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Syntheses and characterization of cubane-type clusters, $[Mo_4S_4(edta)_2]^{n-}$ ($n=2$–4), $[Mo_4S_4(H_2O)_{12}]^{n+}$ ($n=4$–6) and $[Mo_4S_4(NH_3)_{12}]^{4+}$. X-ray structures of $Na_2[Mo_4S_4(edta)_2]\cdot 6H_2O$, $Ca_{1.5}[Mo_4S_4(edta)_2]\cdot 13H_2O$, $Mg_2[Mo_4S_4(edta)_2]\cdot 20H_2O$, $[Mo_4S_4(H_2O)_{12}](CH_3C_6H_4SO_3)_5\cdot 14H_2O$ and $[Mo_4S_4(NH_3)_{12}]Cl_4\cdot 7H_2O$

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Abstract

Sulfur-bridged cubane-type molybdenum clusters, $[Mo_4S_4(edta)_2]^{3-}$ (**1B**), $[Mo_4S_4(H_2O)_{12}]^{5+}$ (**2B**) and $[Mo_4S_4(NH_3)_{12}]^{4+}$ (**4C**), are obtained from $[Mo_2O_2S_2(edta)]^{2-}$ and $NaBH_4$, from $Mo_2O_2S_2^{2+}$(aq) and $NaBH_4$, and from **2B** and ammonia–water, respectively. The reduced and oxidized forms of **1B**, $[Mo_4S_4(edta)_2]^{n-}$ ($n=4$ (**1C**) and 2 (**1A**)), and those of **2B**, $[Mo_4S_4(H_2O)_{12}]^{n+}$ ($n=4$ (**2C**) and 6 (**2A**)), are isolated and characterized. The clusters **1B** and **2B** show two quasi-reversible, one-electron waves. The crystallographic results obtained are as follows: $Na_2[Mo_4S_4(edta)_2]\cdot 6H_2O$ (**Na1A**), monoclinic, $P2_1/n$, $a=25.171(4)$, $b=11.231(3)$, $c=13.417(3)$ Å, $\beta=98.28(1)°$, $V=3753.4(15)$ Å^3, $Z=4$, $R=4.41\%$, $Ca_{1.5}[Mo_4S_4(edta)_2]\cdot 13H_2O$ (**Ca1B**), monoclinic, $P2_1/c$, $a=15.726(8)$, $b=12.447(4)$, $c=28.10(2)$ Å, $\beta=123.16(3)°$, $V=4604.6(43)$ Å^3, $Z=4$, $R=5.53\%$; $Mg_2[Mo_4S_4(edta)_2]\cdot 20H_2O$ (**Mg1C**), monoclinic, $P2_1/m$, $a=14.358(6)$, $b=13.680(6)$, $c=12.990(5)$ Å, $\beta=96.56(2)°$, $V=2534.8(19)$ Å^3, $Z=2$, $R=4.79\%$; $[Mo_4S_4(H_2O)_{12}](CH_3C_6H_4SO_3)_5\cdot 14H_2O$ (**2Bpts**) (Hpts = paratoluenesulfonic acid), triclinic, $P\bar{1}$, $a=16.352(4)$, $b=16.715(3)$, $c=13.109(4)$ Å, $\alpha=91.05(2)$, $\beta=98.73(2)$, $\gamma=89.37(2)°$, $V=3540.8(16)$ Å^3, $Z=2$, $R=4.06\%$; $[Mo_4S_4(NH_3)_{12}]Cl_4\cdot 7H_2O$ (**4C′**), triclinic $P\bar{1}$, $a=10.529(3)$, $b=17.470(4)$, $c=9.967(3)$ Å, $\alpha=96.74(2)$, $\beta=116.26(2)$, $\gamma=82.91(2)°$, $V=1627.4(8)$ Å^3, $Z=2$, $R=4.50\%$. The electronic structures of **2A**, **2B** and **2C** were investigated using the spin-polarized discrete variational (DV)-Xα method. The binding energies (eV) of Mo3$d_{3/2}$ and Mo3$d_{5/2}$ obtained by XPS measurements are: **Na1A**, 232.7, 229.7; $Na_3[Mo_4S_4(edta)_2]\cdot 10H_2O$ (**Na1B**), 232.1, 229.0; **Mg1C**, 232.1, 229.0; **2Bpts**, 233.0, 230.0; **4C′**, 232.1, 228.9.

Introduction

We have made preliminary reports on the syntheses and properties of cubane-type clusters, $[Mo_4S_4(edta)_2]^{n-}$ ($n=2$ (**1A**), 3 (**1B**), 4 (**1C**); edta = ethylenediaminetetraacetate(4−)) [1, 2], $[Mo_4S_4(H_2O)_{12}]^{n+}$ ($n=4$ (**2C**), 5 (**2B**), 6 (**2A**)) [3, 4], $[Mo_4S_4(NCS)_{12}]^{6-}$ (**3A**) [2] and $[Mo_4S_4(NH_3)_{12}]^{4+}$ (**4C**) [5]**. X-ray structures of some of the clusters have also been determined. Sykes and co-workers [6] also reported on the syntheses and properties (including kinetics) of **1A**, **1B**, **1C**, **2A**, **2B**, **2C** and **3A**. A report on the aqua and thiothianato clusters with Mo_4S_4 cores by Cotton *et al.* is also well known [7]. Many reports on discrete clusters with cubane-type Mo_4S_4 cores have appeared [8], where the oxidation state of molybdenum varied from 5 to 3, that is, the total oxidation number of four molybdenum atoms (Mo_4) was between 20 and 12. The formation of discrete cubane-type clusters, $[Mo_4(\mu_3\text{-}S)_4O_4(dtc)_4]^{1-/2-}$, was proposed by Sawyer and co-workers in 1975 through the result of electrochemistry [9], and the first discrete compound with an Mo_4S_4 core, $[Mo_4S_4(Ntol)_4(Et_2dtp)_4]$, was isolated in 1980 by Edelblut and Wentworth [10]. The Mo_4S_4 core has the possibility of being an electron reservoir, however,

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**The letters A, B and C in abbreviations indicate that the total numbers of 4d-electrons in Mo_4S are 10, 11 and 12, respectively.

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$[Mo_4S_4(\eta\text{-}C_5H_4Pr^i)_4]^{n+}$ ($n=0$ (**5C**), 1 (**5B**) and 2 (**5A**)) is the only case isolated so far to form a set of consecutive oxidation numbers of molybdenum [11, 2j]. It is very interesting that the cyclic voltammograms of the clusters **1B** and **2B** show two quasi-reversible, one-electron waves. We describe here in detail the syntheses, X-ray structure determinations and properties of the cubane-type Mo_4S_4 clusters with edta, H_2O or NH_3 ligands.

