

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)
$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

| | x | y | z | U_{eq} |
|-------|-------------|-------------|------------|-----------------|
| Zr | 0 | 0.1003 (1) | 1/4 | 0.043 (1) |
| Cl | -0.0256 (1) | -0.1544 (1) | 0.3514 (1) | 0.061 (1) |
| C(1) | 0.1066 (1) | 0.2467 (5) | 0.1953 (2) | 0.051 (1) |
| C(2) | 0.1287 (1) | 0.0414 (6) | 0.1871 (2) | 0.060 (1) |
| C(3) | 0.1584 (1) | 0.0391 (7) | 0.1137 (3) | 0.072 (2) |
| C(4) | 0.1356 (1) | 0.0923 (8) | 0.0231 (3) | 0.082 (2) |
| C(5) | 0.1140 (1) | 0.2959 (8) | 0.0266 (3) | 0.075 (2) |
| C(6) | 0.0854 (1) | 0.3049 (6) | 0.1018 (2) | 0.058 (1) |
| C(7) | 0.1378 (1) | 0.4127 (6) | 0.2281 (2) | 0.063 (1) |
| C(8) | 0.1642 (1) | 0.3689 (7) | 0.3155 (3) | 0.078 (2) |
| C(9) | 0.1911 (2) | 0.5298 (9) | 0.3543 (3) | 0.099 (2) |
| C(10) | 0.2149 (2) | 0.4685 (11) | 0.4405 (3) | 0.125 (3) |
| C(11) | 0.2171 (2) | 0.6368 (9) | 0.2951 (4) | 0.127 (3) |
| C(12) | 0.0753 (1) | 0.2354 (5) | 0.2649 (2) | 0.046 (1) |
| C(13) | 0.0482 (1) | 0.3919 (5) | 0.2849 (2) | 0.050 (1) |
| C(14) | 0.0297 (1) | 0.3438 (6) | 0.3634 (2) | 0.056 (1) |
| C(15) | 0.0448 (1) | 0.1553 (6) | 0.3934 (2) | 0.058 (1) |
| C(16) | 0.0718 (1) | 0.0856 (5) | 0.3317 (2) | 0.052 (1) |

Table 2. Selected geometric parameters (\AA , $^\circ$)

| | | | |
|------------------------------|-----------|------------------------------|-----------|
| Zr—Cl | 2.460 (1) | Zr—CEN† | 2.224 (1) |
| Zr—C(12) | 2.599 (3) | Zr—C(13) | 2.508 (3) |
| Zr—C(14) | 2.468 (4) | Zr—C(15) | 2.506 (3) |
| Zr—C(16) | 2.539 (3) | C(1)—C(2) | 1.544 (5) |
| C(1)—C(6) | 1.549 (6) | C(1)—C(7) | 1.542 (5) |
| C(1)—C(12) | 1.521 (5) | C(2)—C(3) | 1.526 (6) |
| C(3)—C(4) | 1.524 (6) | C(4)—C(5) | 1.520 (7) |
| C(5)—C(6) | 1.523 (5) | C(7)—C(8) | 1.525 (5) |
| C(8)—C(9) | 1.463 (7) | C(9)—C(10) | 1.496 (7) |
| C(9)—C(11) | 1.461 (8) | C(12)—C(13) | 1.410 (5) |
| C(12)—C(16) | 1.417 (5) | C(13)—C(14) | 1.402 (5) |
| C(14)—C(15) | 1.397 (5) | C(15)—C(16) | 1.406 (5) |
| CEN—Zr—Cl | 105.3 (1) | CEN—Zr—Cl ¹ | 108.3 (1) |
| Cl—Zr—Cl ¹ | 93.7 (1) | CEN—Zr—CEN ¹ | 130.1 (1) |
| C(12)—Zr—C(12 ¹) | 139.9 (1) | C(16)—Zr—C(12 ¹) | 151.0 (1) |
| C(1)—C(12)—C(13) | 125.5 (3) | C(1)—C(12)—C(16) | 128.1 (3) |
| C(13)—C(12)—C(16) | 105.7 (3) | C(12)—C(13)—C(14) | 109.6 (3) |
| C(13)—C(14)—C(15) | 107.7 (3) | C(14)—C(15)—C(16) | 107.8 (3) |
| C(15)—C(16)—C(12) | 109.1 (3) | C(12)—C(1)—C(7) | 106.3 (3) |
| C(12)—C(1)—C(6) | 110.9 (3) | C(12)—C(1)—C(2) | 110.9 (3) |
| C(2)—C(1)—C(6) | 108.5 (3) | C(2)—C(1)—C(7) | 110.6 (3) |
| C(6)—C(1)—C(7) | 109.6 (3) | C(1)—C(2)—C(3) | 113.3 (3) |
| C(2)—C(3)—C(4) | 110.2 (3) | C(4)—C(5)—C(6) | 112.1 (4) |
| C(5)—C(6)—C(1) | 113.8 (3) | C(1)—C(7)—C(8) | 116.1 (3) |
| C(7)—C(8)—C(9) | 118.2 (4) | C(8)—C(9)—C(10) | 112.9 (5) |
| C(8)—C(9)—C(11) | 118.1 (4) | C(10)—C(9)—C(11) | 111.6 (4) |

