

The preparation and structural characterisation of bis(*N,N*-diethylmonothiocarbamato)complexes of cadmium and of the novel tetrameric complex $[\text{Et}_4\text{Zn}_4(\text{OSCNEt}_2)_2(\text{NEt}_2)_2]$: two new bonding modes for the monothiocarbamato ligand

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Bis(diethylmonothiocarbamato) complexes of cadmium (**1**) and zinc (**2**) were prepared by the reaction of sodium monothiocarbamate with cadmium acetate or zinc chloride. Compound **1** crystallises as clear needles and a single crystal X-ray analysis showed it to be monoclinic (space group $C2/c$, no. 15), $a = 22.143(2)$, $b = 9.239(2)$, $c = 7.553(3)$ Å, $\beta = 101.41(2)^\circ$ and $Z = 4$. The coordination at the cadmium centre is distorted trigonal prismatic with two S,O-bidentate and two O-monodentate diethylmonothiocarbamato ligands. This new, O-binucleating, bonding mode for the monothiocarbamato ligand results in polymeric chains which are co-aligned to give a distorted close-packed hexagonal array.

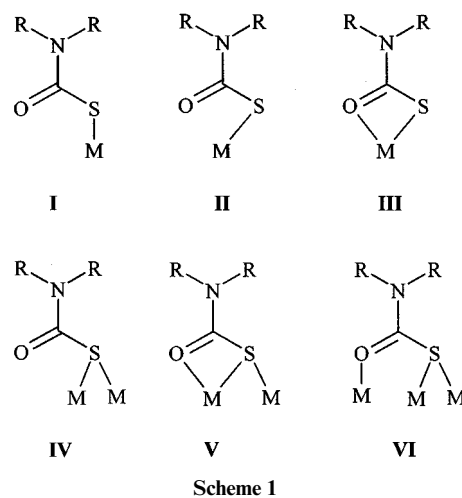
The cage complex $[\text{Et}_4\text{Zn}_4(\text{OSCNEt}_2)_2(\text{NEt}_2)_2]$ **3** is formed as the only isolable product from the reaction of EtZnNEt_2 with carbonyl sulfide. Clear rhombic crystals (space group $P2_1/n$, no. 14) were formed [$a = 10.818(1)$, $b = 14.732(1)$, $c = 11.758(2)$ Å, $\beta = 103.25(1)^\circ$ and $Z = 2$]. The cage is comprised of two six-membered Zn_2CNOS metalocycles that are linked by pairs of Zn–S and Zn–O bonds. In **3** a second new bonding mode for the monothiocarbamato ligand is observed in which both the oxygen and sulfur atoms are binucleating. Molecules of **3** pack to form a slightly distorted cubic close-packed array. The variable temperature ^1H NMR of **3** is also reported and shows the cluster to remain intact in solution.

Introduction

Dithiocarbamate complexes of metal ions are well known^{1–6} and find applications in the rubber⁷ and petrochemical industries,⁸ chemical analysis⁹ and in the deposition of ZnS or CdS thin films by metal organic chemical vapour deposition.^{1,6,10–12} The dithiocarbamate (dtc) ligand, R_2NCS_2^- (R = alkyl) is a formal three-electron donor and has the ability to stabilise metal centres in a variety of oxidation states.¹ There are several methods for the preparation of such carbamates and the most popular are the reaction of a metal salt with CE_2 (E = O, S or Se) in the presence of a secondary amine¹³ or the formal insertion of CE_2 across an M–NR₂ bond in an alkylamide.^{14,15} Mixed alkyl species formed by cadmium or zinc, $[\text{RM}(\text{E}_2\text{CNR}'_2)]_2$ (E = S or Se, R = Me or Et and R' = alkyl), are generally dimeric in the solid state and are readily formed by the reaction of CE_2 with $\text{RM}(\text{NRR}')$. However, the insertion of CO_2 into such alkylamides leads to unusual species such as, with zinc, the tetramers $[\text{Me}_2\text{Zn}_4(\text{O}_2\text{CNEt}_2)_6]$ and $[\text{Me}_4\text{Zn}_4(\text{O}_2\text{CNEt}_2)_4]$.^{16,17}

Here we report further studies of the coordination chemistry of carbamato ligands. Complexes of monothiocarbamates (Et_2NCOS^- diethylmonothiocarbamate mtc) have been much less extensively studied than those of thiocarbamates and only a handful of reports have appeared. It has been suggested, on the basis of spectroscopic results, that the monothiocarbamate group forms chelates with both zinc and cadmium.¹⁸ Monothiocarbamates are known to adopt several modes of coordination; six have been reported so far^{19–26} (Scheme 1). The ligands have been shown to form polymeric complexes involving bridging to adjacent metals through either oxygen or sulfur.