Experimental

Syntheses

$Na_3[Mo_4S_4(edta)_2]\cdot 10H_2O$ (Na1B)

The μ-sulfido Mo(V) dimer $Na_2[Mo_2S_2(edta)_2]\cdot 2H_2O$ [12] (2.0 g, 0.003 mol) was dissolved in water (200 ml) in a Erlenmeyer flask, and $NaBH_4$ (1 g) was added with stirring. Then, 1 M HCl (6 ml) was added producing a brown solution, which was allowed to stand overnight. The solution was then subjected to air oxidation in a water bath over 90 °C; the color of the solution gradually turned to dark green in a couple of hours. After an additional one hour of air oxidation, the solution was cooled to room temperature and filtered. The purification of the green solution was effected by Sephadex G-10 column chromatography by elution with water. The green band was collected and the volume of the solution was reduced to *c.* 10 ml, then acetone (*c.* 2 ml) was added to the concentrated solution. After standing a few days at room temperature it gave dark green crystals, which were collected by filtration and air-dried; yield 0.30 g (15%). *Anal.* Found: Na, 5.29; N, 4.19; C, 17.92; H, 2.97. Calc.: Na, 5.16; N, 4.19; C, 17.96; H, 3.31%.

$Ca_{1.5}[Mo_4S_4(edta)_2]\cdot 13H_2O$ (Ca1B)

The corresponding sodium salt **Na1B** was dissolved in water and, from the solution, recrystallized in the form of calcium salt by the addition of solid $CaCl_2$. *Anal.* Found: N, 3.93; C, 17.02; H, 3.20. Calc.: N, 4.05; C, 17.34; H, 3.65%.

$Na_2[Mo_4S_4(edta)_2]\cdot nH_2O$ ($n=5$ and 6 (Na1A))

A few drops of bromine water were added to the green aqueous solution (10 ml) containing **Na1B** (0.11 g). Addition of sodium chloride (0.1 g) to the resultant red solution and allowing the solution to stand for a few days in a refrigerator gave dark red needle-like crystals, which were filtered off. Yield 0.05 g (50%). *Anal.* Found: N, 4.55; C, 19.81; H, 2.60. Calc. for penta hydrate: N, 4.58; C, 19.62; H, 2.80%. The filtrate was allowed to stand for several days at room temperature to give hexagonal red crystals. *Anal.* Found: N, 4.47; C, 19.09; H, 2.50. Calc. for hexa hydrate: N, 4.51; C, 19.33; H, 2.92%.

$Ca[Mo_4S_4(edta)_2]\cdot 8H_2O$ (Ca1A)

Na1B (0.10 g) was dissolved in water (*c.* 10 ml) and the solution was poured on to a cation exchanger Dowex 50W-X8 (H^+ form). To the eluate, a few drops of bromine water were added. Addition of a small amount of solid $CaCl_2$ and allowing the solution to stand at room temperature gave dark red crystals. *Anal.* Found: N, 4.43; C, 18.92; H, 3.28. Calc.: N, 4.40; C, 18.88; H, 3.17%.

$Mg[Mo_4S_4(edta)_2]\cdot 12H_2O$ (Mg1A)

The method used was similar to the preparation of **Ca1A**, but $MgCl_2$ was added instead of $CaCl_2$. *Anal.* Found: N, 4.20; C, 17.87; H, 2.97. Calc.: N, 4.21; C, 18.07; H, 3.64%.

$(NH_4)_2[Mo_4S_4(edta)_2]\cdot 4H_2O$ (NH₄1A)

The method used was similar to that for **Ca1A**, but NH_4Cl was added instead of $CaCl_2$. *Anal.* Found: N, 6.89; C, 20.02; H, 3.39. Calc.: N, 7.02; C, 20.80; H, 3.37%.

$Na_4[Mo_4S_4(edta)_2]\cdot 19H_2O$ (Na1C)

Under a dinitrogen atmosphere, **Na1B** (0.10 g) in water (5 ml) was transferred into a flask containing $NaBH_4$ (0.1 g) to give an orange solution. Ethanol was added to the solution until the solution became turbid. Allowing the solution to stand in a refrigerator overnight it gave orange crystals, which were filtered off. Yield 0.07 g (64%). *Anal.* Found: Na, 6.28; N, 3.63; C, 15.77; H, 2.92. Calc.: Na, 6.04; N, 3.68; C, 15.77; H, 4.10%.

$Mg_2[Mo_4S_4(edta)_2]\cdot 20H_2O$ (Mg1C)

Under a dinitrogen atmosphere, **Na1B** (0.10 g) in water (5 ml) was transferred into a flask containing $NaBH_4$ (0.1 g). Addition of $MgCl_2$ (0.05 g) gave orange crystals, which were filtered off. *Anal.* Found: N, 3.72; C, 16.02; H, 3.72. Calc.: N, 3.74; C, 16.04; H, 4.31%.

$Mn_2[Mo_4S_4(edta)_2]\cdot 22H_2O$ (Mn1C)

The procedure used was similar to that for the preparation of **Mg1C**, but $MnCl_2$ was used instead of $MgCl_2$. *Anal.* Found: N, 3.51; C, 14.61; H, 3.48; Calc.: N, 3.51; C, 15.04; H, 4.30%.

$[Mo_4S_4(H_2O)_{12}]^{5+}$ (2B) and $[Mo_4S_4(H_2O)_{12}](CH_3C_6H_4SO_3)_5\cdot 14H_2O$ (2Bpts)

Two methods were applied.

Method 1. According to the procedure described in the literature [15], the compound was prepared from the Mo(V) aqua dimer $Mo_2O_2S_2{}^{2+}$(aq) by $NaBH_4$ reduction. *Anal.* Found: C, 23.08; H, 4.60. Calc.: C, 22.89; H, 4.77%.

Method 2. **Na1B** (0.2 g) was dissolved in concentrated HCl (10 ml) and allowed to stand for a couple of days. After dilution the solution was absorbed on a Dowex 50W-X2 cation exchanger, which was washed with 1 M HCl. A green eluent was obtained by the use of 2 M HCl [2].

$[Mo_4S_4(H_2O)_{12}]^{6+}$ (2A)

Controlled potential electrolysis (one equivalent) of **2B** in 2 M HCl at +0.60 V (versus SCE, Pt electrode) gave the oxidized form.

$[Mo_4S_4(H_2O)_{12}]^{4+}$ (2C)

Controlled potential electrolysis of **2B** in 2 M Hpts at −0.12 V (versus SCE, Hg pool) gave the reduced form [2].

$(pyH)_6[Mo_4S_4(NCS)_{12}]\cdot 4H_2O$ (3A′)

Addition of KNCS (1.0 g) to 2 M HCl solution of green **2B** (5.7 mM, 18 ml; $NCS^-/Mo = c.$ 10) gave a brown solution, which turned to purple on standing overnight in the air. Addition of a drop of pyridine to the solution gave purple plate-like crystals. *Anal.* Found: N, 14.35; C, 28.76; H, 2.07. Calc.: N, 14.31; C, 28.63; H, 2.51%.

