

A series of soluble, discrete homo and heteroleptic Ca(II) complexes of hexanuclear sulfidochloride rhenium clusters,  $[\text{Ca}(\text{X})_n(\text{Y})_m][\text{Re}_6\text{S}_6\text{Cl}_8]$ , ( $n = 6, m = 0, \text{X} = \text{DMF}, \text{THF}, \text{DMSO}; n = 4, m = 3, \text{X} = \text{MeCN}, \text{Y} = \text{THF}, \text{dioxane}$ ) and the 1D co-ordination polymer  $[\text{Ca}(\text{MeCN})_3(\text{OH}_2)_2(\text{dioxane})_2][\text{Re}_6\text{S}_6\text{Cl}_8] \cdot (\text{dioxane})(\text{MeCN})$

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Dedicated to Professor François Mathey on the occasion of his 60th birthday

## Abstract

Six homo- and heteroleptic calcium complexes involving different ligands such as dimethylformamide, dimethylsulfoxide, acetonitrile, tetrahydrofuran, dioxane or water and the hexanuclear sulfidochloride rhenium cluster  $[\text{Re}_6\text{S}_6\text{Cl}_8]^{2-}$  as counter-ion have been synthesised and structurally characterised by X-ray diffraction on single crystals. The coordination geometry around the calcium centre is of octahedral type within the three homoleptic complexes  $\text{Ca}(\text{DMF})_6$  (**1**),  $\text{Ca}(\text{THF})_6$  (**2**) and  $\text{Ca}(\text{DMSO})_6$  (**3**), while in the heteroleptic complexes  $\text{Ca}^{2+}$  is seven-coordinated either in a monocapped trigonal prism (**4** and **5**) geometry or in a pentagonal bipyramid (**6**) one. The compound **6** is a 1D co-ordination polymer formed via  $\text{O}_{\text{diox}} \cdots \text{H}-\text{OH}$  hydrogen bonds. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Calcium complexes; Rhenium clusters; Crystal structures; Co-ordination polymer

## 1. Introduction

The chemistry of discrete, molecular forms of hexanuclear chalcogenide rhenium clusters is in a stage of rapid development [1], driven by the opportunity to unravel the organic solution phase and redox chemistry of electron rich mineral molecular forms and explore their substitution patterns and coordination chemistry which vary with the chalcogen–halogen ratio within the  $\mu_3$ -ligand shell surrounding the octahedral metal cluster core.

A representative example of this chemistry is the simultaneous  $\mu_3$ -Cl and  $\mu_1$ -Cl displacement reactions of

the dianionic cluster form  $[\text{Re}_6(\mu_3\text{-S})_6(\mu_3\text{-Cl})_2(\mu_1\text{-Cl})_6]^{2-}$ , shown in Fig. 1, upon reaction with silylated derivatives  $\text{E}[\text{SiMe}_3]_2$ ,  $\text{E} = \text{O}, \text{S}, \text{Se}, \text{NH}$  or  $\text{E}'[\text{SiMe}_3]_3$ ,  $\text{E}' = \text{P}, \text{As}$ , which, in the presence of  $\text{PPr}_3$ , give either neutral  $\mu_3$ -imido-chalcogenido,  $\mu_3$ -oxo-chalcogenido and  $\mu_3$ -sulfido-chalcogenido cluster forms,  $[\text{Re}_6\text{S}_6\text{E}_2(\text{PPr}_3)_6]$  ( $\text{E} = \text{NH}, \text{O}, \text{S}$ ), or dicationic  $\mu_3$ -phosphido-chalcogenido and  $\mu_3$ -arsenido-chalcogenido clusters,  $[\text{Re}_6\text{S}_6\text{E}_2(\text{PPr}_3)_6]^{2+}[\text{Re}_6\text{S}_6\text{Cl}_8]^{2-}$  ( $\text{E} = \text{As}, \text{P}$ ) [2].

The alkaline-earth salts of the divalent cluster forms proved to be the point of entry of choice into this ligand displacement chemistry since they are highly soluble in a large variety of polar organic solvents such as alcohol, acetonitrile, tetrahydrofuran, dimethylformamide, dioxane and acetone [1]. Note that hydrated solid phases such as  $[\text{Ca}(\text{H}_2\text{O})_n][\text{Re}_6\text{Q}_6\text{Cl}_8] \cdot m\text{H}_2\text{O}$  ( $\text{Q} = \text{S}, \text{Se}$ ) readily crystallise out of the organic phase con-

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taining even minute amounts of water and are found to be in turn highly soluble in water [3].