The present work concerns the preparation and the first single crystal X-ray structural analyses of $[\{\text{Cd}(\text{OSCNEt}_2)_2\}_n]$ **1** and of an unusual tetrameric mixed alkyl/alkylamido/mono-



thiocarbamato compound $[\text{Et}_4\text{Zn}_4(\text{OSCNEt}_2)_2(\text{NEt}_2)_2]$ **3**, a cage complex obtained as the only crystalline product from the insertion reactions of carbonyl sulfide (OCS) into zinc–amide bonds. Compounds **1** and **3** both show new coordination modes for the mtc ligand.

Experimental

Materials

All chemicals were purchased from Aldrich Chemical Co. Ltd., and were used without further purification. All solvents were dried and distilled before use and reactions were carried out under an inert atmosphere using standard Schlenk line techniques.

Preparation of $[\text{Et}_2\text{NH}_2]^+[\text{SCONEt}_2]^-$

The salt was prepared by bubbling carbonyl sulfide into diethylamine (50 mL) while keeping the reaction temperature below 10 °C. The salt precipitates upon saturation of the diethylamine solution (yield 19.23 g, 42%). The product was filtered and washed thoroughly with diethyl ether giving a fine white crystalline solid, and dried under vacuum for *ca.* 10 min. The salt sublimes at room temperature under vacuum. The salt is quite hygroscopic and was converted to the corresponding sodium salt immediately or reacted with cadmium or zinc salts to form the respective bis-complexes **1** or **2**.

Preparation of $\text{Na}^+[\text{SCONEt}_2]^-$

The diethylammonium salt of diethylmonothiocarbamate was prepared as above. The diethylammonium salt (45.00 g, 218 mmol) was then dissolved in dry benzene (100 mL) to which was added slowly sodium hydride (5.00 g, 208 mmol). The suspension was allowed to stir overnight by which time a white solid had precipitated out (27.31 g, 84% theoretical). The solid was isolated by filtration and washed with two 50 ml aliquots of benzene. Microanalysis. Found: C, 38.61; H, 6.45; N, 8.96. Calc. for $\text{C}_5\text{H}_{10}\text{NNaOS}$: C, 38.70; H, 6.49; N, 9.03%.

Preparation of $\text{Cd}[\text{SCONEt}_2]_2$ **1**

To the diethylammonium salt in water was added a stoichiometric amount of cadmium acetate, which gave a coagulated white precipitate. The precipitate was isolated and recrystallised from chloroform–pentane (1:1) giving colourless needles of bis(diethylmonothiocarbamate)cadmium(II), mp 167 °C. The yield was quantitative.

Microanalysis. Found: C, 32.05; H, 5.04; N, 7.28. Calc. for $\text{C}_{10}\text{H}_{20}\text{CdN}_2\text{O}_2\text{S}_2$: C, 31.88; H, 5.35; N, 7.43%. ^1H NMR (270 MHz, CDCl_3 , 20 °C): δ 1.24 (t, 3H), 1.36 (t, 3H), 3.53 (q, 2H), 3.79 (q, 2H). ^{13}C NMR (127 MHz, CDCl_3 , 20 °C): δ 13.00 (CH_2CH_3), 13.00 (CH_2CH_3), 42.58 (CH_2CH_3), 46.39 (CH_2CH_3), 181.37 [OC(S)N]. X-Ray powder results [$d(\text{\AA})$ (% intensity)]: 10.53 (94), 8.3 (100), 5.62 (38), 4.84 (11), 4.2 (13), 3.89 (21), 3.79 (20), 3.48 (24), 2.92 (10), 2.82 (13), 2.69 (13), 2.31 (13), 2.15 (16).

Preparation of $\text{Zn}[\text{SCONEt}_2]_2$ **2**

Compound **2** was prepared by reacting a suspension of sodium *N,N*-diethylmonothiocarbamate (4.59 g, 29.6 mmol) in benzene, with anhydrous zinc chloride (2 g, 14.8 mmol) dissolved in dry diethyl ether. The precipitate (4.19 g, 86% theoretical) was washed with ethanol and recrystallised from benzene–hexane (1:1), mp 110 °C.

Microanalysis. Found: C, 36.81; H, 5.97; N, 8.46. Calc. for $\text{C}_{10}\text{H}_{20}\text{N}_2\text{O}_2\text{S}_2\text{Zn}$: C, 36.58; H, 6.14; N, 8.54%. ^1H NMR (270 MHz, CDCl_3 , 20 °C): δ 1.09 (t, 3H), 1.20 (t, 3H), 3.37 (q, 2H), 3.67 (q, 2H). ^{13}C NMR (127 MHz, CDCl_3 , 20 °C): δ 13.09 (CH_2CH_3), 13.09 (CH_2CH_3), 42.56 (CH_2CH_3), 46.64 (CH_2CH_3), 181.53 [OC(S)N]. X-Ray powder results [$d(\text{\AA})$ (% intensity)]: 10.35 (96), 8.19 (100), 5.56 (40), 4.8 (12), 4.17 (13), 3.86 (22), 3.75 (20), 3.46 (25), 2.91 (10), 2.81 (13), 2.68 (12), 2.31 (11), 2.15 (12).

