | 2879(3)   | 2315(5) |
| N(4)  | 3282(5)  | 2219(3)   | 2895(5) |
| CÌÌ   | 1783(7)  | -994(4)   | 3964(6) |
| C(2)  | -1499(7) | 975(5)    | 39(8)   |
| C(3)  | 1138(6)  | 2206(3)   | 2786(6) |
| C(4)  | 2270(6)  | 1811(3)   | 2632(6) |
| C(5)  | - 74(6)  | 3400(3)   | 2325(6) |
| C(6)  | -838(7)  | 3611(4)   | 1035(6) |
| C(7)  | -1851(7) | 4178(4)   | 1031(8) |
| C(8)  | -1321(9) | 4866(4)   | 1791(7) |
| C(9)  | - 544(8) | 4645(4)   | 3069(7) |
| C(10) | 486(6)   | 4089(4)   | 3082(6) |
| C(11) | 4473(6)  | 1990(4)   | 2728(5) |
| C(12) | 5509(6)  | 2498(5)   | 3480(7) |
| C(13) | 6744(7)  | 2307(5)   | 3285(7) |
| C(14) | 6626(7)  | 2328(4)   | 1938(7) |
| C(15) | 5590(6)  | 1816(4)   | 1183(7) |
| C(16) | 4353(6)  | 2003(4)   | 1368(6) |

and 3 in most common solvents prevented the characterization of the complexes in solution. The structures of these new molecules were first deduced from spectroscopic data and microanalysis. Single-crystal X-ray structural studies have been carried out on complexes 1 and 3. The structure of 2 could not Published on 01 January 1995. Downloaded by University of California - San Francisco on 05/09/2014 22:24:03

**Table 3** Atomic coordinates  $(\times 10^4)$  for  $[{HgCl_2(H_2L)}_{2}]$  EtOH 3

120.3(11)

124.4(12)

121.5(10)

C(1)-C(8)-S(2)

N(3)-C(15)-S(3)

C(15)-C(22)-S(4)

N(4)-C(22)-C(15) 114.1(14)