$[Mo_4S_4(NH_3)_{12}]Cl_4\cdot 7H_2O$ (4C′)

Concentrated ammonia water (20 ml) was added with stirring to the aqua ion **2B** (0.05 M, 20 ml) in 2 M HCl which had been cooled with ice water under dinitrogen atmosphere. The solution was filtered and the filtrate was allowed to stand for a few days at room temperature. Orange crystals were obtained by filtration; yield 38%. *Anal.* Found: N, 17.39; H, 4.75. Calc.: N, 17.07; H, 5.11% [5].

*Structural determinations of $Na_2[Mo_4S_4(edta)_2]\cdot 6H_2O$ (**Na1A**), $Ca_{1.5}[Mo_4S_4(edta)_2]\cdot 13H_2O$ (**Ca1B**), $Mg_2[Mo_4S_4(edta)_2]\cdot 20H_2O$ (**Mg1C**), $[Mo_4S_4(H_2O)_{12}](CH_3C_6H_4SO_3)_5\cdot 14H_2O$ (**2Bpts**) and $[Mo_4S_4(NH_3)_{12}]Cl_4\cdot 7H_2O$ (**4C′**)*

A dark red crystal (dimensions 0.15×0.35×0.35 mm) of **Na1A**, a green crystal (dimensions 0.15×0.3×0.3 mm) of **Ca1B**, an orange crystal (dimensions 0.2×0.3×0.3 mm) of **Mg1C**, a green crystal (dimensions 0.42×0.36×0.26 mm) of **2Bpts** and an orange crystal (dimensions 0.40×0.30×0.30 mm) of **4C′** were mounted in glass capillaries. The crystallographic data are given in Table 1. Cell constants and orientation matrixes for the crystals were obtained from least-squares refinement, by using setting angles of 20 reflections for **Na1A**, **Ca1B**, and **Mg1C** in the range $20 < 2\theta < 30°$ measured on a Phillips 1100 diffractometer by use of Mo Kα radiation ($\lambda = 0.71073$ Å). Those for **2Bpts** and **4C′** were obtained similarly by using setting angles of 25 reflections measured on a Rigaku AFC-6A diffractometer. The intensities of standard reflections monitored (after every 100 reflections for **Na1A**, **Ca1B** and **Mg1C**; after every 150 reflections for **2Bpts** and **4C′**) did not show any appreciable decay. Intensities were corrected for polarization and Lorentz factors but not for absorption. All the structures were solved by MULTAN

TABLE 1. Crystallographic data for $Na_2[Mo_4S_4(edta)_2]\cdot 6H_2O$ (**Na1A**), $Ca_{1.5}[Mo_4S_4(edta)_2]\cdot 13H_2O$ (**Ca1B**), $Mg_2[Mo_4S_4(edta)_2]\cdot 20H_2O$ (**Mg1C**), $[Mo_4S_4(H_2O)_{12}](CH_3C_6H_4SO_3)_5\cdot 14H_2O$ (**2Bpts**) and $[Mo_4S_4(NH_3)_{12}]Cl_4\cdot 7H_2O$ (**4C′**)

	Na1A	**Ca1B**	**Mg1C**	**2Bpts**	**4C′**
Formula	$Mo_4S_4O_{22}N_4C_{20}H_{36}Na_2$	$Mo_4S_4O_{29}C_{20}N_4H_{50}Ca_{1.5}$	$Mo_4S_4O_{36}N_4C_{20}H_{64}Mg_2$	$Mo_4S_9O_{41}C_{35}H_{87}$	$Mo_4Cl_4S_4O_7N_{12}H_{50}$
Molecular weight	1242.52	1382.77	1497.37	1836.41	984.31
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	triclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/m$	$P\bar{1}$	$P\bar{1}$
a (Å)	25.171(4)	15.726(8)	14.358(6)	16.352(4)	10.529(3)
b (Å)	11.231(3)	12.447(4)	13.680(6)	16.715(3)	17.470(4)
c (Å)	13.417(3)	28.10(2)	12.990(5)	13.109(4)	9.967(3)
α (°)				91.05(2)	96.74(2)
β (°)	98.28(1)	123.16(3)	96.56(2)	98.73(2)	116.26(2)
γ (°)				89.37(2)	82.91(2)
V (Å^3)	3753.4(15)	4604.6(43)	2534.8(19)	3540.8(16)	1627.4(8)
Z	4	4	2	2	2
D_{calc} (g/cm^3)	2.199	1.995	1.962	1.722	2.009
D_{obs} (g/cm^3)	2.19	2.00	1.98	1.71	
Radiation (Mo Kα, Å)	0.71073	0.71073	0.71073	0.71073	0.71073
R (%)	4.41	5.53	4.79	4.06	4.50
R_w (%)	5.74	7.76	7.61	6.60	7.65

and refined by the block-diagonal least-squares method. Computations were performed on a FACOM M380 at Okayama University of Science and on a FACOM 230-60 computer at Osaka City University using the programs in the UNICS system [13] and the program ORTEP [14]. No attempt was made to locate hydrogen atoms for any of the compounds. The atomic coordinates and thermal parameters for **Na1A**, **Ca1B**, **Mg1C**, **2Bpts** and **4C′** are listed in Tables 2–6, respectively.

Other physical measurements

UV, visible and near-IR spectra were recorded on a Hitachi 330, 320 or U2000 spectrophotometer. XPS measurements were carried out on a Shimadzu ESCA-850 electron spectrometer which was installed at the Analytical Center of Okayama University of Science: Mg Kα (1253.6 eV) radiation was used taking carbon binding energy (1s$_{1/2}$, 285.0 eV) as standard. Cyclic voltammograms were recorded on a Yanaco P1100 polarographic analyzer or a BAS 100A electrochemical analyzer. The working electrode for cyclic voltammetry was a glassy carbon (GC), platinum or mercury (Hg) electrode. The reference electrode used was a saturated calomel electrode (SCE) or an Ag/AgCl (3 M NaCl) electrode.