Preparation of $[\text{Et}_2\text{Zn}_4(\text{OSCNEt}_2)_2(\text{NEt}_2)_2]$ **3**

One equivalent of diethylamine was added slowly (dropwise) to diethyl zinc at –78 °C. The resulting clear solution was allowed to warm to room temperature and refluxed at 40 °C for 3 h. The solution was then cooled to –78 °C and OCS was bubbled into it. After several minutes the solution turned pale yellow in colour and a white solid precipitated. Recrystallisation from toluene afforded clear colourless hexagonal and cubic

crystals. Microanalysis. Found: C, 33.95; H, 5.78; N, 6.52. Calc. for $\text{C}_{26}\text{H}_{60}\text{N}_4\text{O}_2\text{S}_2\text{Zn}_4$: C, 35.73; H, 5.75; N, 6.95%. ^1H NMR (270 MHz, CDCl_3 , 80 °C): δ 0.43 (q, ZnCH_2CH_3), 1.36 (t, ZnCH_2CH_3), 1.18 (t, $\text{ZnNCH}_2\text{CH}_3$), 2.77 (q, $\text{ZnNCH}_2\text{CH}_3$), 0.91–1.04 (q, $\text{OSCNCH}_2\text{CH}_3$), 3.14–3.50 (q, $\text{OSCNCH}_2\text{CH}_3$). ^{13}C NMR (127 MHz, CDCl_3 , 20 °C): δ 2.59 (ZnCH_2CH_3), 12.73 (ZnCH_2CH_3), 13.11 ($\text{OSCNCH}_2\text{CH}_3$), 15.81 ($\text{ZnNCH}_2\text{CH}_3$), 42.95 ($\text{OSCNCH}_2\text{CH}_3$), 46.35 ($\text{OSCNCH}_2\text{CH}_3$), 47.28 ($\text{ZnNCH}_2\text{CH}_3$), 180.74 (OSCN), 181.13 (OSCN).

Attempted preparations of $\text{RZn}(\text{OSCNEt}_2)$ (R = Me **4**, Et **5**)

To a solution of R_2Zn (R = Me **4** or Et **5**) in toluene was added dropwise an equimolar equivalent of **2** in toluene at –78 °C. The mixture was allowed to attain room temperature and left to stir overnight. The solution was then reduced *in vacuo* to leave a very viscous oil. The oil was left to stand for several months in pentane, no crystallisation was observed. ^1H and ^{13}C NMR analysis of the oil in each case showed the presence of the species **4** or **5**.

Physical measurements

IR spectra were recorded on a Mattson-Polaris FT spectrometer as Nujol mulls between KBr plates or as KBr pellets. ^1H and ^{13}C NMR spectra were recorded using Bruker AM500 or DX400 pulsed FT/NMR instruments, in either CDCl_3 or C_6D_6 . Variable temperature NMR were recorded on a JEOL EX270. The internal reference used was Me_4Si . Mass spectral data were run on Micromass Autospec and Micromass Platform2 spectrometers. Microanalysis were carried out at Imperial College. X-Ray diffraction patterns were obtained using secondary graphite monochromated $\text{Cu-K}\alpha$ radiation on a Philips PW1700 series automated diffractometer.

X-Ray crystallographic analysis

Table 3 provides a summary of the crystal data, data collection and refinement parameters for **1** and **3**. The structures were solved by the heavy atom method and by direct methods for **1** and **3** respectively. In **3** disorder was found in the position of the terminal methyl group of one of the ethyl groups. This was resolved into two partial occupancy positions, the major occupancy non-hydrogen atom of which was refined anisotropically. The remaining non-hydrogen atoms in both structures were refined anisotropically. In each structure the C–H hydrogen atoms were placed in calculated positions, assigned isotropic thermal parameters, $U(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ [$U(\text{H}) = 1.5U_{\text{eq}}(\text{C-Me})$], and allowed to ride on their parent atoms. Computations were carried out using the SHELXTL PC program system.²⁷

CCDC reference number 186/1163.

Results and discussion

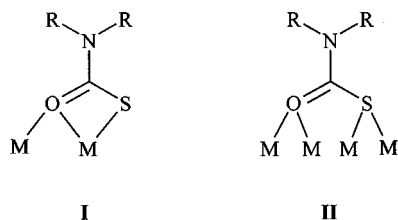
Synthesis of complexes

Stoichiometric amounts of cadmium acetate and the ammonium salt $[\text{Et}_2\text{NH}_2]^+[\text{Et}_2\text{NCOS}]^-$ were reacted in water to give a white precipitate of the bis-mtc complex of cadmium (**1**) which was isolated and recrystallised from a 1:1 chloroform pentane mixture to give colourless needles. The preparation of $\text{Zn}(\text{OSCNEt}_2)_2$ **2** when attempted by the above route resulted in the formation of a mixture of **2** and a fine insoluble precipitate characterised as ZnS by X-ray powder diffraction. The bis-mtc complex of zinc was prepared by a non-aqueous route involving the metathesis reaction of a suspension of sodium diethyl-mtc in benzene with zinc chloride solution in diethyl ether. The solution was filtered and the volume reduced *in vacuo* to yield a white powder, which was recrystallised from benzene to give