Symmetry code: (i) $-x, y, \frac{1}{2} - z$.

† CEN is the centroid of the cyclopentadienyl ring.

The structure was solved by heavy-atom methods and refined by block-diagonal least squares with anisotropic displacement parameters for all non-H atoms. H atoms were introduced at calculated positions and fixed with isotropic displacement parameters ($U_{\text{iso}} = 0.06 \text{\AA}^2$) in the final cycles of refinement.

Data collection and cell refinement: *P3 Program* (Nicolet XRD Corporation, 1985). Data reduction, structure solution and refinement, molecular graphics and preparation of material for publication: *SHELXTL Users Manual* (Sheldrick, 1985).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1008). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Chien, J. C. W. & Razavi, A. (1988). *J. Polym. Sci. Polym. Chem.* **26**, 2369–2380.
- Erker, G., Nolte, R., Aul, R., Wilker, S., Krüger, C. & Noe, R. (1991). *J. Am. Chem. Soc.* **113**, 7594–7602.
- Erker, G., Nolte, R., Krüger, C., Schlund, R., Benn, R., Grondey, H. & Mynott, R. (1989). *J. Organomet. Chem.* **364**, 119–132.
- Gelmini, L., Puddephatt, R. J. & Vittal, J. J. (1993). *Acta Cryst.* **C49**, 30–33.
- Howie, R. A., Mcquillan, G. P., Thompson, D. W. & Lock, G. A. (1986). *J. Organomet. Chem.* **303**, 213–220.
- Kaminsky, W. (1986). *Angew. Makromol. Chem.* **145/146**, 149–160.
- Kaminsky, W., Engehausen, R., Zoumisk, K., Spaleck, W. & Rohrmann, J. (1992). *Makromol. Chem.* **193**, 1643–1651.
- Nicolet XRD Corporation (1985). *P3 Program. Crystallographic System User's Guide*. Nicolet XRD Corporation, Madison, Wisconsin, USA.
- Ogasa, M., Mallin, D. T., Macomber, D. W., Rausch, M. D., Rogers, R. D. & Rollins, A. N. (1991). *J. Organomet. Chem.* **405**, 41–52.
- Prout, K., Cameron, T. S., Forder, R. A., Critchley, S., Denton, B. & Rees, G. V. (1974). *Acta Cryst.* **B30**, 2290–2304.
- Sheldrick, G. M. (1985). *SHELXTL Users Manual*. Revision 5.1. Nicolet XRD Corporation, Madison, Wisconsin, USA.
- Sinn, H. & Kaminsky, W. (1980). *Adv. Organomet. Chem.* **18**, 99–149.
- Sinn, H., Kaminsky, W., Vollmer, H. J. & Woldt, R. (1980). *Angew. Chem. Int. Ed. Engl.* **19**, 39–41.
- Tian, J. & Huang, B. T. (1994). *Macromol. Rapid Commun.* **15**, 923.