Results and discussion

Syntheses, properties and electrochemistry of $[Mo_4S_4(edta)_2]^{n-}$ *(n=2 (1A), 3 (1B), 4 (1C)),* $[Mo_4S_4(H_2O)_{12}]^{n+}$ *(n=4 (2C), 5 (2B), 6 (2A)),* $[Mo_4S_4(NCS)_{12}]^{6-}$ *(3A) and* $[Mo_4S_4(NH_3)_{12}]^{4+}$ *(4C)*

Reduction of the molybdenum(V) dimer $[Mo_2(O_t)_2(\mu\text{-}S)_2(edta)]^{2-}$ with $NaBH_4$ followed by air oxidation gave a water-soluble green compound $Na_3[Mo_4S_4(edta)_2]\cdot 10H_2O$ (**Na1B**), no air-free techniques being required. The calcium salt of **1B** was obtained from the corresponding sodium salt. The cyclic voltammogram (Fig. 1(a)) of the calcium salt indicated the existence of both the one-electron oxidant, $[Mo_4S_4(edta)_2]^{2-}$ (**1A**), and the one-electron reductant, $[Mo_4S_4(edta)_2]^{4-}$ (**1C**) [1, 2]. Then, it was attempted to isolate the oxidant and the reductant, and they could both be obtained electrolytically and chemically. Controlled potential electrolyses of **1B** gave the oxidized form **1A** and the reduced form **1C**; one electron per four molybdenum was transferred for each case. Chemically the oxidized form and the reduced one were obtained more easily. The oxidized form $Na_2[Mo_4S_4(edta)_2]\cdot 5H_2O$ was prepared by the oxidation of **Na1B** with bromine–water. The corresponding hexa hydrate **Na1A** was synthesized from a more diluted solution of **Na1B**, similar to the synthesis of the penta hydrate. Sodium, magnesium and manganese salts of the reduced form were obtained

TABLE 2 Atomic coordinates and equivalent isotropic temperature factors[a] for $Na_2[Mo_4S_4(edta)_2]\cdot 6H_2O$ (**Na1A**)

Atom	x	y	z	B_{eq} (Å^2)
Mo1	0.47090(3)	0.0796(1)	0.2418(1)	1.02(2)
Mo2	0.39991(3)	−0.1218(1)	0.2198(1)	1.07(2)
Mo3	0.38101(3)	0.0867(1)	0.0999(1)	0.99(2)
Mo4	0.37211(3)	0.0947(1)	0.3107(1)	1.07(2)
S1	0.4532(1)	−0.0461(2)	0.1004(2)	1.3(1)
S2	0.4404(1)	−0.0372(2)	0.3705(2)	1.3(1)
S3	0.3195(1)	−0.0176(2)	0.1820(2)	1.3(1)
S4	0.4111(1)	0.2399(2)	0.2178(2)	1.2(1)
O11	0.5163(2)	0.1737(6)	0.3603(5)	1.7(2)
O12	0.5210(3)	0.1810(6)	0.1621(5)	1.6(2)
O13	0.5980(3)	0.1946(6)	0.4476(5)	2.3(2)
O14	0.6066(3)	0.2222(6)	0.1564(5)	2.0(2)
O21	0.3555(3)	−0.2340(6)	0.2997(5)	1.8(2)
O22	0.3771(3)	−0.2542(6)	0.1121(5)	2.2(2)
O23	0.3505(3)	−0.4136(7)	0.3640(7)	3.4(2)
O24	0.3966(3)	−0.4280(7)	0.0479(6)	3.5(2)
O31	0.4086(3)	0.1940(6)	−0.0101(5)	1.5(2)
O32	0.3474(3)	−0.0042(6)	−0.0301(5)	1.6(2)
O33	0.3943(3)	0.3545(6)	−0.1062(5)	2.2(2)
O34	0.2868(3)	−0.0008(6)	−0.1667(5)	2.2(2)
O41	0.3957(3)	0.1911(6)	0.4420(5)	1.8(2)
O42	0.3232(3)	0.0180(6)	0.4080(5)	1.7(2)
O43	0.3669(3)	0.3103(8)	0.5552(6)	3.4(2)
O44	0.2481(3)	0.0296(7)	0.4735(6)	2.9(2)
N1	0.5488(3)	−0.0263(6)	0.2689(5)	1.0(2)
N2	0.4598(3)	−0.2687(7)	0.2648(6)	1.4(2)
N3	0.3089(3)	0.2033(7)	0.0453(6)	1.3(2)
N4	0.3032(3)	0.2277(7)	0.3053(6)	1.2(2)
C11	0.5631(4)	0.1354(9)	0.3971(7)	1.6(2)
C12	0.5718(4)	0.1515(9)	0.1712(7)	1.5(2)
C13	0.5738(4)	0.0040(8)	0.3752(7)	1.5(2)
C14	0.5841(4)	0.0212(9)	0.1969(7)	1.7(3)
C15	0.5512(4)	−0.1605(8)	0.2535(7)	1.4(2)
C21	0.3766(4)	−0.3330(9)	0.3341(8)	2.1(3)
C22	0.4082(4)	−0.3449(9)	0.1066(8)	2.0(3)
C23	0.4375(4)	−0.342(1)	0.3444(9)	2.4(3)
C24	0.4618(4)	−0.3435(9)	0.1714(8)	2.0(3)
C25	0.5184(3)	−0.2420(9)	0.3138(7)	1.6(2)
C31	0.3817(4)	0.2873(8)	−0.0418(7)	1.4(2)
C32	0.3055(4)	0.0388(9)	−0.0823(7)	1.4(2)
C33	0.3320(4)	0.3157(9)	0.0062(7)	1.5(2)
C34	0.2757(4)	0.139(1)	−0.0400(7)	2.1(3)
C35	0.2672(4)	0.2364(9)	0.1148(7)	1.5(2)
C41	0.3634(4)	0.269(1)	0.4696(7)	2.0(3)
C42	0.2763(4)	0.0633(9)	0.4111(7)	1.7(3)
C43	0.3196(4)	0.3158(9)	0.3901(7)	1.9(3)
C44	0.2563(4)	0.1558(8)	0.3322(7)	1.5(2)
C45	0.2866(4)	0.3022(8)	0.2130(7)	1.3(2)
Na1	0.2968(2)	−0.2014(4)	−0.2134(3)	2.1(1)
Na2	0.3988(2)	−0.4339(4)	−0.1287(3)	3.5(1)
OW1	0.1962(3)	0.3654(7)	−0.1176(5)	2.6(2)
OW2	0.3143(3)	−0.4112(7)	−0.2481(6)	3.1(2)
OW3	0.4955(4)	−0.4042(9)	−0.0713(9)	6.5(4)
OW4	0.2115(3)	0.2480(9)	0.5455(6)	4.0(3)
OW5	0.6987(3)	−0.2892(9)	0.2677(6)	4.1(3)
OW6A[b]	0.1404(6)	0.049(1)	0.921(1)	2.2(3)
OW6B[b]	0.0511(7)	0.064(2)	0.781(1)	3.6(3)

[a] Equivalent isotropic temperature factors ($B_{eq} = \frac{4}{3}\{\Sigma\Sigma B_{ij}a_ia_j\}$)

[b] Isotropic temperature factors were used. The following occupancy factors were used for the disordered atoms OW6A, 0.5; OW6B, 0.5.