very fine crystals of **2**. Crystals of **2** suitable for single crystal X-ray analysis could not be prepared. The preparation of $RZn(SOCNET_2)$ ($R = Me$ **4** or Et **5**) was attempted by the comproportionation reaction²⁸ of **2** with either dimethyl or diethyl zinc respectively. However, these reactions produced viscous liquids which when characterised showed the presence of the above species **4** and **5** (*cf.* Experimental section). The insertion of carbonyl sulfide across a metal–amide bond is a well established route to many transition metal monothiocarbamates,²⁹ hence bubbling carbonyl sulfide into a solution of ethylzinc diethylamide³⁰ was expected to afford the mixed alkyl species **5**. However after bubbling carbonyl sulfide through a solution for several minutes at (-78 °C, toluene) clear crystals of **3** began to precipitate. Recrystallisation from toluene gave isomorphous hexagonal and rectangular crystals of $[Et_4Zn_4(OSCNET_2)_2(NEt_2)_2]$ **3**. The insertion of OCS gas was also carried out at higher temperatures and with various ethylzinc diethylamide concentrations; in each case crystals of **3** began to form. When left in contact with air, **3** decomposes slowly to give the air stable bis-complex **2**.

Molecular structure of $Cd[SCONET_2]_2$ **1**

The X-ray structure of **1** reveals the complex to have crystallographic C_2 symmetry, the cadmium being bound to two ‘bidentate’ diethyl-mtc ligands and ‘monodentately’ to the oxygen atoms of two further mtc ligands (Fig. 1). The oxygen atoms of each ligand (all of which are crystallographically equivalent) are also binucleating and bridge adjacent cadmium centres to form the extended polymer chain shown in Fig. 2. This is a new bonding mode for the mtc ligand and is represented in Scheme 2-I. The geometry at cadmium is distorted



Scheme 2

trigonal prismatic (Fig. 3) with Cd–S distances of 2.498(1) Å and Cd–O distances of 2.587(4) Å (bidentate) and 2.347(4) Å (monodentate), *i.e.* the oxygen bridging is asymmetric. The geometry within the mtc ligand is unexceptional, exhibiting the expected pattern of N–C=O bond delocalisation, the C=O distance being unaffected by its dual coordinating and bridging roles (Table 1). The coordination planes of the two ‘bidentate’ mtc ligands subtend an angle of *ca.* 133° at cadmium. Along the polymer axis (the crystallographic c direction) the Cd atoms describe a zigzag chain, the Cd···Cd vectors subtending an angle of 151° (transannular Cd···Cd separation 3.90 Å), and with adjacent planar Cd_2O_2 rings being inclined by 52° to each other. Adjacent polymer chains are parallel and are arranged to give a distorted close-packed hexagonal array (Fig. 4). The outer surfaces of each chain are dominated by the hydrophobic ethyl groups and thus there are no interchain interactions other than normal van der Waals. This absence of strong intermolecular interactions clearly contributes to the low melting point of the solid.

In the IR spectrum the $\nu(C-S)$ mode is observed at 680 cm^{-1} (medium) and 695 cm^{-1} (medium) for **1** and **2**, respectively. The broad band at 1510–1525 cm^{-1} (very strong) seen for **1** and at 1510–1530 cm^{-1} (very strong) for **2** is assigned to the $\nu(C-O)$ mode that may also include the $\nu(C-N)$ mode. Although crystals for **2** suitable for single crystal X-ray analysis could not be grown, the powder X-ray data (*cf.* experimental) and IR data suggest that the coordinating behaviour of the

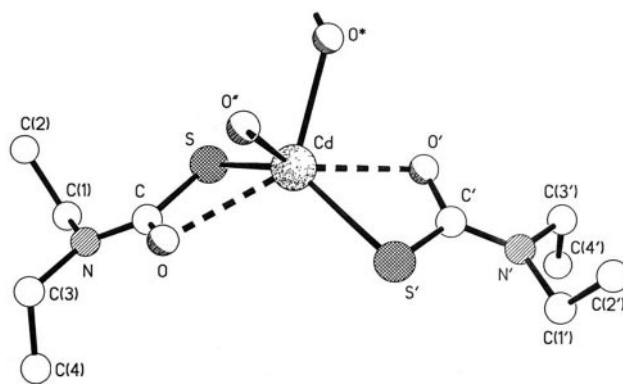


Fig. 1 The coordination at cadmium in the structure of **1**.