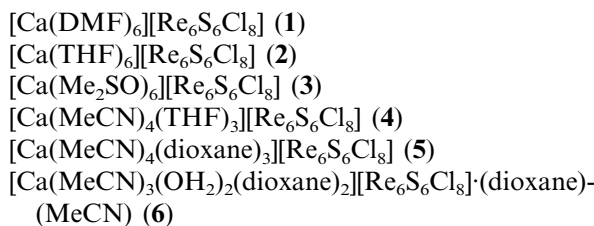
In this paper, we report the results of our exploration of the chemistry of  $\text{Ca}[\text{Re}_6\text{S}_6\text{Cl}_8]$  in organic solvents such as MeCN, DMF, THF and DMSO, where, remarkably, low range ordered, high quality crystalline assemblies are readily constructed. The salient coordination features of the series of homo-ligand or mixed (or hetero)-ligands-Ca(II) complex salts are reported. Such solvated alkaline-earth metal complexes and inorganic polymers based on metal ion complexation and covalent or hydrogen bonding in organic solvents have become the focus of a recent interest as they can be regarded as model aggregates of larger more complex and somewhat disordered assemblies obtain, for example, by the sol-gel process [4]. The ready formation and inherent network-forming ability of the title complex salts, also expressed by their different stoichiometries and spatial arrangements, all are indications that other macroscopically ordered crystalline complexes should be accessible from these precursors in different, eventually constrained environments.

## 2. Experimental

### 2.1. Designation

The formulation and numbering of the six Ca(II) solvent ligand complex salts of the hexanuclear sulfi-

dochloride rhenium cluster dianion reported in this paper are as follows:



### 2.2. Synthesis

Standard Schlenk and vacuum line techniques were employed for all manipulations of dioxygen- and/or moisture sensitive compounds. Solvents were distilled under Ar atmosphere from  $\text{P}_2\text{O}_5$  for MeCN and Na and benzophenone for dioxane and tetrahydrofuran (THF).  $\text{Ca}[\text{Re}_6\text{S}_6\text{Cl}_8]$  was prepared by high temperature solid state reaction of a  $\text{CaCl}_2$ , Re, S and  $\text{ReCl}_5$ , as described earlier [3].

$\text{Ca}[\text{Re}_6\text{S}_6\text{Cl}_8]$  (ca. 40 mg) were dissolved in MeCN. Slow condensing THF into the solution give ruby red crystals of **2**.

Crude pellets of  $\text{Ca}[\text{Re}_6\text{S}_6\text{Cl}_8]$  containing a total of 3 mmol of Re (from Re metal and  $\text{ReCl}_5$ ) are grounded and stirred in 500 ml of MeCN at room temperature (r.t.) for 24 h. The suspension is filtered on Celite to eliminate black residues. The orange solution is concentrated to half its initial volume prior to addition of THF (**4**) or dioxane (**5**, **6**) which results in the precipitation of an orange solid. The solution is then heated until dissolution and slow cooling gives beautiful ruby red polyhedral crystals of **4** and **5**; slow evaporation under  $\text{N}_2$  flow gives red platelet of **6** (yield 75% for all three compounds).

### 2.3. X-ray crystallography

Experimental details for compounds **1–6** are given in Table 1. In each case a suitable single-crystal was mounted on a glass fiber in a random orientation. Except for **1** which is stable in the air, the crystals of other compounds were thermally unstable and placed rapidly under a cold nitrogen flow to prevent decomposition by loss of solvent or crystallisation. Data collection were performed at r.t. for **1** or low temperature for **2–6** on a  $\kappa$ -axis Enraf-Nonius CAD4-F diffractometer **1**, **3** or single  $\phi$ -axis Stoe-IPDS system (**2**, **4–6**) using graphite monochromatised Mo-K $\alpha$  radiation. In all cases an absorption correction was applied using either empirical procedures based on azimuthal psi-scans of some reflexions [5] or numerical procedures based on face indexing [6]. In some cases, the highest peaks revealed by the final difference-Fourier maps are in the