TABLE 3. Atomic coordinates and equivalent isotropic temperature factors[a] for $Ca_{1.5}[Mo_4S_4(edta)_2]\cdot 13H_2O$ (**Ca1B**)

Atom	x	y	z	B_{eq} (Å^2)
Mo1	0.3458(1)	0.7639(1)	0.29571(4)	1.48(4)
Mo2	0.2191(1)	0.8418(1)	0.18590(4)	1.37(4)
Mo3	0.1364(1)	0.7339(1)	0.24101(4)	1.41(4)
Mo4	0.2369(1)	0.6220(1)	0.19948(4)	1.46(4)
S1	0.2227(2)	0.8992(2)	0.2674(1)	1.7(1)
S2	0.3691(2)	0.7411(2)	0.2200(1)	1.8(1)
S3	0.0838(2)	0.7183(3)	0.1449(1)	1.7(1)
S4	0.2628(2)	0.6023(3)	0.2902(1)	1.9(1)
O11	0.4903(6)	0.6863(7)	0.3477(4)	2.4(3)
O12	0.3781(6)	0.7786(7)	0.3801(3)	2.4(3)
O13	0.6570(7)	0.7075(8)	0.4009(4)	4.2(4)
O14	0.4848(8)	0.8480(8)	0.4643(4)	4.0(5)
O21	0.1973(6)	0.8378(7)	0.1045(3)	2.2(3)
O22	0.1109(6)	0.9691(7)	0.1421(4)	2.3(3)
O23	0.2221(8)	0.9231(8)	0.0436(4)	4.0(5)
O24	0.0878(6)	1.1406(7)	0.1155(4)	2.6(4)
O31	0.1330(6)	0.7523(7)	0.3154(3)	2.2(4)
O32	−0.0052(6)	0.8168(7)	0.2087(4)	2.1(3)
O33	0.0723(8)	0.6981(9)	0.3652(4)	3.9(5)
O34	−0.1638(6)	0.8022(8)	0.1841(4)	3.3(4)
O41	0.3409(6)	0.4910(7)	0.2243(4)	2.5(4)
O42	0.2276(6)	0.5910(7)	0.1222(4)	2.2(4)
O43	0.3648(7)	0.3148(8)	0.2400(5)	3.9(5)
O44	0.1592(9)	0.4951(8)	0.0425(4)	4.4(5)
N1	0.4588(7)	0.9031(8)	0.3327(4)	1.7(4)
N2	0.3154(7)	0.9831(8)	0.1901(4)	1.4(4)
N3	0.0278(7)	0.6000(8)	0.2318(4)	1.5(4)
N4	0.1349(7)	0.4730(8)	0.1644(4)	1.9(4)
C11	0.5711(9)	0.743(1)	0.3681(5)	2.4(5)
C12	0.4434(9)	0.848(1)	0.4129(5)	2.3(5)
C13	0.5586(9)	0.857(1)	0.3468(6)	2.5(5)
C14	0.466(1)	0.937(1)	0.3856(5)	2.3(5)
C15	0.4395(9)	1.007(1)	0.2987(5)	2.4(5)
C21	0.2421(9)	0.908(1)	0.0935(5)	2.1(5)
C22	0.1438(9)	1.064(1)	0.1432(5)	1.8(5)
C23	0.3265(9)	0.971(1)	0.1407(5)	2.2(5)
C24	0.2573(9)	1.083(1)	0.1822(5)	2.1(5)
C25	0.4256(9)	0.999(1)	0.2410(5)	2.0(5)
C31	0.0828(9)	0.687(1)	0.3248(5)	2.2(5)
C32	−0.0833(9)	0.763(1)	0.1947(5)	2.1(5)
C33	0.040(1)	0.590(1)	0.2882(6)	2.7(6)
C34	−0.0780(9)	0.641(1)	0.1888(6)	2.4(5)
C35	0.037(1)	0.486(1)	0.2156(5)	2.2(5)
C41	0.309(1)	0.397(1)	0.2228(6)	2.4(6)
C42	0.170(1)	0.517(1)	0.0895(5)	2.4(5)
C43	0.197(1)	0.381(1)	0.2004(6)	2.6(6)
C44	0.105(1)	0.455(1)	0.1040(6)	2.8(6)
C45	0.0313(9)	0.471(1)	0.1598(5)	1.9(5)
OW1	0.0980(7)	0.4704(8)	0.4265(4)	3.6(4)
OW2	0.4843(9)	0.304(1)	0.3557(6)	5.9(6)
OW3	0.2117(8)	0.9036(9)	0.4045(5)	5.0(6)
OW4	0.3357(8)	0.0793(9)	0.4405(5)	5.3(5)
OW5	0.178(1)	0.113(1)	0.4619(6)	8.4(9)
OW6	0.3299(8)	0.1783(9)	0.3493(5)	4.9(6)
OW7	0.152(1)	0.295(2)	0.5029(6)	9.1(8)
OW8	0.3563(8)	0.665(1)	0.0866(5)	4.9(5)
OW9	0.143(2)	0.841(1)	0.4675(6)	11.(1)
OW10	0.262(1)	0.436(2)	0.4089(8)	12.(1)
OW11	0.027(1)	0.786(2)	0.0027(5)	14.(1)
Ca1	0.0943(2)	0.6535(2)	0.4526(1)	2.4(1)
Ca2[b]	0.4513(5)	0.4881(6)	0.4808(3)	4.5(1)
OW12A[b]	0.471(2)	0.319(2)	0.465(1)	6.7(6)
OW12B[b]	−0.270(2)	0.189(2)	0.022(1)	5.9(6)
OW13A[b]	0.490(2)	0.498(2)	0.410(1)	7.1(6)
OW13B[b]	0.610(3)	0.537(3)	0.461(1)	7.6(9)

[a] Equivalent isotropic temperature factors ($B_{eq} = \frac{4}{3}\{\Sigma\Sigma B_{ij}a_ia_j\}$). [b] Isotropic temperature factors were used. The following occupancy factors were used for the disordered atoms Ca2, 0.5; OW12A, 0.5; OW12B, 0.5; OW13A, 0.6; OW13B, 0.4.