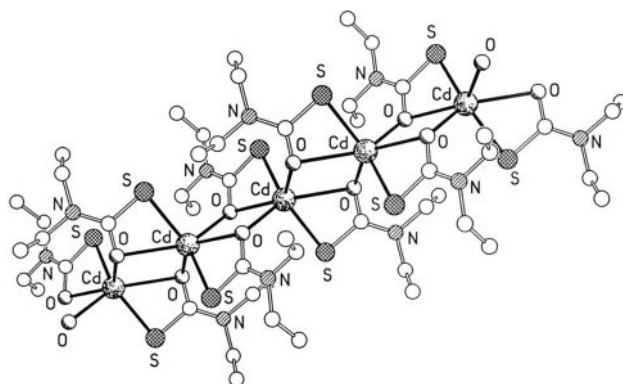


Fig. 2 Part of one of the extended polymer chains present in the crystals of **1**.

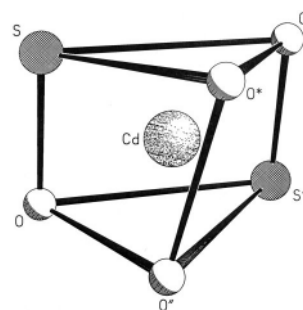


Fig. 3 The trigonal prismatic coordination polyhedron present in **1**.

Table 1 Selected bond lengths (Å) and angles (°) for **1**

| | | | |
|-----------|----------|-----------|----------|
| Cd–O* | 2.347(4) | Cd–O | 2.587(4) |
| Cd–S | 2.498(1) | C–O | 1.268(6) |
| S–C | 1.740(5) | Cd–S' | 2.498(1) |
| O''–Cd' | 2.347(4) | Cd–O' | 2.587(4) |
| Cd–O'' | 2.347(4) | C–N | 1.341(7) |
| O''–Cd–O* | 83.5(2) | O'–Cd–O'' | 134.0(1) |
| O''–Cd–S | 117.6(1) | S–Cd–O' | 104.8(1) |
| O''–Cd–O | 75.7(1) | C–O–Cd | 93.2(3) |
| S–Cd–O | 61.6(1) | O*–Cd–S' | 117.6(1) |
| S'–Cd–O' | 61.6(1) | S'–Cd–S | 136.9(1) |
| C–O–Cd' | 130.7(3) | S'–Cd–O | 104.8(1) |
| O''–Cd–S' | 94.9(1) | O'–Cd–O* | 75.7(1) |
| O*–Cd–S | 94.9(1) | O–Cd–O' | 145.2(2) |
| O*–Cd–O | 134.0(1) | Cd–O–Cd' | 104.4(1) |

mtc ligand to both cadmium and zinc metal centres is similar and that the two compounds are isomorphous.

Molecular structure of **3**

The X-ray analysis of the product of the reaction between $EtZnNET_2$ and OCS reveals the formation of the fascinating

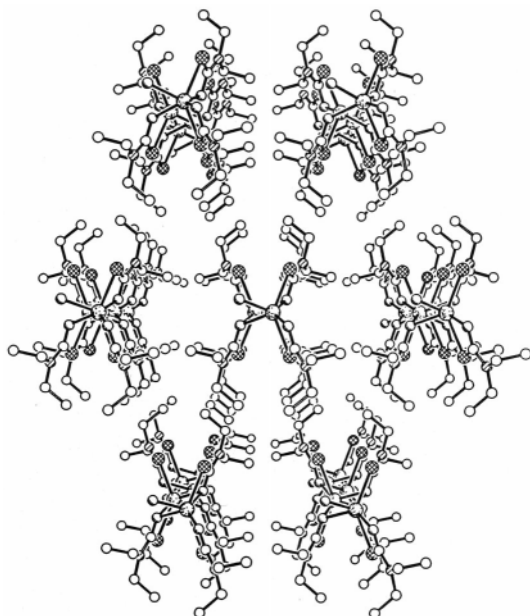


Fig. 4 The slightly flattened close-packed hexagonal array of polymer chains in **1** viewed down the chain axes.

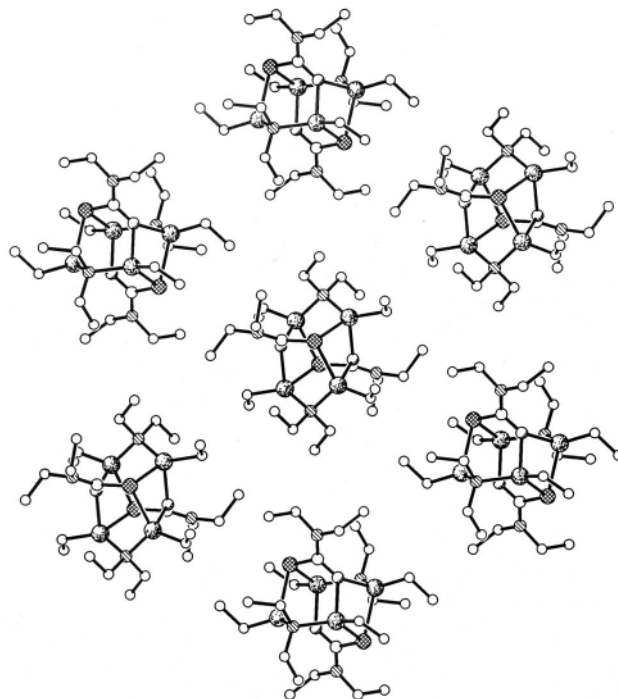


Fig. 6 Part of one of the close-packed hexagonal sheets in the crystals of **3**. Adjacent sheets pack to form an ABC cubic close-packed arrangement.