Acta Cryst. (1996). **C52**, 21–24

catena- $\{[\text{HgCl}_2([\text{18}] \text{aneS}_2\text{O}_4)]\text{HgCl}_2\}$ at 150 K: a Redetermination and Reinterpretation

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Abstract

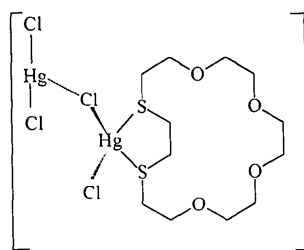
The structure of the title compound $\{[\text{HgCl}_2([\text{18}] \text{aneS}_2\text{O}_4)]\text{HgCl}_2\}_n$ ($[\text{18}] \text{aneS}_2\text{O}_4 = 1,4,7,10\text{-tetraoxa-13,16-dithiacyclooctadecane}$), $[\text{Hg}_2\text{Cl}_4(\text{C}_{12}\text{H}_{24}\text{O}_4\text{S}_2)]_n$, has been redetermined and reinterpreted as a one-dimensional polymeric thread comprising linked Hg_4Cl_4

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macrocyclic moieties with pendant macrocyclic ligands {the compound may be named *catena*-poly[(chloro-mercury)-di- μ -chloro-bis[(1,4,7,10-tetraoxa-13,16-dithiacyclooctadecane-*S,S*)mercury]-di- μ -chloro-(chloro-mercury)-di- μ -chloro]}.

Comment

We are currently investigating the coordination chemistry of mixed O/S donor ionophores, such as [18]-aneS₂O₄, with a range of transition and main group metal ions (Blake, Reid & Schröder, 1990, 1992; Blake, Gould, Radek & Schröder, 1994; Blake, Gould, Reid, Radek, Taylor & Schröder, 1993; Reid, 1989). We report herein an improved single-crystal structure determination, a revised structural description and spectroscopic data for the title compound, (1). The structure of (1) has been reported previously by Dalley &



(1)

Larson (1981), who described it in terms of isolated molecules of [HgCl₂([18]aneS₂O₄)]HgCl₂. The asymmetric unit in the low-temperature single-crystal structure of (1) (Fig. 1) contains the binuclear fragment [HgCl₂([18]aneS₂O₄)]HgCl₂. The structure features two Hg^{II} ions with very different coordination geometries. The macrocyclic ligand adopts a typical bidentate coordination mode *via* the thioether S donors [Hg1—S1 = 2.664 (2), Hg1—S4 = 2.511 (2) Å; Hg1—Cl11 = 2.472 (2), Hg1—Cl12 = 2.440 (2) Å]. The coordination geometry at Hg1 can be described as distorted tetrahedral [S1—Hg1—S4 = 86.09 (6) and Cl11—Hg1—Cl12 = 109.43 (7)°]. Similar geometry has been reported for the binuclear Hg^{II}Cl₂ complex with 1,4,8,11-tetrathiacyclotetradecane ([14]aneS₄) (Alcock, Herron & Moore, 1978); however, the Cl—Hg—Cl angle in [(HgCl₂)₂([14]aneS₄)] is significantly wider [117.54 (9)°], and this supports our reinterpretation of the structure of (1) as a polymeric network involving bridging Cl⁻ ligands.