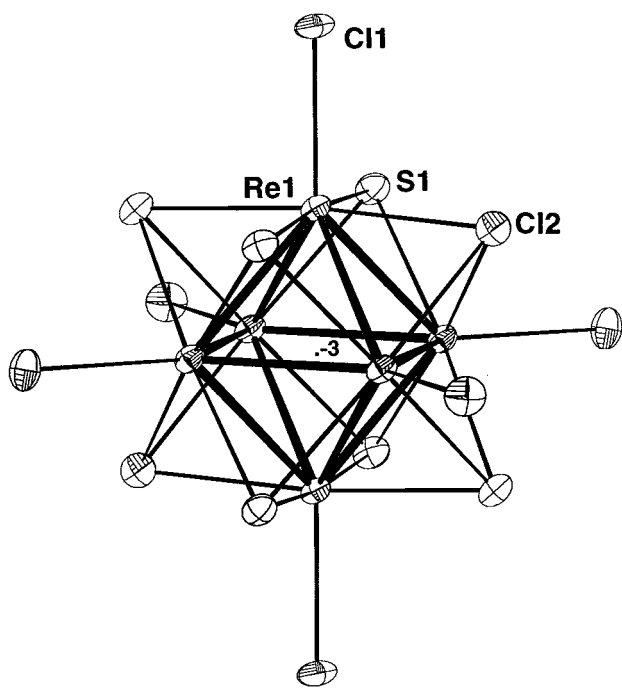


Fig. 1. Structure of the discrete, molecular cluster dianion, common to all compounds **1–6**, and shown here in  $[\text{Ca}(\text{THF})_6][\text{Re}_6\text{S}_6\text{Cl}_8]$  (**2**). The thermal ellipsoids are drawn at the 50% probability level.

Table 1  
Crystal data as well as data collection and refinement details for calcium complexes 1–6

Crystal data						
Compound	[Ca(DMF) <sub>6</sub> ] [Re <sub>6</sub> S <sub>6</sub> Cl <sub>8</sub> ] (1)	[Ca(THF) <sub>6</sub> ] [Re <sub>6</sub> S <sub>6</sub> Cl <sub>8</sub> ] (2)	[Ca(Me <sub>2</sub> SO) <sub>6</sub> ] [Re <sub>6</sub> S <sub>6</sub> Cl <sub>8</sub> ] (3)	[Ca(MeCN) <sub>4</sub> - (THF) <sub>3</sub> ]- [Re <sub>6</sub> S <sub>6</sub> Cl <sub>8</sub> ] (4)	[Ca(MeCN) <sub>4</sub> - (dioxane) <sub>3</sub> ]- [Re <sub>6</sub> S <sub>6</sub> Cl <sub>8</sub> ] (5)	[Ca(MeCN) <sub>3</sub> (OH) <sub>2</sub> - (dioxane) <sub>2</sub> ][Re <sub>6</sub> S <sub>6</sub> Cl <sub>8</sub> ] (dioxane)(MeCN) (6)
Empirical formula	C <sub>18</sub> H <sub>42</sub> CaCl <sub>8</sub> N <sub>6</sub> O <sub>6</sub> Re <sub>6</sub> S <sub>6</sub>	C <sub>24</sub> H <sub>48</sub> CaCl <sub>8</sub> O <sub>6</sub> Re <sub>6</sub> S <sub>6</sub>	C <sub>12</sub> H <sub>36</sub> CaCl <sub>8</sub> O <sub>6</sub> Re <sub>6</sub> S <sub>12</sub>	C <sub>20</sub> H <sub>36</sub> CaCl <sub>8</sub> N <sub>4</sub> O <sub>3</sub> Re <sub>6</sub> S <sub>6</sub>	C <sub>20</sub> H <sub>36</sub> CaCl <sub>8</sub> N <sub>4</sub> O <sub>6</sub> Re <sub>6</sub> S <sub>6</sub>	C <sub>20</sub> H <sub>40</sub> CaCl <sub>6</sub> N <sub>4</sub> O <sub>8</sub> Re <sub>6</sub> S <sub>8</sub>
Formula weight	2071.94	2065.98	2102.19	2013.89	2025.60	2093.89
T (K)	293	170	220	250	250	200
Crystal system	Triclinic	Trigonal	Trigonal	Monoclinic	Monoclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>R</i> $\bar{3}$	<i>R</i> $\bar{3}$	<i>P</i> 2 <sub>1</sub> / <i>m</i>	<i>P</i> 2 <sub>1</sub> / <i>m</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	10.1397(15)	10.4900(10)	10.549(2)	9.6345(8)	9.8155(6)	9.6854(10)
<i>b</i> (Å)	12.3419(17)			23.6733(14)	24.3841(17)	14.3100(15)
<i>c</i> (Å)	10.1276(14)			10.5620(8)	10.4703(6)	18.142(2)
$\alpha$ (°)	103.386(13)	96.91(2)	99.460(19)			73.145(13)
$\beta$ (°)	98.303(12)			110.749(9)	113.555(6)	82.047(13)
$\gamma$ (°)	98.248(13)					83.210(12)
<i>V</i> (Å <sup>3</sup> )	1199.3(3)	1126.9(2)	1119.9(4)	2252.7(3)	2297.2(3)	2375.2(5)
<i>Z</i>	1	1	1	2	2	2
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	2.869	3.044	3.117	2.969	2.928	2.928
$\mu$ (Mo–K $\alpha$ ) (mm <sup>-1</sup> )	15.930	16.950	17.328	16.952	16.630	16.091
Data collection						
$\theta_{\min}$ – $\theta_{\max}$ (°)	1.7–27.0	2.0–24.2	2.0–27.0	1.6–26.0	1.6–26.0	1.6–26.0
Collected data	5501	7119	5131	17 616	18 106	17 065
Unique data	5198	1161	1636	4458	4552	8644
<i>R</i> <sub>int</sub>	0.023	0.075	0.041	0.081	0.056	0.051
Reflections observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	3825	948	1245	3514	3728	5047
Refinement						
<i>N</i> <sub>ref</sub> – <i>N</i> <sub>par</sub>	5198–5238	1161–1179	1636–1688	4458	4552–4272	8644–8483
<i>R</i>	0.0491	0.0221	0.0556	0.0477	0.0376	0.0461
<i>R</i> <sub>w</sub>	0.1353	0.0476	0.1345	0.1169	0.0924	0.0945
<i>S</i>	1.00	0.91	1.01	1.00	0.99	1.07
Shift/error max-average	0.00–0.00	0.00–0.00	0.00–0.00	0.01–0.01	0.00–0.00	0.00–0.00
$\rho_{\min}$ – $\rho_{\max}$ (e Å <sup>-3</sup> )	–4.47–+5.62	–0.76–+0.85	–3.61–+4.34	–3.36–+4.19	–2.51–+2.35	–2.63–+3.69