| Atom   | x                        | У                      | Z                        | Atom   | x                        | у                        | z                |                    |  |
|--|--------------------------|------------------------|--------------------------|--|--------------------------|--------------------------|------------------|--------------------|--|
| Hg(1)  | 16 443(1)                | 22 882                 | 15 233(1)                | C(10)  | 11 040(19)               | 24 173(10)               | 13 669(          | 16)                |  |
| $H_{g}(2)$   | 18 977(1)                | 24 528(1)              | 16 959(1)                | Càn  | 10 259(29)               | 24 366(8)                | 6(8) 12 422(17   |                    |  |
| S(1)   | 16 369(7)                | 23 249(3)              | 17 236(5)                | C(12)  | 10 146(22)               | 25 067(7)                | 067(7) 12 287(2: |                    |  |
| S(2)   | 16 384(5)                | 24 499(3)              | 15 233(5)                | C(13)  | 11 783(23)               | 25 347(9)                | 7(9) 12 759(15   |                    |  |
| S(3)   | 18181(7)                 | 21 864(3)              | 15 810(5)                | C(14)  | 12 555(23)               | 25 148(7)                | 13 999(16)       |                    |  |
| S(4)   | 17 765(6)                | 22 985(3)              | 13 524(4)                | C(15)  | 19 516(19)               | 22 085(9)                | 15 0130          | 13)                |  |
|  | 13 568(7)                | 22,903(3)<br>22,677(3) | 14 136(6)                | C(16)  | 21 888(22)               | 21 620(8)                | 16 3800          | 16 380(14)         |  |
| Cl(2)  | 20.671(7)                | 22 648(3)              | 16 556(6)                | C(17)  | 22 655(30)               | 22 058(10)               | 17 3580          | 17 358(17)         |  |
| Cl(2)  | 20 071(7)                | 25 554(3)              | 16 272(6)                | C(18)  | 22 035(30)               | 21 697(12)               | 18 433(          | 71)                |  |
| Cl(3)  | 18 000(10)               | 23 334(3)<br>24 716(4) | 18 960(6)                | C(10)  | 24 764(25)               | 21.097(12)<br>21.261(10) | 18 1600          | 20)                |  |
| $\mathbf{N}(1)$  | 10,909(10)<br>14,864(18) | 24710(4)<br>24214(7)   | 17 879(12)               | C(20)  | 23 962(30)               | 20 828(10)               | 17 184(          | 17 184(16)         |  |
| N(1)   | 14.004(10)<br>12.267(17) | 24 214(7)<br>24 224(8) | 15 210(12)               | C(20)  | 23 105(26)               | 21 175(10)               | 16 0910          | 17)                |  |
| N(2)   | 13.307(17)               | 24 234(8)              | 15 317(13)<br>15 212(12) | C(21)  | 18 963(20)               | 21 175(10)               | 13 7900          | 12)                |  |
| IN(5)  | 21001(17)                | 21 900(8)              | 13313(13)<br>12072(13)   | C(22)  | 10.903(20)<br>10.040(24) | 22 332(8)                | 11 7040          | 12)                |  |
| N(4)   | 19 409(18)               | 22 040(7)              | 12.972(13)<br>17.020(12) | C(23)  | 20 050(26)               | 22 193(0)                | 11 444()         | 15)                |  |
| C(1)   | 15 300(21)               | 23 910(8)              | 17020(12)                | C(24)  | 10.607(21)               | 22 7 52(3)               | 10 1460          | 15)                |  |
| C(2)   | 15 105(25)               | 23 900(0)              | 19 100(12)               | C(25)  | 19 007(31)               | 22.090(14)               | 0 4000           | 77)                |  |
| C(3)   | 15 020(31)               | 24 512(10)             | 19 939(10)               | C(20)  | 19 /0/(33)               | 22 331(14)<br>21 769(15) | 9 400(2          | 22)<br>10)         |  |
| C(4)   | 15 263(34)               | 24 288(12)             | 21 199(18)               | C(27)  | 10 220(27)               | 21 /06(13)               | 9 727(.          | 19)                |  |
| C(5)   | 14 21 /(32)              | 23 743(10)             | 21 343(19)               | C(28)  | 19 320(37)               | 21017(10)                | 11 032(          | 19)<br><b>7</b> 0) |  |
| C(6)   | 14 334(30)               | 23 227(9)              | 20 490(13)               | O(15)  | 15 / 59(24)              | 25 401(9)                | 17 303(2         | 20)                |  |
| C(7)   | 13931(27)                | 23 477(11)             | 19 240(15)               | C(1S)  | 14 681(39)               | 25 897(14)               | 17 102(2         | 28)                |  |
| C(8)   | 14 908(18)               | 24 228(9)              | 15 830(13)               | C(2S)  | 15 362(58)               | 20 337(10)               | 18 025(2         | 29)                |  |
| 1  | i oona ienguis (A)       |                        | (112E)(5C11)2]           | EtOH 3   | etted bond tengtins      | (rt) und ungles (        | ) tor L(Inge     | ,12(112L)}2J       |  |