The second Hg^{II} ion is part of an HgCl₂ unit with Hg2—Cl21 = 2.327 (2), Hg2—Cl22 = 2.317 (2) Å, Cl21—Hg2—Cl22 = 166.90 (7)°. These values are similar to those found in the single-crystal structure of HgCl₂ (Subramanian & Seff, 1980) [Hg—Cl1 = 2.292 (10), Hg—Cl2 = 2.274 (10) Å, Cl1—Hg—Cl2 = 178.6 (4)°]. Hg2 participates in four additional long-

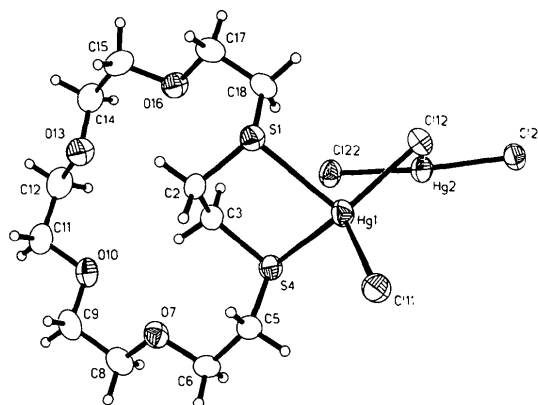


Fig. 1. A view of the contents of the asymmetric unit of (1) showing the atom-numbering scheme. Displacement ellipsoids enclose 50% probability surfaces and H atoms are drawn as spheres of arbitrary radii.

range interactions involving Cl11 [3.054 (2) Å] at $(-x, 1 - y, 1 - z)$, Cl12 [2.863 (2) Å] and Cl21 [3.281 (2) Å] at $(-x - 1, -y, z - 1)$ and S1 [3.153 (2) Å] at $(x - 1, y, z)$. All four lie well within the sum of the van der Waals radii of the relevant atoms [Hg 1.50, Cl 1.80 and S 1.85 Å; Bondi, 1964] and may be considered at least partially covalent in nature. However, it seems likely that there is an ionic contribution to the stability of this structure.

Fig. 2 shows the formation of eight-membered Hg₄Cl₄ macrocycles *via* bridging Cl⁻ ligands. Other long-range Hg \cdots Cl⁻ interactions link these into one-dimensional polymeric threads, which are weakly cross-linked *via* S1 \cdots Hg2 contacts to form a two-dimensional sheet structure. The structure of (1) can be regarded as a co-crystallization product between HgCl₂ and the metal macrocyclic complex [HgCl₂([18]aneS₂O₄)].

Interestingly, in the complex [HgCl₂(1,4,7,10-tetraoxa-13,16-dithiacyclooctadec-14-en-14,15-dicarbonitrile)], (2), (Silbert, Lange, Stern, Hoffman & Barrett, 1994), which contains a related ligand, the Hg^{II} ion is coordinated by two axial chlorides and four equatorial O atoms; two of the latter are closely bound [Hg—

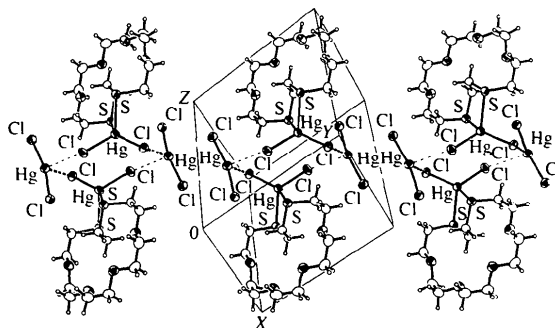
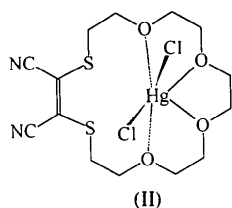


Fig. 2. A packing diagram of (1) illustrating the infinite chain structure.