vicinity of the rhenium atoms. The structures were solved by direct-methods and refined by full-matrix least-squares based on  $F^2$ , by using the program SHELX-97 [7]. All non-hydrogen atoms were refined anisotropically. Although most of the hydrogen atoms were identified on difference-Fourier maps, they were simply included for 1–4 and 6 in structure factors calculations at idealised positions and assigned to ride on the atoms to which they were bound. This proved impossible in the case of 5 because of significant disorder.

### 3. Results and discussion

#### 3.1. General structural considerations

In compounds 1–6, the geometrical characteristics of the [Re<sub>6</sub>S<sub>6</sub>Cl<sub>8</sub>]<sup>2-</sup> cluster (Fig. 1) are similar and typical

of this di-anion cluster form [1]. The mean distances Re–Re<sub>cis</sub> and Re–Re<sub>trans</sub> are 2.60 and 3.65 Å, respectively. The inner or  $\mu_3$ -Cl<sup>-</sup> are each localised on one cluster face only (and not seen by X-ray diffraction as distributed on a uniform pattern over all eight face-capping sites) and the mean distance between rhenium and apical chlorine atoms is 2.37 Å. This value agree with those found for other structures of dianionic hexanuclear sulphidochloride rhenium clusters [1].

##### 3.1.1. [Ca(DMF)<sub>6</sub>][Re<sub>6</sub>S<sub>6</sub>Cl<sub>8</sub>] (1)

In compound 1, the asymmetric unit contains one half cluster anion and one Ca(II) located on an inversion centre and surrounded by three dimethylformamide molecules. The calcium cation is found six-coordinated by oxygen atoms of six DMF solvent molecules and the coordination geometry around the calcium centre can be described as a slightly distorted octahedron (Fig. 2), as exemplified by Ca–O bond

lengths ranging from 2.278 to 2.341 Å (mean distance  $\langle \text{Ca-O} \rangle = 2.313(32)$  Å and  $\text{O-Ca-O}_{\text{cis}}$  bond angles ranging from 85.35 to 94.65°. The distortion is likely to reflect relative steric hindrances of the ligands. The full geometrical characteristics of this co-ordination polyhedron are given in Table 2.