| Hg-S(1)  | 2.494(2)                 | Hg-S(2)                | 2.500(2)                 | Hg(1)–S(1)   | 2.476(5)                 | Hg(1)-5                  | S(4)             | 2.521(5)           |  |
| Hg-S(4)  | 2.551(2)                 | Hg-S(3)                | 2.577(2)                 | Hg(1)-Cl(1)  | 2.532(6)                 | Hg(1)9                   | S(3)             | 2.637(6)           |  |
| S(1)-C(1)  | 1.654(8)                 | S(2) - C(2)            | 1.642(8)                 | Hg(2)-Cl(4)  | 2.380(7)                 | Hg(2)-4                  | Cl(2)            | 2.489(7)           |  |
| S(3)-C(3)  | 1.691(7)                 | S(4)C(4)               | 1.687(6)                 | Hg(2)-Cl(3)  | 2.585(6)                 | Hg(2)9                   | S(2)             | 2.623(5)           |  |
| N(1)-C(1)  | 1.134(8)                 | N(2)-C(2)              | 1.130(8)                 | S(1)-C(1)  | 1.68(2)                  | S(2)-C(                  | (8)              | 1.68(2)            |  |
| N(3)–C(3)  | 1.298(7)                 | N(3)-C(5)              | 1.475(7)                 | S(3) - C(15)   | 1.70(2)                  | S(4)-C(22)               |                  | 1.68(2)            |  |
| N(4)C(4)   | 1.304(7)                 | N(4)-C(11)             | 1.480(7)                 | N(1)-C(1)  | 1.316(14)                | N(1)-C                   | (2)              | 1.483(14)          |  |
| C(3)-C(4)  | 1.521(9)                 |                        |                          | N(2)C(8)   | 1.314(14)                | N(2)-C                   | (9)              | 1.474(14)          |  |
|  |                          |                        |                          | N(3)-C(15)   | 1.311(14)                | N(3)-C                   | (16)             | 1.477(14)          |  |
| S(1)-Hg-S(2)   | 108.19(7)                | S(1)-Hg- $S(4)$        | 119.67(7)                | N(4)-C(22)   | 1.317(13)                | N(4)-C                   | (23)             | 1.474(14)          |  |
| S(2)-Hg- $S(4)$  | 114.41(8)                | S(1)-Hg-S(3)           | 115.51(7)                | C(1)-C(8)  | 1.505(11)                | C(15)-C(22)              |                  | 1.505(11)          |  |
| S(2)-Hg-S(3)   | 111.42(7)                | S(4)-Hg- $S(3)$        | 86.27(6)                 |  |                          |                          |                  |                    |  |
| C(1)-S(1)-Hg   | 97.7(2)                  | C(2)-S(2)-Hg           | 98.0(3)                  | S(1) - Hg(1) - S(1)  | (4) 146.3(2)             | S(1)-H                   | g(1) - Cl(1)     | 107.1(2)           |  |
| C(3)-S(3)-Hg   | 95.9(2)                  | C(4)-S(4)-Hg           | 99.1(2)                  | S(4)-Hg(1)-C   | 1(1) 100.4(2)            | S(1)-H                   | g(1)-S(3)        | 99.2(2)            |  |
| C(3) - N(3) - C(5)   | 127.1(6)                 | C(4)-N(4)-C(1)         | 1) 125.8(5)              | S(4)-Hg(1)-S(  | (3) 86.7(2)              | Cl(1)-H                  | Ig(1)-S(3)       | 114.2(2)           |  |
| N(3)-C(3)-C(4)   | 114.4(6)                 | N(3)-C(3)-S(3)         | ) 124.3(5)               | Cl(4)-Hg(2)-0  | Cl(2) 117.6(3)           | Cl(4)-H                  | Ig(2)-Cl(3)      | 104.6(3)           |  |
| C(4)-C(3)-S(3)   | 121.3(4)                 | N(4)-C(4)-C(3)         | ) 115.2(5)               | Cl(2)-Hg(2)-Cl(2 | CI(3) 108.5(2)           | Cl(4)-H                  | Ig(2)-S(2)       | 123.0(3)           |  |
| N(4)-C(4)-S(4)   | 122.4(5)                 | C(3)-C(4)-S(4)         | 122.3(5)                 | Cl(2)-Hg(2)-S  | S(2) = 105.3(2)          | Cl(3)-H                  | Ig(2)-S(2)       | 94.8(2)            |  |
|  |                          |                        |                          | C(1)-S(1)-Hg   | (1) 105.1(5)             | C(8)–S(                  | 2)-Hg(2)         | 105.9(5)           |  |
|  |                          |                        |                          | C(15)-S(3)-H   | g(1) 92.4(6)             | C(22)-S                  | 5(4)-Hg(1)       | 98.7(5)            |  |
| ha datamain - 1 -  | undan tha are            | imantal aanditiana     | amplaued or              | C(1)-N(1)-C(   | 2) 125(2)                | C(8)-N                   | (2)-C(9)         | 124(2)             |  |
| be determined  | under ine exper          | intental conditions    | employed as              | C(15)-N(3)-C   | 2(16) 125(2)             | C(22)-1                  | N(4) - C(23)     | 124.4(14)          |  |
| its single crystals decomposed readily upon X-ray irradiation in |                          |                        | N(1)-C(1)-C(1)           | N(1)-C(1)-C(8) 116.2(14) $N(1)-C(1)-S(1)$  |                          | (1)-S(1)                 | 122.8(12)        |                    |  |
| the process of   | data collection,         | presumably due 1       | to the loss of           | C(8)-C(1)-S(1)   | 1) 120.9(11)             | N(2)C                    | (8)-C(1)         | 114.0(14)          |  |