O = 2.657 (4), 2.681 (5) Å, the other two markedly less so [Hg—O = 2.932 (4), 2.980 (4) Å]. This preferential coordination by O donors is unusual since Hg^{II} tends to bind to thioether S donors. The distance between the Hg^{II} centre and the two S donors is greater than 3.3 Å and therefore well beyond typical values for Hg—S bonding distances [2.50–2.75 Å (Sato, Habata, Sato & Akabori, 1989; Dalley & Larson, 1981; Blake, Holder, Hyde, Reid & Schröder, 1989; Heinzl & Mattes, 1992; Jones, Sokol, Rohrabacher & Glick, 1979; Blake, Pasteur, Reid & Schröder, 1991; Byriel, Gahan, Kennard & Sunderland, 1993; Sobhia *et al.*, 1992; Alcock, Herron & Moore, 1978)].



Experimental

The macrocyclic ligand [18]aneS₂O₄ was prepared according to a published method (Bradshaw *et al.*, 1974). HgCl₂ (272 mg, 1.0 mmol) was added to a refluxing solution of [18]aneS₂O₄ (148 mg, 0.5 mmol) in MeOH/MeCN (50 cm³, 5:1 v/v) to obtain a colourless solution. Removal of the solvent *in vacuo* yields the product as a white microcrystalline solid. Recrystallization of the initial product by slow concentration of a solution in MeCN afforded colourless tabular crystals suitable for X-ray diffraction studies (yield: 377 mg, 90%). Microanalysis for C₁₂H₂₄Cl₄Hg₂O₄S₂: calculated C 17.2, H 2.88%; found C 17.1, H 2.84%. Fast-atom bombardment mass spectrum (DMSO/3-nitrobenzoic acid/trifluoroacetic acid) *m/z*: 533; calculated for [²⁰²Hg³⁵Cl([18]aneS₂O₄)]⁺ 533. ¹H NMR spectrum (*d*₆-DMSO, 297 K, 250.130 MHz): 2.86, 3.22, 3.54 and 3.72 p.p.m. ¹³C NMR spectrum (*d*₆-DMSO, 297 K, 62.900 MHz): 30.59 (double intensity), 69.37, 69.63, 70.14 and 70.55 p.p.m. IR (KBr disc): 2980*m*, 2880*m*, 1470*m*, 1450*m*, 1400*m*, 1355*s*, 1295*m*, 1250*s*, 1200*w*, 1125*vs*, 1085*vs*, 1040*s*, 945*m*, 890*m*, 840*m*, 690*w*, 670*w*, 620*w*, 540*w*, 490*w* and 450*w* cm⁻¹.

Crystal data

[Hg₂Cl₄(C₁₂H₂₄O₄S₂)]

M_r = 839.41

Triclinic

P $\bar{1}$

a = 8.269 (4) Å

b = 11.310 (5) Å

c = 12.332 (5) Å

α = 92.45 (3)°

β = 95.02 (3)°

γ = 105.78 (4)°

V = 1102.9 (8) Å³

Z = 2

D_x = 2.528 Mg m⁻³

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 24

reflections

θ = 15–16°

μ = 14.59 mm⁻¹

T = 150.0 (2) K

Tablet

0.43 × 0.43 × 0.31 mm

Colourless

Data collection

Stoe Stadi-4 four-circle diffractometer

ω–2θ scans using on-line profile fitting (Clegg, 1981)

Absorption correction: ψ scans (North, Phillips & Mathews, 1968)

*T*_{min} = 0.003, *T*_{max} = 0.020

4859 measured reflections

3886 independent reflections

3585 observed reflections

[*I* > 2σ(*I*)]

*R*_{int} = 0.0173

θ_{max} = 25.01°

h = –9 → 9

k = –13 → 13

l = 0 → 14

3 standard reflections

frequency: 60 min

intensity decay: 3%

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.0342

wR(*F*²) = 0.0933

S = 1.109

3868 reflections

218 parameters

H atoms riding on C atoms with *U*(H) = 1.2*U*_{eq}(C)

w = 1/[σ²(*F*_o²) + (0.057*P*)² + 2.17*P*]

where *P* = (*F*_o² + 2*F*_c²)/3

(Δ/σ)_{max} = –0.15

Δρ_{max} = 1.84 e Å⁻³
(close to Hg)