### 3.1.2. $[\text{Ca}(\text{THF})_6][\text{Re}_6\text{S}_6\text{Cl}_8]$ (**2**)

The asymmetric unit of compound **2** consists of one sixth of a hexanuclear cluster anion, one sixth of a  $\text{Ca}^{2+}$  cation and one THF molecule in general position. In the Ca(II) complex the metal is six coordinated by the oxygen atoms of the six THF molecules (Fig. 3). The absence of disorder on the coordinated THF molecules and the location of the alkaline earth on a

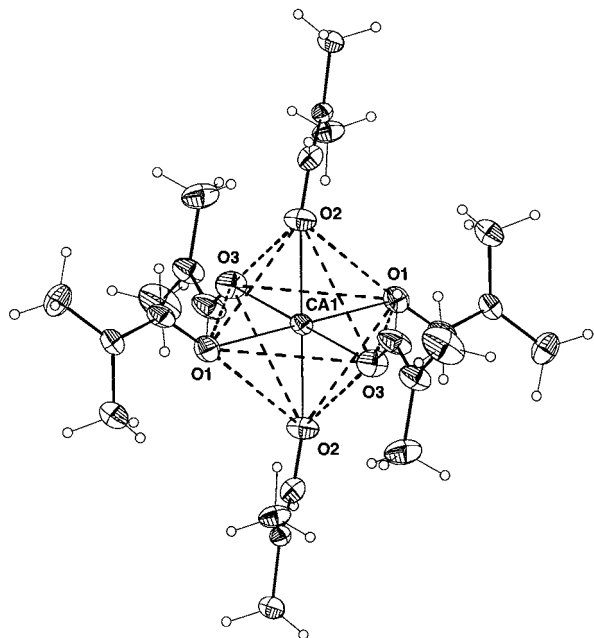


Fig. 2. The complex cation in  $[\text{Ca}(\text{DMF})_6][\text{Re}_6\text{S}_6\text{Cl}_8]$  (**1**). Thermal ellipsoids are shown at the 50% probability level.

Table 2

Selected bond distances (Å) and angles (°) for the cationic complex  $[\text{Ca}(\text{DMF})_6]^{2+}$  in (**1**)

#### Bond distances

Ca1–O1 ( $\times 2$ )	2.321(0.010)
Ca1–O2 ( $\times 2$ )	2.278(0.011)
Ca1–O3 ( $\times 2$ )	2.341(0.010)

#### Bond angles

O1–Ca1–O1 <sup>i</sup>	180.00(0.35)
O1–Ca1–O2 ( $\times 2$ )	85.35(0.42)
O1–Ca1–O2 <sup>i</sup> ( $\times 2$ )	94.65(0.42)
O1–Ca1–O3 ( $\times 2$ )	89.75(0.46)
O1–Ca1–O3 <sup>i</sup> ( $\times 2$ )	90.25(0.46)
O2–Ca1–O2 <sup>i</sup>	180.00(0.54)
O2–Ca1–O3 ( $\times 2$ )	87.34(0.43)
O2–Ca1–O3 <sup>i</sup> ( $\times 2$ )	92.66(0.43)
O3–Ca1–O3 <sup>i</sup>	180.00(0.00)

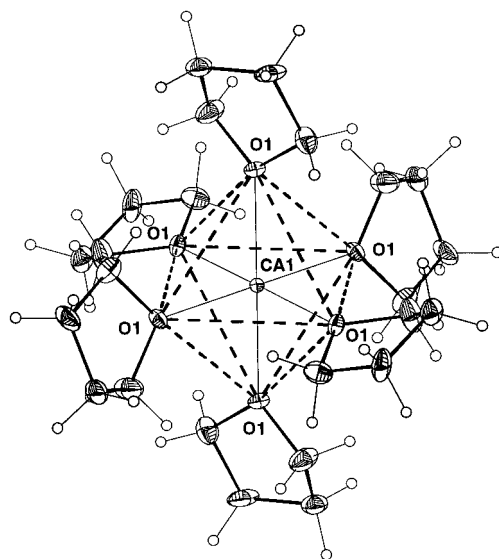


Fig. 3. The complex cation in  $[\text{Ca}(\text{THF})_6][\text{Re}_6\text{S}_6\text{Cl}_8]$  (**2**). Thermal ellipsoids are shown at the 50% probability level.

– 3 symmetry site of the trigonal space group  $R\bar{3}$  make for a quasi regular octahedron with one single Ca–O independent distance of 2.341(5) Å and two bond angles values  $\text{O-Ca-O}_{\text{cis}}$  at 90.96(18) and 89.04(17)°.

### 3.1.3. $[\text{Ca}(\text{DMSO})_6][\text{Re}_6\text{S}_6\text{Cl}_8]$ (**3**)

There is one independent, disordered ligand out of the six which constitute the co-ordination sphere of the complex cation in **3**. The flip-flop disorder (disordered oxygen and sulphur atoms and ordered methyl groups) is two-fold with equal populations (one half each). If one considers one orientation of the DMSO molecule only, the co-ordination polyhedron is a regular octahedron (Fig. 4) in accordance with the location of Ca(II) on a – 3 symmetry site of the trigonal space group  $R\bar{3}$ . The Ca–O bond lengths are 2.291(25) and 2.439(43) Å for the two half populated sites of the oxygen atom O1A and O1B, respectively.