be d its s the process of data collection, presumably due to the loss of volatile molecules of crystallization (see Experimental section).

Structure of [Hg(H<sub>2</sub>L)(SCN)<sub>2</sub>] 1.—The structure of complex 1 consists of discrete molecular units with the basic tetrahedral  $HgS_4$  co-ordination core determined by S(1) and S(2), one sulfur atom from each thiocyanate ligand, and by the two sulfur atoms S(3) and S(4) from the N,N'-dicyclohexyldithiooxamide molecule acting as a bidentate S, S'-chelating ligand (Fig. 1). The Hg-S bond lengths of the S-thiocyanate ligands are 2.494(2) and 2.500(2) Å whereas the values for the chelating  $H_2L$  ligand are 2.577(2) and 2.551(2) Å, respectively. The former two are in the range reported for terminal Hg-SCN bonds in tetrahedral units  $[2.49(4) Å]^{27}$  and the latter are slightly longer than the sum of the covalent radii (ca. 2.52 Å)<sup>28</sup> but substantially shorter than the sum of the van der Waals radii between the Hg and S atoms, which have been accepted <sup>29</sup> to be *ca*. 3.60 Å and is certainly indicative of a bonding interaction. The main departure from tetrahedral symmetry is the S(3)-Hg-S(4) angle of 86.3° instead of 109.5°, due to the restricted bite angle of the H<sub>2</sub>L ligand with the remaining S-Hg-S angles in the range 108.2-119.7°. This

type of HgS<sub>4</sub> group falls into the Metacinnabarite, HgS, type in which there are four Hg-S bonds in the range 2.49-2.66 Å with the Hg atom in a nearly tetrahedral environment.<sup>30</sup> The dihedral angle  $\theta$  between the planes containing the two thioamide groups of the S,S'-chelated  $H_2L$  ligand in complex 1 is 47.5° Similar configurations were also reported for the related complexes  $[ZnCl_2(H_2L^1)]$  ( $\theta = 38.4^\circ$ ) and  $[{Cu(H_2L^2)_2}]$  $(ClO_4)_{2}$   $[\theta = 35.0^{\circ}]$   $(H_2L^1 = N, N'$ -dimethyl- and  $H_2L^2 =$ N,N'-dibenzyl-dithiooxamide). The torsion around the C-C bond in the latter complexes was ascribed to the steric hindrance between the two thioamide protons. In fact, in the deprotonated [Pd(HL)<sub>2</sub>] ( $\theta = 0.8^{\circ}$ ) and [Pd(HL<sup>3</sup>)<sub>2</sub>] ( $\theta$ = 2.7°) (H<sub>2</sub>L<sup>3</sup> =  $\tilde{N}, N'$ -dicyclopentyldithiooxamide) the thioamide moieties are nearly coplanar. Bond lengths and angles for

125.6(12)

113.6(14)

121.4(12)

124.4(12)

N(2)-C(8)-S(2)

N(3)-C(15)-C(22)

C(22)-C(15)-S(3)

N(4)-C(22)-S(4)

the remainder of the ligand are within the normal values for neutral S,S'-chelated complexes of N,N'-disubstituted dithiooxamide ligands.<sup>21</sup> An interesting feature in the structure of compound 1 is the short non-bonding interaction of the sulfur atom of the S-bonded SCN group S(1) on one molecule with S(1') on the symmetry-related adjacent molecule in the unit cell. The  $S(1) \cdots S(1')$  non-bonding distance of 3.39 Å is significantly shorter than the sum of the van der Waals radii, ca. 3.60 Å. These secondary interactions may be responsible for the low solubility observed for 1 in most common solvents. In addition, the two N-H groups in the molecule appear to be involved in intermolecular hydrogen bonds with the nitrogen atoms of the SCN ligands of adjacent molecules [N(3') · · · N(1) 1.98 Å, N(3)-H(3') · · · N(1) 162° and N(4') · · · N(2) 2.02 Å, N(4)-H(4') · · · N(2) 159°]. A drawing of the unit-cell packing diagram of complex 1 is given in Fig. 2.

Structure of  $[{HgCl_2(H_2L)}_2]$ -EtOH 3.—The structure of complex 3, a monoethanol solvate, consists of a binuclear



Fig. 1 Structure of  $[Hg(H_2L)(SCN)_2]$  1, with partial labelling scheme. Hydrogen atoms are omitted for clarity