Δρ_{min} = –1.11 e Å⁻³
(close to Hg)

Extinction correction:

SHELXL93 (Sheldrick, 1993)

Extinction coefficient:

0.0019 (3)

Atomic scattering factors

from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

| | <i>x</i> | <i>y</i> | <i>z</i> | <i>U</i> _{eq} |
|------|--------------|-------------|--------------|------------------------|
| Hg1 | 0.11766 (4) | 0.36502 (2) | 0.45074 (2) | 0.03734 (13) |
| Hg2 | –0.35796 (3) | 0.16701 (3) | 0.44384 (2) | 0.03694 (13) |
| Cl12 | –0.0331 (2) | 0.2088 (2) | 0.56426 (14) | 0.0373 (4) |
| Cl21 | –0.5073 (2) | 0.1339 (2) | 0.59634 (15) | 0.0410 (4) |
| Cl11 | 0.2669 (3) | 0.5536 (2) | 0.56653 (15) | 0.0424 (4) |
| Cl22 | –0.2626 (2) | 0.1662 (2) | 0.2727 (2) | 0.0411 (4) |
| S1 | 0.3166 (2) | 0.2458 (2) | 0.36280 (14) | 0.0330 (4) |
| C2 | 0.3283 (9) | 0.3199 (6) | 0.2352 (6) | 0.036 (2) |
| C3 | 0.1629 (9) | 0.3374 (6) | 0.1844 (5) | 0.0336 (14) |
| S4 | 0.0650 (2) | 0.4326 (2) | 0.26276 (14) | 0.0330 (4) |
| C5 | 0.2159 (9) | 0.5839 (6) | 0.2756 (6) | 0.037 (2) |
| C6 | 0.2137 (10) | 0.6507 (6) | 0.1726 (6) | 0.037 (2) |
| O7 | 0.2739 (6) | 0.5863 (5) | 0.0918 (4) | 0.0383 (11) |
| C8 | 0.2481 (11) | 0.6251 (8) | –0.0149 (6) | 0.044 (2) |
| C9 | 0.3198 (10) | 0.5511 (8) | –0.0908 (6) | 0.043 (2) |
| O10 | 0.2365 (7) | 0.4238 (5) | –0.0887 (4) | 0.0419 (12) |
| Cl1 | 0.2972 (11) | 0.3523 (8) | –0.1650 (6) | 0.045 (2) |
| Cl2 | 0.2233 (11) | 0.2187 (8) | –0.1526 (6) | 0.047 (2) |
| O13 | 0.2913 (7) | 0.1846 (5) | –0.0530 (4) | 0.0434 (12) |
| C14 | 0.2386 (12) | 0.0535 (8) | –0.0479 (7) | 0.049 (2) |
| C15 | 0.2968 (11) | 0.0197 (8) | 0.0624 (7) | 0.046 (2) |
| O16 | 0.2012 (7) | 0.0585 (5) | 0.1410 (4) | 0.0391 (11) |
| C17 | 0.2325 (10) | 0.0186 (7) | 0.2457 (6) | 0.040 (2) |
| C18 | 0.1707 (9) | 0.0939 (6) | 0.3284 (6) | 0.037 (2) |

Table 2. Selected geometric parameters (Å, °)

| | | | |
|----------|-----------|-----------|------------|
| Hg1—S1 | 2.664 (2) | C6—O7 | 1.412 (9) |
| Hg1—S4 | 2.511 (2) | O7—C8 | 1.422 (9) |
| Hg1—Cl11 | 2.472 (2) | C8—C9 | 1.493 (12) |
| Hg1—Cl12 | 2.440 (2) | C9—O10 | 1.420 (10) |
| Hg2—Cl12 | 2.863 (2) | O10—Cl11 | 1.425 (10) |
| Hg2—Cl21 | 2.327 (2) | Cl11—Cl12 | 1.488 (12) |
| Hg2—Cl22 | 2.317 (2) | Cl12—O13 | 1.419 (9) |