TABLE 4. Atomic coordinates and equivalent isotropic temperature factors[a] for $Mg_2[Mo_4S_4(edta)_2]\cdot 20H_2O$ (**Mg1C**)

Atom	x	y	z	B_{eq} (Å^2)
Mo1[b]	0.2970(1)	0.25	−0.1250(1)	1.83(2)
Mo2[b]	0.2847(1)	0.25	−0.3393(1)	1.55(2)
Mo3	0.15180(5)	0.35111(5)	−0.24016(5)	1.64(2)
S1	0.3130(1)	0.3876(2)	−0.2312(2)	2.2(1)
S3[b]	0.1222(2)	0.25	−0.3876(2)	1.8(1)
S4[b]	0.1381(2)	0.25	−0.0960(2)	2.0(1)
O11	0.3216(5)	0.1512(5)	0.0063(4)	3.9(2)
O13	0.4294(8)	0.0759(9)	0.1119(8)	12.1(5)
O21	0.2951(4)	0.1504(4)	−0.4689(4)	2.6(2)
O23	0.3884(6)	0.0804(7)	−0.5671(7)	8.3(3)
O31	0.1389(6)	0.4755(5)	−0.1361(5)	4.8(2)
O32	0.1267(4)	0.4771(4)	−0.3453(4)	2.4(1)
O33	0.0409(9)	0.5868(7)	−0.0918(6)	11.4(5)
O34	0.0183(4)	0.5854(4)	−0.4042(4)	2.9(2)
N1[b]	0.4565(7)	0.25	−0.0882(8)	3.8(3)
N2[b]	0.4426(6)	0.25	−0.3564(7)	2.6(3)
N3	−0.0063(5)	0.3757(6)	−0.2491(6)	3.5(2)
C11	0.4074(9)	0.1291(9)	0.0352(9)	5.6(4)
C13	0.4824(8)	0.1616(9)	−0.025(1)	5.6(4)
C21	0.3747(7)	0.1277(7)	−0.4908(7)	3.5(3)
C23	0.4600(6)	0.1601(7)	−0.4177(8)	3.6(3)
C31	0.052(1)	0.5033(9)	−0.1305(8)	7.2(5)
C32	0.0409(5)	0.5037(6)	−0.3663(6)	2.0(2)
C33	−0.0262(8)	0.433(1)	−0.1613(9)	6.8(4)
C34	−0.0342(6)	0.4324(6)	−0.3450(7)	2.9(2)
Mg1[b]	0.1663(3)	0.25	0.2498(3)	2.3(1)
Mg2[b]	−0.2624(3)	0.25	0.3847(4)	3.5(1)
OW1	0.1567(4)	0.1422(4)	0.3614(4)	2.9(2)
OW2[b]	0.3119(6)	0.25	0.2790(8)	4.5(3)
OW3	0.1769(5)	0.1408(5)	0.1388(5)	4.0(2)
OW4[b]	0.0209(6)	0.25	0.2081(8)	4.3(3)
OW5	−0.2685(5)	0.0981(5)	0.3838(6)	4.8(2)
OW6[b]	−0.1203(7)	0.25	0.4280(9)	4.8(3)
OW7[b]	−0.2916(9)	0.25	0.5357(9)	5.8(4)
OW8[b]	−0.4026(9)	0.25	0.336(1)	9.4(6)
OW9[b]	−0.235(1)	0.25	0.232(1)	9.2(6)
OW10	−0.5258(5)	−0.0710(5)	−0.3057(6)	5.0(2)
OW11	−0.2860(6)	0.0855(6)	−0.3479(7)	6.7(3)
OW12	0.2940(9)	−0.0971(8)	−0.0977(9)	12.0(5)
OW13	−0.2916(9)	0.066(1)	−0.1391(9)	13.5(6)
C15	0.517(1)	0.211(1)	−0.174(1)	3.5(4)
C25	0.514(1)	0.279(1)	−0.268(1)	2.3(3)
C35A[c]	−0.068(1)	0.196(1)	−0.214(1)	2.4(3)
C35B[c]	−0.078(1)	0.282(1)	−0.288(1)	2.7(3)

[a] Equivalent isotropic temperature factors ($B_{eq} = \frac{4}{3}\{\Sigma\Sigma B_{ij}a_ia_j\}$). [b] Atoms on a mirror plane. [c] Isotropic temperature factors were used. The following occupancy factors were used for the disordered atoms: C35A, 0.5; C35B, 0.5

TABLE 5 Atomic coordinates and equivalent isotropic temperature factors[a] for $[Mo_4S_4(H_2O)_{12}](CH_3C_6H_4SO_3)_5 \cdot 14H_2O$ (**2Bpts**)