zwitterionic complex with two different tetrahedral moieties, Fig. 3. One moiety with one chlorine atom, two sulfur atoms of a chelating H<sub>2</sub>L and one sulfur atom of a bridging H<sub>2</sub>L ligand around Hg(1), is positively charged. The other, with three chlorine atoms and the second sulfur atom of the bridging H<sub>2</sub>L ligand around Hg(2) is negatively charged. It represents to our knowledge the first crystallographically characterized structure in which a chelating and a bridging dithiooxamide ligand coexist in a binuclear unit. The Hg(1) atom is surrounded by an asymmetrically chelating  $H_2L$  ligand [Hg(1)-S(3) 2.637(6) and Hg(1)-S(4) 2.521(5) Å] and a chlorine atom [Hg(1)-Cl(1) 2.532(6) Å]. A relatively strong Hg(1)-S(1) bond [2.476(5) Å] with the bridging H<sub>2</sub>L partially compensates the co-ordinative unsaturation of the Hg(1) atom. The three Hg(2)-Cl distances are 2.585(6), 2.489(7) and 2.380(7) Å respectively. In spite of the wide range of Hg-Cl bond distances in complex 3 the average value of 2.50 Å is in good agreement with the distance reported for tetrahedral terminal Hg-Cl bonds.<sup>27</sup> Tetrahedral co-ordination around Hg(2) is completed through a weak Hg(2)-S(2) bond of 2.623(5) Å with the second sulfur atom of the bridging H<sub>2</sub>L ligand and reflects a relief from electron oversaturation on Hg(2). The two  $Hg^{2+}$  ions have markedly distorted tetrahedral co-ordination as evidenced by the bond angles at mercury, varying from 86.7(2) to 146.3(2)°.



Fig. 2 Stereoview of the packing diagram of complex 1. Heavy dashed lines represent  $S \cdots S$  bonds



Fig. 3 Structure of  $[{HgCl_2(H_2L)}_2]$ -EtOH 3, with partial labelling scheme. Hydrogen atoms are omitted for clarity

The calculated dihedral angle  $\theta$  between the thioamide groups for the chelating and the bridging  $H_2L$  ligands are 52.6 and 66.4°, respectively. The former is comparable to that reported above for the chelating H<sub>2</sub>L in mononuclear complex 1. The latter value indicates that the bridging ligand in which the sulfur atoms are free from any constraints arising from chelation is also strongly distorted, contrasting with the nearly planar trans conformation found in polymeric  $SbCl_3L'_{4.5}$  [L' = RNHC(S)C(S)NHR, R = Et or  $Pr^{i}$ , the only reported cases where the ligands form S,S'-bonded links between metal centres. A trans conformation ( $\theta = 180^\circ$ ) was also reported for several free N, N'-disubstituted dithiooxamide molecules (R = H, Et or Pr<sup>i</sup>).<sup>18</sup> For comparison, we have also determined the crystal structure of N, N'-dicyclohexyldithiooxamide and have confirmed the planar geometry of this ligand.<sup>31</sup> In order to account for the rather complex structural arrangement exhibited by the S,S'-bridged H<sub>2</sub>L ligand in 3, non-bonding distances were examined for any evidence of unusually short distances that might be indicative of secondary interactions. Thus Hg(1). S(2) and Hg(2)  $\cdots$  S(1) distances, at 3.464 and 3.596 Å respectively, are at the limit of the sum of the van der Waals radii, 3.60 Å. If these intramolecular interactions are taken into account, then the bridging dithiooxamide ligand participates with both sulfur atoms in co-ordination to each mercury atom, through one primary and one secondary bond. The two mercury atoms can alternatively, be regarded as having highly distorted five-co-ordinate environments. The Hg(1) atom with S(1), S(2), S(3) and S(4) in a narrow belt and Cl(1) in an apical position is nearly square pyramidal, whereas Hg(2) with Cl(2), Cl(4) and S(2) in an equatorial plane and Cl(3) and S(1) in apical positions is nearly trigonal bipyramidal. Mercury five-co-ordination has been reported before in other mercury-sulfur systems.<sup>32</sup> The bridging H<sub>2</sub>L ligand in its folded configuration spans a  $Hg(1) \cdot \cdot \cdot Hg(2)$  separation of 4.373 Å which precludes any metal-metal interaction. All four N-H groups in complex 3 appear to be involved in hydrogen bonding: three of them to chlorine atoms  $H(3') \cdots Cl(1) (2.34), H(2') \cdots Cl(2) (2.37) and H(4) \cdots Cl(3)$ (2.53 Å) and one to the oxygen atom of the ethanol solvate molecule  $H(1') \cdots O(1S)$  (1.84 Å). In addition, the rather short O(1S) · · · Cl(3) distance of 3.14 Å is indicative of an additional hydrogen-bonding interaction involving the ethanol molecule and Cl(3). The wide range in the Hg-Cl distances in 3 may be largely associated with the particularly hydrogenbonding pattern described. The shortest bond [Hg(2)-Cl(4) 2.380(7) Å] is not involved in any hydrogen bonding, the two medium-length bonds [Hg(1)-Cl(1) 2.532(6) and Hg(2)-Cl(2) 2.489(7) Å] are associated with single hydrogen bonds, whereas the longest bond [Hg(2)-Cl(3) 2.585(6) Å] is involved in two hydrogen bonds. In a way complex 3 can be regarded as the result of the rearrangement of the coordinatively unsaturated complex 2 in a more donor media to adopt a different configuration on crystallization. The network of secondary interactions found in 3 does not persist upon dissolution in most common solvents, and decomposition occurs yielding the reactants.