| | | | |
|---------------|------------|-----------------|------------|
| S1—C2 | 1.812 (7) | O13—C14 | 1.432 (10) |
| S1—C18 | 1.819 (7) | C14—C15 | 1.502 (12) |
| C2—C3 | 1.520 (10) | C15—O16 | 1.429 (9) |
| C3—S4 | 1.809 (7) | O16—C17 | 1.411 (9) |
| S4—C5 | 1.814 (7) | C17—C18 | 1.510 (11) |
| C5—C6 | 1.507 (10) | | |
| C11—Hg1—C112 | 109.43 (7) | C3—S4—C5 | 104.6 (3) |
| C112—Hg1—S4 | 136.22 (6) | C6—C5—S4 | 112.6 (5) |
| C11—Hg1—S4 | 106.40 (7) | O7—C6—C5 | 107.6 (6) |
| C112—Hg1—S1 | 100.42 (7) | C6—O7—C8 | 113.5 (6) |
| C11—Hg1—S1 | 115.19 (7) | O7—C8—C9 | 107.5 (6) |
| S1—Hg1—S4 | 86.06 (6) | O10—C9—C8 | 110.3 (6) |
| C122—Hg2—C121 | 166.90 (7) | C9—O10—C11 | 111.0 (6) |
| C122—Hg2—C112 | 95.87 (7) | O10—C11—C12 | 110.1 (6) |
| C121—Hg2—C112 | 94.86 (7) | O13—C12—C11 | 110.4 (7) |
| Hg1—C112—Hg2 | 96.07 (7) | C12—O13—C14 | 110.4 (6) |
| C2—S1—C18 | 104.6 (3) | O13—C14—C15 | 109.8 (7) |
| Hg1—S1—C2 | 96.9 (2) | O16—C15—C14 | 108.3 (6) |
| C18—S1—Hg1 | 101.4 (3) | C17—O16—C15 | 112.8 (6) |
| S1—C2—C3 | 115.3 (5) | O16—C17—C18 | 108.7 (6) |
| C2—C3—S4 | 117.1 (5) | C17—C18—S1 | 112.7 (5) |
| C18—S1—C2—C3 | 61.8 (6) | C9—O10—C11—C12 | 173.5 (6) |
| S1—C2—C3—S4 | 61.5 (7) | O10—C11—C12—O13 | -70.0 (8) |
| C2—C3—S4—C5 | 62.9 (6) | C11—C12—O13—C14 | -172.0 (7) |
| C3—S4—C5—C6 | 76.9 (6) | C12—O13—C14—C15 | -174.3 (7) |
| S4—C5—C6—O7 | -66.8 (7) | O13—C14—C15—O16 | 70.0 (9) |
| C5—C6—O7—C8 | 168.5 (6) | C14—C15—O16—C17 | 173.2 (6) |
| C6—O7—C8—C9 | 179.1 (6) | C15—O16—C17—C18 | 162.9 (6) |
| O7—C8—C9—O10 | 60.4 (8) | O16—C17—C18—S1 | -78.7 (7) |
| C8—C9—O10—C11 | 176.9 (6) | C2—S1—C18—C17 | 61.4 (6) |

Data collection: *DIF4* (Stoe & Cie, 1990a). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1990b). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1992). Software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CF1033). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CHI 2HU, England.