Atom	x	y	z	B_{eq} (Å^2)
Mo1	0.23902(3)	0.43636(3)	0.60553(4)	2.02(1)
Mo2	0.19554(3)	0.55953(3)	0.73847(4)	2.06(1)
Mo3	0.35389(3)	0.55500(3)	0.68463(4)	1.95(1)
Mo4	0.30687(3)	0.43828(3)	0.81365(4)	2.10(1)
S1	0.2295(1)	0.5739(1)	0.5714(1)	2.28(4)
S2	0.1663(1)	0.4229(1)	0.7453(1)	2.46(4)
S3	0.3210(1)	0.5760(1)	0.8512(1)	2.29(4)
S4	0.3789(1)	0.4169(1)	0.6729(1)	2.24(4)
O11	0.1217(3)	0.4249(3)	0.5029(4)	3.2(1)
O12	0.2808(3)	0.4197(3)	0.4551(3)	3.0(1)
O13	0.2261(3)	0.3060(3)	0.5861(4)	3.0(1)
O21	0.0662(3)	0.5755(3)	0.6661(4)	3.0(1)
O22	0.1354(3)	0.5735(3)	0.8756(4)	3.4(1)
O23	0.1780(3)	0.6886(2)	0.7418(4)	2.8(1)
O31	0.4844(3)	0.5620(3)	0.7504(4)	2.9(1)
O32	0.4148(3)	0.5663(3)	0.5464(3)	2.8(1)
O33	0.3714(3)	0.6854(2)	0.6826(4)	2.7(1)
O41	0.4284(3)	0.4238(3)	0.9100(4)	3.1(1)
O42	0.2734(3)	0.4273(3)	0.9678(4)	3.5(1)
O43	0.3118(3)	0.3090(2)	0.8317(4)	3.0(1)
SP1	0.3533(1)	0.7953(1)	0.9230(2)	3.3(1)
SP2	0.4256(1)	0.2053(1)	0.6194(2)	3.4(1)
SP3	0.1932(1)	0.7933(1)	0.5099(2)	3.3(1)
SP4	0.1129(1)	0.2097(1)	0.7930(2)	4.0(1)
SP5	0.2525(1)	0.2962(1)	0.2081(2)	3.9(1)
OP11	0.3579(4)	0.7624(3)	1.0252(4)	5.0(2)
OP12	0.4159(3)	0.7616(3)	0.8657(4)	4.1(2)
OP13	0.2708(3)	0.7883(3)	0.8646(5)	5.3(2)
OP21	0.3510(4)	0.2151(3)	0.5443(4)	5.0(2)
OP22	0.4935(4)	0.2492(3)	0.5902(6)	6.4(2)
OP23	0.4120(4)	0.2239(3)	0.7235(4)	4.8(2)
OP31	0.1296(3)	0.7543(3)	0.5576(4)	3.8(1)
OP32	0.2708(3)	0.7970(3)	0.5787(4)	4.3(2)
OP33	0.2018(4)	0.7586(3)	0.4097(4)	5.0(2)
OP41	0.1777(4)	0.2380(4)	0.8693(5)	5.8(2)
OP42	0.0377(4)	0.2505(4)	0.798(1)	13.3(5)
OP43	0.1383(7)	0.2122(4)	0.6949(6)	10.8(4)
OP51	0.2196(4)	0.3264(4)	0.1060(5)	5.8(2)
OP52	0.3412(3)	0.3085(4)	0.2338(5)	5.2(2)
OP53	0.2092(3)	0.3287(4)	0.2891(4)	5.1(2)
CP11	0.3727(4)	0.8986(4)	0.9394(5)	2.8(2)
CP12	0.3683(5)	0.9457(5)	0.8501(6)	3.7(2)
CP13	0.3806(5)	1.0274(5)	0.8603(6)	3.9(2)
CP14	0.3951(4)	1.0625(4)	0.9590(7)	3.8(2)
CP15	0.3987(5)	1.0152(4)	1.0456(6)	3.9(2)
CP16	0.3883(5)	0.9325(4)	1.0351(6)	3.5(2)
CP17	0.4053(6)	1.1536(5)	0.9719(8)	5.2(3)
CP21	0.4539(4)	0.1042(4)	0.6198(5)	2.8(2)
CP22	0.3944(5)	0.0474(4)	0.5747(6)	3.6(2)
CP23	0.4161(5)	−0.0345(5)	0.5864(6)	4.3(2)
CP24	0.4923(5)	−0.0592(5)	0.6378(6)	4.4(3)
CP25	0.5507(5)	0.0009(5)	0.6787(6)	4.2(2)
CP26	0.5303(5)	0.0818(4)	0.6685(6)	3.5(2)
CP27	0.5112(7)	−0.1473(5)	0.6515(8)	6.2(3)
CP31	0.1580(4)	0.8935(4)	0.4901(5)	2.9(2)
CP32	0.1917(5)	0.9542(4)	0.5528(6)	3.9(2)
CP33	0.1613(5)	1.0332(5)	0.5365(7)	4.5(3)
CP34	0.0982(5)	1.0488(4)	0.4557(6)	3.9(2)
CP35	0.0641(5)	0.9847(5)	0.3948(6)	4.2(2)
CP36	0.0916(5)	0.9083(5)	0.4107(6)	3.9(2)
CP37	0.0655(6)	1.1342(5)	0.4359(8)	5.6(3)
CP41	0.0974(4)	0.1084(4)	0.8198(6)	3.3(2)
CP42	0.1583(5)	0.0511(5)	0.8068(7)	4.5(3)
CP43	0.1451(5)	−0.0280(5)	0.8249(7)	4.8(3)
CP44	0.0733(5)	−0.0532(5)	0.8592(6)	4.4(2)
CP45	0.0121(5)	0.0046(5)	0.8748(7)	4.6(3)
CP46	0.0254(5)	0.0867(5)	0.8549(6)	4.2(2)
CP47	0.0600(7)	−0.1411(6)	0.8804(9)	6.5(3)
CP51	0.2361(5)	0.1926(5)	0.2012(6)	3.7(2)
CP52	0.2145(5)	0.1548(5)	0.1070(6)	4.4(2)
CP53	0.2063(5)	0.0701(5)	0.1027(7)	4.8(3)
CP54	0.2196(4)	0.0263(5)	0.1940(7)	4.5(3)
CP55	0.2383(5)	0.0656(5)	0.2875(7)	4.6(3)
CP56	0.2481(5)	0.1478(6)	0.2933(6)	4.7(3)
CP57	0.2120(6)	−0.0652(5)	0.1882(9)	6.5(4)
OW1	0.4494(3)	0.3424(3)	0.0959(4)	3.4(1)
OW2	0.0070(3)	0.3229(3)	0.5592(4)	3.9(1)
OW3	0.4314(3)	0.3598(3)	0.4267(4)	3.6(1)
OW4	0.7361(4)	0.4607(4)	0.8925(5)	5.6(2)
OW5	0.5367(4)	0.3233(4)	0.8378(5)	5.8(2)
OW6	0.3536(3)	0.6724(3)	0.4024(4)	4.8(2)
OW7	0.5982(4)	0.4447(4)	0.7399(6)	8.2(3)
OW8	−0.1276(5)	0.2794(6)	0.7955(6)	9.8(3)
OW9	0.1966(4)	0.6817(3)	1.0308(5)	5.6(2)
OW10	0.0532(3)	0.5356(3)	0.3730(4)	4.1(2)
OW11	0.0303(4)	0.3226(4)	0.2509(7)	8.8(3)
OW12	0.0246(6)	0.4729(6)	0.9146(8)	12.5(4)
OW13	0.0500(6)	0.3267(6)	0.022(1)	13.7(5)
OW14	0.1323(7)	0.5027(7)	0.2080(9)	14.4(5)

[a] Equivalent isotropic temperature factors ($B_{eq} = \frac{4}{3}\{\Sigma\Sigma B_{ij}a_ia_j\}$).

by the reduction of **Na1B** with $NaBH_4$ under a dinitrogen atmosphere. Electronic spectra of **1A**, **1B** and **1C** are shown in Fig. 2(a).

Four methods have been reported for the synthesis of **2B**. Method 1: reduction of $[Mo_2O_2S_2(cys)_2]^{2-}$ or $Mo_2O_2S_2^{2+}$(aq) in diluted HCl with $NaBH_4$ [4, 5, 15]. Method 2: aquation of **1B** in concentrated HCl [2]. Method 3: electrolytic reduction of $[Mo_2O_2S_2(cys)_2]^{2-}$ in 2 M HCl [6a]. Method 4: refluxing a mixture of $Mo(CO)_6$ and Na_2S in acetic anhydride [7]. The aqua ion **2B** was crystallized as $[Mo_4S_4(H_2O)_{12}](pts)_5 \cdot 14H_2O$ (**2Bpts**) and the X-ray structure analysis confirmed the cubane-type Mo_4S_4 core [3].

The cyclic voltammogram of **2B** in 2 M Hpts (Fig. 1(b)) showed two quasi-reversible, one-electron waves ($E_{pc,1} = 0.621$, $E_{pa,1} = 0.690$; $E_{pc,2} = -0.045$, $E_{pa,2} = 0.012$ V) indicating the existence of the oxidized form, $[Mo_4S_4(H_2O)_{12}]^{6+}$ (**2A**), and the reduced form, $[Mo_4S_4(H_2O)_{12}]^{4+}$ (**2C**), through comparison with the cyclic voltammogram of **1B** [2, 6a]. E_ps are shifted toward the positive as compared to the corresponding ones of **1B** [1, 2].