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*IR Spectra.*—The infrared spectral data of complexes 1–3 show the distinct vibrational features associated with the dithiooxamide ligands<sup>24</sup> (see Experimental section). The free H<sub>2</sub>L shows a medium to strong band at 1507 cm<sup>-1</sup> which has been assigned to vibrations of predominantly C–N character of the thioamide group (RHN–C=S). In contrast, complexes 1–3 exhibit new v(C–N) bands at higher energies (1550–1560 cm<sup>-1</sup>). Similar shifts have been reported for *S*,*S*-bidentate dithiooxamide complexes<sup>21</sup> of palladium(II), nickel(II) and copper(II). Another noticeable feature in the free ligand and in the new complexes is the v(N–H) stretching vibration, which is present as a medium and broad band with a maximum at *ca.* 3150 cm<sup>-1</sup>. In addition, in the infrared spectrum of complex 1, a single, strong v(C=N) stretch is clearly observed at 2124 cm<sup>-1</sup>, 991

indicative of an S-bonded metal-thiocyanate bond.<sup>33</sup> This is in accordance with the 'hard-soft' rule which implies a preference for the S-bonding mode of the thiocyanate ligand to mercury, as confirmed by X-ray crystallography. Further evidence for adduct formation was obtained from the examination of the low-frequency spectra (200-650 cm<sup>-1</sup>) where the metal-to-ligand sensitive modes are expected. Comparison of the spectra of the reactants with those of the adducts may provide an effective criterion for metal-ligand bonding. Although there can be no clear distinction between the Hg-S and the Hg-Cl modes in complexes 2 and 3, they may be broadly described as metal-toligand vibrations coupled with angular motions. Adduct 1 shows new bands in the range 220–250 cm<sup>-1</sup> [Fig. 4(a)], and because of their position and intensity are attributed to the prevailing contribution of the Hg-S terminal modes in a tetrahedral environment as confirmed above by X-ray crystallography. The values for v(Hg-S) are about the same as those reported for the tetrahedral HgS<sub>4</sub> environment in polymeric<sup>3</sup>  $Hg(SBu^{n})_{2}$  for which the Hg-S bond lengths (Hg-S average = 2.54 Å) are comparable to those found in 1 (Hg–S average = 2.53 Å). The similarity of the low-frequency vibrational features of adduct 2 [Fig. 5(b)] and 1 [Fig. 5(a)] suggests that the two compounds may be isostructural. Although on the basis of the spectroscopic data alone we cannot exclude the presence of more complex sulfur- or halide-bridged structures, they strongly support the presence of mononuclear units in 2. In contrast, the low-frequency spectrum of complex 3 [Fig. 5(c)] contains a number of new poorly structured bands in the range 200-380 cm<sup>-1</sup> associated with Hg-S and Hg-Cl vibrations in tetrahedral environments. These results are consistent with the



**Fig. 4** Far-infrared spectra of  $[Hg(H_2L)(SCN)_2](a)$ ,  $H_2L(b)$  and  $[Hg(SCN)_2](c)$ 



**Fig. 5** Far-infrared spectra of  $[Hg(H_2L)(SCN)_2](a)$ ,  $[HgCl_2(H_2L)](b)$  and  $[{HgCl_2(H_2L)}_2]$ -EtOH (c)

rather large variations in the Hg-Cl and Hg-S distances found above for 2 by X-ray analysis.

# Conclusion

The present work describes the first examples as well as the first structural determinations of neutral mercury(II) N,N'disubstituted dithiooxamide complexes. One of the interesting aspects of the structures is the presence in complex 3 of two different conformations of the neutral H<sub>2</sub>L ligand, which is uncommon in the metal dithiooxamide complexes of other metals. A second point of interest is the observation that the  $H_2L$  and the chloride ligands compete in binding the mercury ion. This bears similarity with the reported fact that mercury(II) binds chloride ions in competition with sulfur amino acids,<sup>16</sup> which is of relevance in several biological processes.

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