References

- Alcock, N. W., Herron, N. & Moore, P. (1978). *J. Chem. Soc. Dalton Trans.* pp. 394–399.
- Blake, A. J., Gould, R. O., Radek, C. & Schröder, M. (1994). *J. Chem. Soc. Chem. Commun.* pp. 985–986.
- Blake, A. J., Gould, R. O., Reid, G., Radek, C., Taylor, A. & Schröder, M. (1993). *The Chemistry of the Copper and Zinc Triads*, edited by A. J. Welch & S. K. Chapman, pp. 95–101. London: The Royal Society of Chemistry.
- Blake, A. J., Holder, A. J., Hyde, T. I., Reid, G. & Schröder, M. (1989). *Polyhedron*, **8**, 2041–2045.
- Blake, A. J., Pasteur, E. C., Reid, G. & Schröder, M. (1991). *Polyhedron*, **10**, 1545–1548.
- Blake, A. J., Reid, G. & Schröder, M. (1990). *J. Chem. Soc. Dalton Trans.* pp. 3849–3856.
- Blake, A. J., Reid, G. & Schröder, M. (1992). *J. Chem. Soc. Chem. Commun.* pp. 1074–1076.
- Bondi, A. (1964). *J. Chem. Phys.* **68**, 441–451.
- Bradshaw, J. S., Hui, J. Y., Chan, Y., Haymore, B. L., Izatt, R. M. & Christensen, J. J. (1974). *J. Heterocycl. Chem.* **11**, 45–49.
- Byriel, K. A., Gahan, L. R., Kennard, C. H. L. & Sunderland, C. J. (1993). *J. Chem. Soc. Dalton Trans.* pp. 625–629.

- Clegg, W. (1981). *Acta Cryst.* **A37**, 22–28.
- Dalley, N. K. & Larson, S. B. (1981). *Acta Cryst.* **B37**, 2225–2227.
- Heinzel, U. & Mattes, R. (1992). *Polyhedron*, **11**, 597–600.
- Jones, T. E., Sokol, L. S. W. L., Rohrabacher, D. B. & Glick, M. D. (1979). *J. Chem. Soc. Chem. Commun.* pp. 140–141.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Reid, G. (1989). PhD thesis, The University of Edinburgh, Scotland.
- Sato, S., Habata, Y., Sato, M. & Akabori, S. (1989). *Bull. Chem. Soc. Jpn.* **62**, 3963–3967.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1992). *SHELXTL/PC*. Version 4.3. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1993). *SHELXL93. Program for Crystal Structure Refinement*. University of Göttingen, Germany.
- Silbert, J. W., Lange, S. J., Stern, C., Hoffman, B. M. & Barrett, A. G. M. (1994). *J. Chem. Soc. Chem. Commun.* pp. 1751–1752.
- Sobhia, M. E., Panneerselvam, K., Chacko, K. K., Suh, I.-H., Weber, E. & Reutel, C. (1992). *Inorg. Chim. Acta*, **194**, 93–97.
- Stoe & Cie (1990a). *DIF4. Diffractometer Control Program*. Version 7.09/DOS. Stoe & Cie, Darmstadt, Germany.
- Stoe & Cie (1990b). *REDU4. Data Reduction Program*. Version 7.03/DOS. Stoe & Cie, Darmstadt, Germany.
- Subramanian, V. & Seff, K. (1980). *Acta Cryst.* **B36**, 2132–2135.

Acta Cryst. (1996). **C52**, 24–27

Potassium Dibenzo-18-crown-6 Triiodide

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Abstract

In (1,4,7,10,13,16-hexaoxa-2,3:11,12-dibenzocyclooctadeca-2,11-diene)potassium triiodide, [K(C₂₀H₂₄O₆)]I₃, the K⁺ ion is coordinated to the six ether O donors of the macrocycle [K—O 2.716(4)–2.779(4) Å] and to atom I3 at a distance of 3.6002(13) Å; I1—I2 is 2.8741(7) and I2—I3 2.9838(7) Å. Pairs of symmetry-related [K(dibenzo-18-crown-6)]I₃ molecules aggregate, with an unusually short distance of 3.184(3) Å between the K⁺ ion and the centroid of one of the benzo groups.

Comment

We are interested in the stabilization of extended polyiodide networks by metal macrocyclic complexes and our work has focused on complexes containing homoleptic S-donor macrocycles (Blake, Devillanova, Lippolis & Schröder, 1994; Blake, Gould, Parsons, Radek & Schröder, 1995).

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