### 3.1.4. $[\text{Ca}(\text{MeCN})_4(\text{THF})_3][\text{Re}_6\text{S}_6\text{Cl}_8]$ (**4**)

The asymmetric unit consists of one half cluster anion, one half Ca(II) located on a mirror plane of the monoclinic cell (space group  $P2_1/m$ ), two acetonitrile and three halves THF molecules. The THF ligands are disordered whereas the acetonitrile ligands are perfectly ordered (Fig. 5). All atoms of the first THF molecule (O1–C5–C6–C7–C8) seemingly lie on a mirror plane but this flat conformation is ruled out in accordance with the elongation of the thermal ellipsoids envelopes of C5 and C8 atoms which extend normal to the to the mirror suggesting a half-chair conformation of the molecule. The two others THF ligands possess the same model of disorder consisting of a folding around a C···C axis whose two carbon atoms are those directly

bounded to the oxygen atom, i.e. C9A...C9A (or C9B...C9B) and C11A...C11A (or C11B...C11B) for the second (O2–C9–C10–C10–C9) and third (O3–C11–C12–C12–C11) molecule, respectively. The co-ordination polyhedron around Ca(II) is an unusual mono-capped trigonal prism (Fig. 5) in which the nitrogen atoms of the four acetonitrile molecules are distributed over the vertices of one rectangular face, two oxygen atoms of two THF molecules forming the rest of the prism and the last THF molecule capping the rectangular face. The mean distances Ca–N and Ca–O are 2.499(6) and 2.380(40) Å, respectively. The Ca–N bonds are in accordance with the values found in the

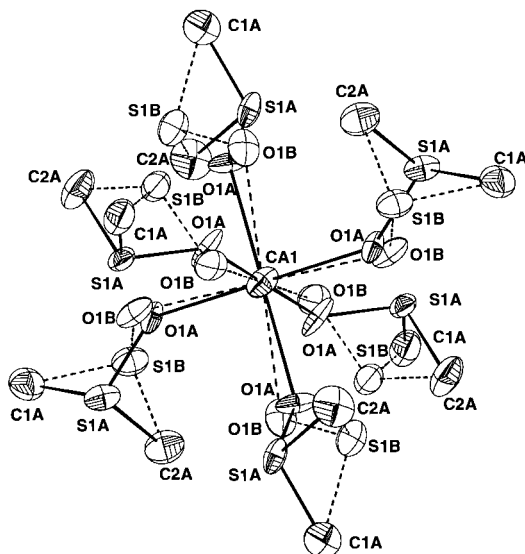


Fig. 4. The two-fold disorder of dimethylsulfoxide ligands  $[\text{Ca}(\text{DMSO})_6][\text{Re}_6\text{S}_6\text{Cl}_8]$  (**3**), leads to two orientations of the co-ordination octahedra (bold and dashed lines). The hydrogen atoms of the methyl groups have been omitted for clarity. The thermal ellipsoids are shown at the 50% probability level.

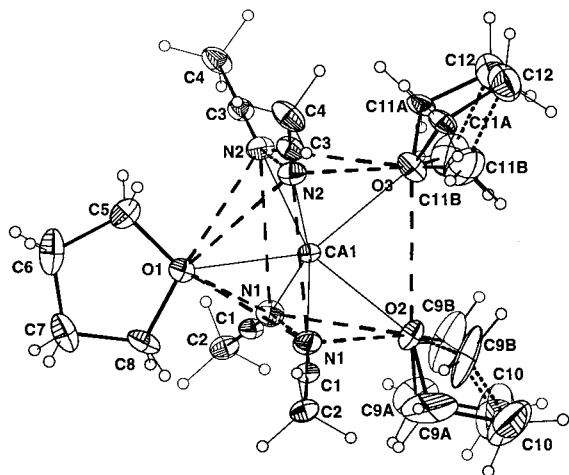


Fig. 5. The seven-monocapped trigonal prism coordination of Ca(II) in  $[\text{Ca}(\text{MeCN})_4(\text{THF})_3][\text{Re}_6\text{S}_6\text{Cl}_8]$  (**4**), with two disordered THF ligands. The thermal ellipsoids are shown at the 50% probability level.