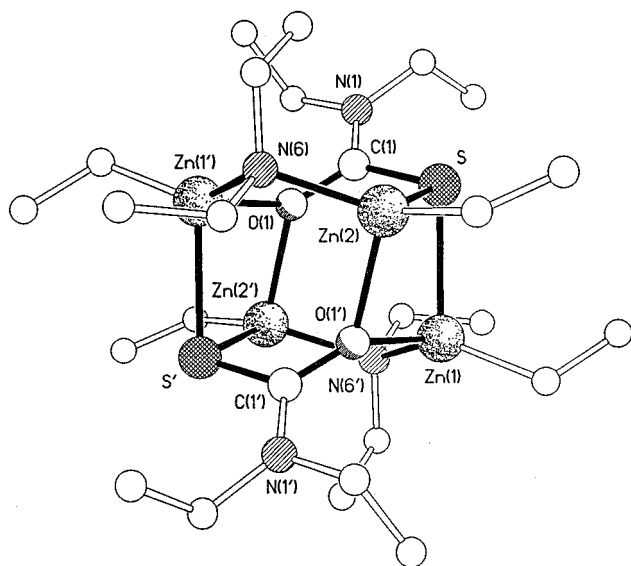


Fig. 5 The cage structure of **3**.

Table 2 Selected bond lengths (Å) and angles (°) for **3**

| | | | |
|--------------------|----------|-------------------|----------|
| Zn(1)–C(11) | 1.981(5) | Zn(2)–S | 2.466(1) |
| Zn(1)–S | 2.527(1) | C(1)–N(1) | 1.329(6) |
| Zn(2)–O(1') | 2.214(3) | Zn(1)–O(1') | 2.213(3) |
| C(1)–O(1) | 1.274(5) | Zn(2)–N(6) | 2.010(4) |
| Zn(1)–N(6') | 1.996(4) | S–C(1) | 1.762(4) |
| Zn(2)–C(13) | 1.958(6) | | |
| C(11)–Zn(1)–N(6') | 136.2(2) | N(6)–Zn(2)–S | 114.1(1) |
| C(13)–Zn(2)–S | 108.9(2) | C(1)–S–Zn(1) | 101.3(1) |
| C(13)–Zn(2)–N(6) | 126.0(3) | C(1)–O(1)–Zn(1') | 129.3(3) |
| C(1)–Zn(2)–S | 112.0(2) | Zn(1')–N(6)–Zn(2) | 111.6(2) |
| C(1)–S(1)–Zn(2) | 102.2(2) | N(6')–Zn(1)–O(1') | 103.6(1) |
| O(1)–C(1)–S | 121.0(3) | O(1')–Zn(1)–S | 87.0(1) |
| Zn(1')–O(1)–Zn(2') | 95.8(1) | N(6)–Zn(2)–O(1') | 97.1(1) |
| C(11)–Zn(1)–O(1') | 105.1(2) | O(1')–Zn(2)–S | 88.5(1) |
| N(6')–Zn(1)–S | 105.0(1) | Zn(2)–S–Zn(1) | 82.2(1) |
| C(13)–Zn(2)–O(1') | 110.9(2) | C(1)–O(1)–Zn(2') | 129.3(3) |

C_i -symmetric cage complex **3** (Fig. 5) which exhibits another new bonding mode for the mtc ligand (Scheme 2-II). The cage is comprised of two six-membered Zn_2CNOS metalocycles each with a slightly twisted 'boat' conformation, the zinc centres

being bridged on one side by the nitrogen atom of the original $EtZnNET_2$ and on the other bidentately by the mtc ligand formed *in situ*. The oxygen and sulfur atoms of this latter ligand are each binucleating, linking the two metalocycles to form the cage (within which all four zinc atoms are perfectly coplanar). The two Zn_2OS faces are arranged in a distorted square prismatic geometry with respect to each other, the two four-membered rings being non-planar (folded by *ca.* 28° about the $Zn \cdots Zn$ vector) with transannular $Zn \cdots Zn$ and $S \cdots O$ separations of 3.28 and 3.27 Å respectively.

The geometry at each zinc centre is distorted tetrahedral with angles ranging between $87.0(1)$ – $136.2(2)^\circ$ at Zn(1) and $88.5(1)$ – $126.0(3)^\circ$ at Zn(2), the acute angles being associated with the four-membered rings whereas the most obtuse ones are for the N–Zn–Et angles. The Zn–C bond lengths are unexceptional (Table 2) and the bridging Zn–N distances [1.996(4) and 2.010(4) Å] are comparable to those observed in, for example, bis(μ -diphenylamido)bis(methylzinc).³¹ The two independent Zn–O distances do not differ significantly, but are markedly longer than those observed in related carbamate species.²⁵ The Zn–S bond lengths on the other hand are noticeably asymmetric with that within the six-membered metalocycle [2.466(1) Å] being shorter than that bridging between the two six-membered rings [2.527(1) Å].

The pattern of bonding within the mtc ligand is little changed from that observed in **1**, there being the expected delocalisation in the N–C=O unit. The C–S distance here is slightly longer than that seen in **1**, reflecting the binucleating role of the sulfur atom, the C=O distance being unaffected. Whereas the sulfur has a pronounced contracted tetrahedral geometry, with angles of $82.2(1)$, $101.3(1)$ and $102.2(2)^\circ$, the oxygen atom adopts a near trigonal planar arrangement [angles of $95.8(1)$, $129.3(3)$ and $129.3(3)^\circ$], the oxygen atom lying 0.23 Å out of the plane of its substituents. For both the sulfur and oxygen atoms, the smallest angles are those associated with the Zn_2OS four-membered ring. The cage molecules have an approximately spherical surface and pack to form an only slightly distorted cubic close-packed array, the shortest centroid \cdots centroid distances within a layer being 10.2, 10.8 and 11.5 Å (Fig. 6).

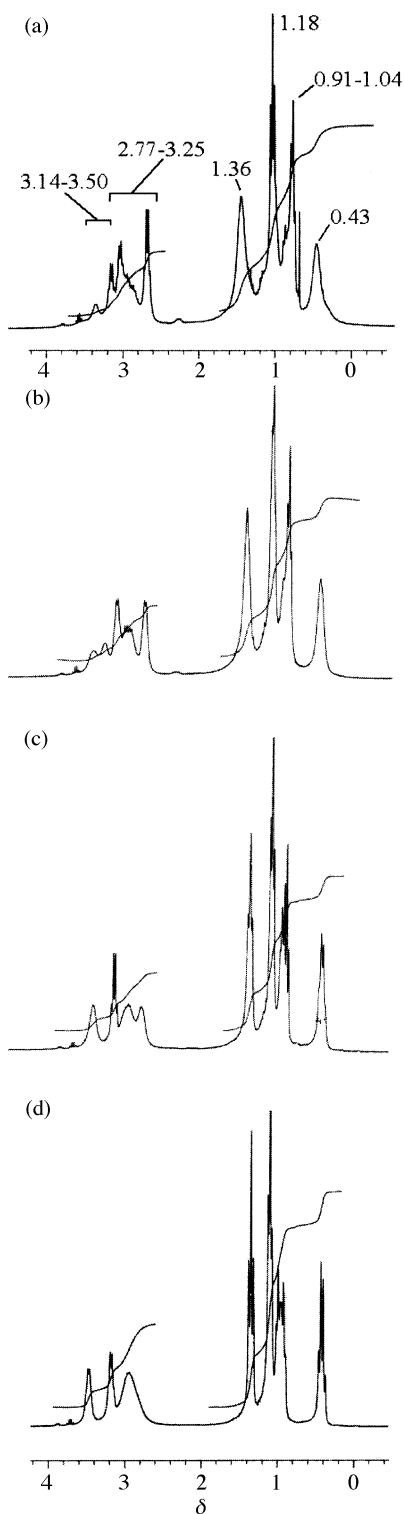


Fig. 7 ^1H Variable temperature NMR of **3** at (a) 20, (b) 40, (c) 60 and (d) 80 °C respectively.

NMR studies

The ^1H NMR spectrum of compound **3**, at room temperature, showed evidence for nine or ten resonance signals some of which were broadened. The cage structure of **3** should lead to only eight proton environments. The spectrum confirmed four resonances at high field and another set at lower field in which the broadening was observed. The highest field signals correspond to the ethyl groups bound to zinc with the methylene protons at δ 0.43 and a signal at a lower field, δ 1.36, for the methyl protons. The monothiocarbamate ligands give two overlapping triplets at δ 0.91–1.04 for the methyl groups

and two lowest field multiplets, δ 3.14–3.50, for the methylene groups. The amidoethyl groups give a well resolved triplet at δ 1.18 for the equivalent methyl groups (12 protons) and two broad quartets (δ 2.77–3.25) for non-equivalent methylene protons [Fig. 7(a), 20 °C]. The 2D proton COSY NMR taken at room temperature confirmed, unequivocally, the correlation of the high and low field resonances.

The ^{13}C NMR spectrum showed nine resonances. Two were assigned to the ethyl group attached to the zinc and the monothiocarbamate ligand gave five resonances (the quaternary carbons of the two mtc ligands are slightly inequivalent, the methyl groups of the mtc ligand are equivalent), the amidoethyl groups gave two environments as expected. The chemical shift assignments are given in the experimental section.

Variable temperature (VT) ^1H NMR analysis of **3**

A VT proton NMR study was undertaken to try to understand the broad signals observed at room temperature. Proton NMR spectra were recorded from 10 to 80 °C at 5 °C intervals, in $[\text{D}_6]\text{benzene}$ (C_6D_6). Four proton NMR spectra taken at 20, 40, 60 and 80 °C are shown [Fig. 7(a)–(d) respectively].