Table 3

Selected bond distances (Å) and bond angles (°) for the complex cations  $[\text{Ca}(\text{MeCN})_4(\text{THF})_3]^{2+}$  in (**4**) and  $[\text{Ca}(\text{MeCN})_4(\text{Diox})_3]^{2+}$  in (**5**)

4		5	
<i>Bond distances</i>			
Ca1–O1	2.335(15)	Ca1–O1	2.383(10)
Ca1–O2	2.398(15)	Ca1–O3	2.469(11)
Ca1–O3	2.406(18)	Ca1–O5	2.439(11)
Ca1–N1 (×2)	2.495(13)	Ca1–N1 (×2)	2.504(12)
Ca1–N2 (×2)	2.503(14)	Ca1–N2 (×2)	2.512(13)
<i>Bond angles</i>			
O1 <sup>III</sup> –Ca1–O2	134.16(63)	O1 <sup>III</sup> –Ca1–O3	147.76(70)
O1 <sup>III</sup> –Ca1–N1 <sup>IV</sup>	77.85(39)	O1 <sup>III</sup> –Ca1–N1	77.85(39)
O1 <sup>III</sup> –Ca1–N2 <sup>VI</sup>	80.61(43)	O1 <sup>III</sup> –Ca1–N2 <sup>VI</sup>	80.61(43)
O2–Ca1–O3	78.08(72)	O2–Ca1–N1 <sup>IV</sup>	76.90(40)
O2–Ca1–N1	77.85(39)	O2–Ca1–N2 <sup>VI</sup>	127.52(38)
O2–Ca1–N2 <sup>VI</sup>	127.52(39)	O3–Ca1–N1 <sup>IV</sup>	117.10(40)
O3–Ca1–N1	117.10(40)	O3–Ca1–N2 <sup>VI</sup>	76.68(52)
O3–Ca1–N2 <sup>VI</sup>	75.02(48)	N1 <sup>IV</sup> –Ca1–N1	111.74(73)
N1 <sup>IV</sup> –Ca1–N2 <sup>VI</sup>	155.25(46)	N1 <sup>IV</sup> –Ca1–N2 <sup>VI</sup>	75.02(48)
N1–Ca1–N2 <sup>VI</sup>	75.02(48)	N1–Ca1–N2 <sup>VI</sup>	155.25(46)
N2 <sup>VI</sup> –Ca1–N2 <sup>VI</sup>	89.61(65)		

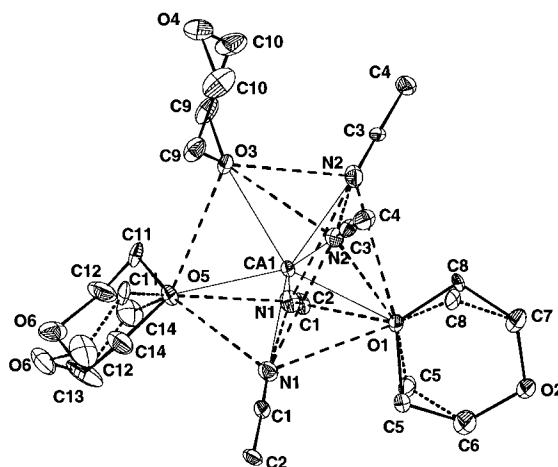


Fig. 6. The seven-monocapped trigonal prism coordination of Ca(II) in  $[\text{Ca}(\text{MeCN})_4(\text{dioxane})_3][\text{Re}_6\text{S}_6\text{Cl}_8]$  (**5**), with two dioxane ligands. The thermal ellipsoids are shown at the 50% probability level.

literature, for example in calcium carbazole derivatives [8]. Note that the capping oxygen O1 is closer to the Ca(II) ion (2.335 Å) than the two oxygen atoms O2 and O3 forming one edge of the trigonal prism (2.398 and 2.406 Å) (Table 3). This is probably due to steric factors.

### 3.1.5. $[\text{Ca}(\text{MeCN})_4(\text{dioxane})_3][\text{Re}_6\text{S}_6\text{Cl}_8]$ (**5**)

The general coordination features of this complex salt are similar to those of the previous compound **4**. Substitution of tetrahydrofuran by dioxane ligands preserves the monoclinic symmetry (space group  $P2_1/m$ ). The cationic complex  $[\text{Ca}(\text{MeCN})_4(\text{dioxane})_3]^{2+}$  in **5** is also partially affected by disorder (Fig. 6). The acetoni-

trile ligands are ordered and two among the three dioxane molecules are affected by disorder.