On reducing the temperature below 20 °C further line broadening was observed resulting in the loss of fine structure which may in part be due to viscosity; at -10 °C in $[\text{D}_8]\text{toluene}$ the compound precipitated. Increasing the temperature to 40 °C [Fig. 7(b)] results in the sharpening of the signals for zinc–ethyl groups, but a considerable loss of the fine structure is observed for all other signals. At 60 °C [Fig. 7(c)] the zinc–ethyl group signals are completely resolved and a similar but smaller effect occurs for the other resonances. The amido-methylene signals are resolved into two broad multiplets. Increasing the temperature to 80 °C [Fig. 7(d)] results in the sharpening of signals for all methyl environments within **3**. Two clear signals are observed for methylene groups of the mtc ligands and one broad signal for amido-methylene groups.

However, the major effect observed in the VT NMR studies is on the broad resonance at δ ca. 2.9. This resonance is associated with the methylene protons of the monothiocarbamate ligand. This peak splits at 60 °C into two distinct resonances and at room temperature a sharp signal is observed. This observation is consistent with restrictive rotation along the C–N bond hence lowering the symmetry of the complex at lower temperatures. At 80 °C the spectra simplifies to that seen in the solid state from X-ray crystallography. The VT NMR studies hence confirm that the tetramer **3** exists in solution, the restriction of rotation around the C–N bond is typical of dynamic variable temperature behaviour.

Conclusion

Two novel group 12 complexes of the monothiocarbamate ligand have been prepared and structurally characterised. Compound $[\{\text{Cd}(\text{OSCNEt}_2)_2\}_n]$ **1** crystallises as clear needles and is polymeric. The coordination at the cadmium centre is distorted trigonal prismatic with two S,O-bidentate and two O-monodentate diethyl-monothiocarbamate ligands. The unique C_1 -symmetric cage complex $[\text{Et}_4\text{Zn}_4(\text{OSCNEt}_2)_2(\text{NEt}_2)_2]$ **3** is comprised of two six-membered Zn_2CNOS metallocycles each with a slightly twisted ‘boat’ conformation. The zinc centres are bridged on one side by the nitrogen of the diethylamide, and on the other bidentately by the mtc ligand. Both compounds **1** and **3** show new bonding modes for the monothiocarbamate ligand.

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Table 3 Crystal data, data collection and refinement parameters^a

| Data | 1 | 3 |
|---|---|--|
| Formula | C ₁₀ H ₂₀ N ₂ O ₂ S ₂ Cd | C ₂₆ H ₆₀ N ₄ O ₂ S ₂ Zn ₄ |
| Formula weight | 376.8 | 790.4 |
| Colour, habit | Clear needles | Clear rhombs |
| Crystal size/mm | 0.43 × 0.13 × 0.13 | 0.33 × 0.27 × 0.22 |
| Lattice type | Monoclinic | Monoclinic |
| Space group, number | C2/c, 15 | P2 ₁ /n, 14 |
| T/K | 293 | 173 |
| Cell dimensions | | |
| a/Å | 22.143(2) | 10.818(1) |
| b/Å | 9.239(2) | 14.732(1) |
| c/Å | 7.553(3) | 11.758(2) |
| β/° | 101.41(2) | 103.25(1) |
| V/Å ³ | 1514.6(6) | 1823.9(3) |
| Z | 4 ^b | 2 ^c |
| D/g cm ⁻³ | 1.652 | 1.439 |
| F(000) | 760 | 832 |
| Radiation used | Cu-Kα | Cu-Kα ^d |
| μ/mm ⁻¹ | 14.08 | 4.25 |
| θ range/° | 4.1–60.0 | 5.9–63.9 |
| No. of unique reflections | | |
| measured | 1138 | 3005 |
| observed, F _o > 4σ(F _o) | 1068 | 2510 |
| Absorption correction | Semi-empirical | Semi-empirical |
| Maximum, minimum transmission | 0.24, 0.11 | 0.29, 0.18 |
| No. of variables | 79 | 177 |
| R ₁ ^e | 0.038 | 0.047 |
| wR ₂ ^f | 0.101 | 0.118 |
| Weighting factors a, b ^g | 0.057, 4.584 | 0.071, 2.442 |
| Largest difference peak, hole/e Å ⁻³ | 0.61, -0.74 | 0.80, -0.64 |

^a Details in common: graphite monochromated radiation, ω-scans, Siemens P4 diffractometer, refinement based on F². ^b The molecule has crystallographic C₂ symmetry. ^c The molecule has crystallographic C_i symmetry. ^d Rotating anode source. ^e R₁ = Σ||F_o| - |F_c||/Σ|F_o|. ^f wR₂ = {Σ[w(F_o² - F_c²)²]/Σ[w(F_o²)²]}^{1/2}. ^g w⁻¹ = σ²(F_o²) + (aP)² + bP.

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