### 3.1.6. $[Ca(MeCN)_3(OH_2)_2(dioxane)_2][Re_6S_6Cl_8] \cdot (dioxane)(MeCN)$ (**6**)

In this heteroleptic complex, two water molecules have entered the Ca(II) co-ordination sphere. The water molecules are likely to have been introduced by a defective dinitrogen flow line used in the process of crystallisation in the acetonitrile–dioxane solution. Three nitrogen atoms of acetonitrile ligands and two oxygen atoms of water molecules form the pentagonal plane of the Ca(II) co-ordination sphere. The additional two co-ordination sites are occupied by two oxygen atoms of two dioxane molecules. Thus, the latter are far from each other at the opposite apexes of the pyramids. All seven molecules co-ordinated to Ca(II) are ordered in **6** (Fig. 7) and form a pentagonal bipyramid. In addition, two, one half dioxane molecules are identified and found to serve as infinite pseudo-linear bridges (Fig. 6) between the former Ca(II) complexes

via  $O_{diox} \cdots H-OH$  hydrogen bonds with both  $OH_2$  water molecules ( $O7 \cdots O5$  2.675(29) and  $O8 \cdots O6$  2.635(35) Å). Thus, a 1D co-ordination polymer develops approximately along the [010] direction (Fig. 8).

### 3.2. Rare Ca(II)–N-donor ligand complexes and a unique hexacoordinated Ca(II)–ether ligand complex

The coordination chemistry of Ca(II) and Mg(II) [9] is essentially one of O-bonded ligands with coordination number ranging from 5 to 9 [10]. Aquo complexes are omnipresent and ligands such as alcohol, ether, phosphates carbonyls, mono- and bi-dentate carboxylates are also largely represented [10]. Thus, the complex salts **4–6** stand out as rare examples of Ca(II)–N-donor ligand complexes. In addition,  $[Ca(THF)_6][Re_6S_6Cl_8]$  (**2**) is perhaps unique as it may represent the first example of an hexacoordinated Ca(II)–ether ligand complex in a class of alkaline earth–cation complexes where octacoordination is prominent and only a few complexes with coordination numbers 5, 7 and 9 have been reported [10].

## 4. Supplementary material

Crystallographic data (excluding structural factors) have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 166937 and 166942 for compounds **1** and **6**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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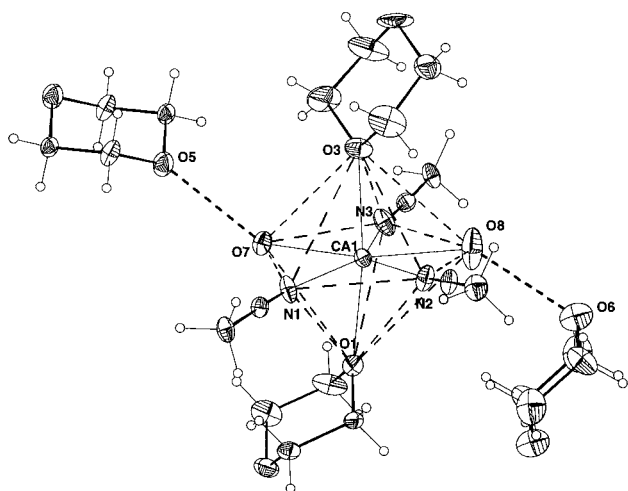


Fig. 7. The seven-pentagonal bipyramid co-ordination polyhedra of Ca(II) in  $[Ca(MeCN)_3(OH_2)_2(dioxane)_2][Re_6S_6Cl_8] \cdot (dioxane)(MeCN)$  (**6**). The thermal ellipsoids are shown at the 50% probability level.

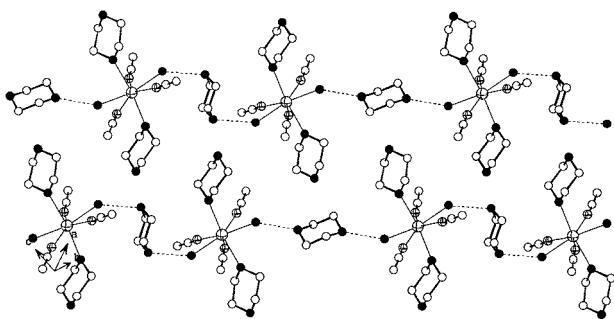


Fig. 8. The polymeric chain in  $[Ca(MeCN)_3(OH_2)_2(dioxane)_2][Re_6S_6Cl_8] \cdot (dioxane)(MeCN)$  (**6**).