TABLE 6 Atomic coordinates and equivalent isotropic temperature factors[a] for $[Mo_4S_4(NH_3)_{12}]Cl_4\cdot 7H_2O$ (**4C′**)

Atom	x	y	z	B_{eq} (Å^2)
Mo1	0.31766(5)	0.19371(2)	0.34120(5)	1.23(1)
Mo2	0.44459(5)	0.31244(3)	0.28998(5)	1.31(1)
Mo3	0.14868(5)	0.30802(3)	0.14716(5)	1.26(1)
Mo4	0.32037(5)	0.19671(2)	0.06289(5)	1.23(1)
S1	0.2903(1)	0.3269(1)	0.4081(1)	1.59(4)
S2	0.5214(1)	0.1794(1)	0.2952(1)	1.53(4)
S3	0.2948(1)	0.3312(1)	0.0336(1)	1.58(4)
S4	0.1246(1)	0.1732(1)	0.1042(2)	1.51(4)
N11	0.4733(5)	0.1836(3)	0.5890(5)	1.9(1)
N12	0.1611(5)	0.1765(3)	0.4359(6)	2.2(2)
N13	0.3413(5)	0.0607(3)	0.3466(6)	2.0(2)
N21	0.6229(5)	0.3235(3)	0.5300(5)	2.2(2)
N22	0.6290(5)	0.3303(3)	0.2361(6)	2.3(2)
N23	0.4461(5)	0.4446(3)	0.3220(6)	2.3(2)
N31	−0.0371(5)	0.3197(3)	−0.0861(5)	2.2(2)
N32	−0.0403(5)	0.3169(3)	0.2077(6)	2.2(2)
N33	0.0960(5)	0.4403(3)	0.1548(6)	2.3(2)
N41	0.1710(5)	0.1828(3)	−0.1856(5)	2.2(2)
N42	0.4777(5)	0.1902(3)	−0.0397(6)	2.1(2)
N43	0.3490(5)	0.0643(3)	0.0208(5)	2.1(2)
C11	0.3632(2)	0.0379(1)	0.6924(2)	2.48(5)
C12	−0.1770(2)	0.1558(1)	0.7086(2)	3.3(1)
C13	−0.0102(2)	0.3319(1)	0.5718(2)	4.2(1)
C14	0.7331(2)	0.4518(1)	−0.0110(2)	3.2(1)
OW1	0.5037(6)	0.3315(3)	−0.1983(7)	4.5(2)
OW2	0.7955(5)	0.1756(3)	0.1731(6)	3.6(2)
OW3	0.7742(5)	0.4728(3)	0.5212(5)	3.5(2)
OW4	−0.1340(5)	0.0887(3)	0.4202(6)	4.2(2)
OW5	−0.1711(6)	0.0598(3)	−0.0323(7)	4.7(2)
OW6	0.2505(6)	0.4384(3)	−0.2855(6)	4.3(2)
OW7	0.0217(7)	0.0133(3)	0.2664(7)	5.3(3)

[a] Equivalent isotropic temperature factors ($B_{eq} = \frac{4}{3}\{\Sigma\Sigma B_{ij}a_i a_j\}$).

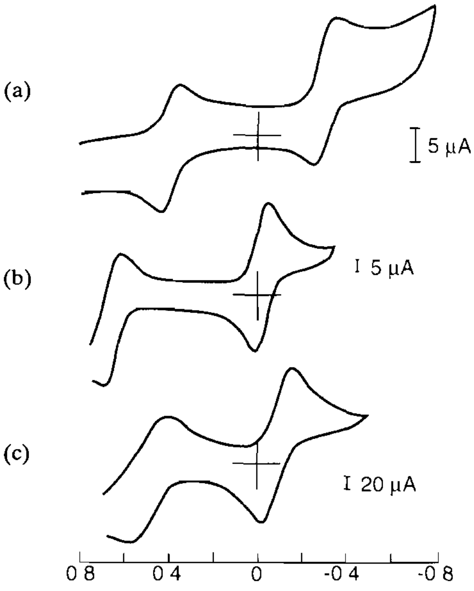

Fig. 1. Cyclic voltammograms at a glassy carbon electrode, E (V) vs. SCE, scan rate 0.1 V/s. (a) $[Mo_4S_4(edta)_2]^{3-}$ (**1B**) (0.8 mM) in 0.1 M $HClO_4$. (b) $[Mo_4S_4(H_2O)_{12}]^{5+}$ (**2B**) (17 mM in 2 M HPTS) (c) $[Mo_4S_4(H_2O)_{12}]^{5+}$ (**2B**) (15 mM in 2M HCl).

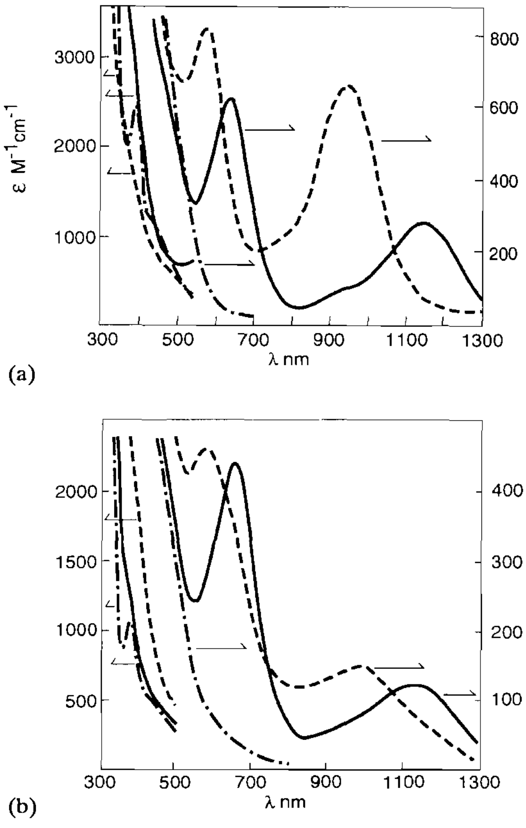

Fig. 2. Electronic spectra (ε values are per tetramer): (a) $[Mo_4S_4(edta)_2]^{2-}$ (**1A**) in water — —, $[Mo_4S_4(edta)_2]^{3-}$ (**1B**) in water ——, $[Mo_4S_4(edta)_2]^{4-}$ (**1C**) in water —·—; (b) $[Mo_4S_4(H_2O)_{12}]^{6+}$ (**2A**) in 2 M HCl – – –, $[Mo_4S_4(H_2O)_{12}]^{5+}$ (**2B**) in 2 M HCl ——, $[Mo_4S_4(H_2O)_{12}]^{4+}$ (**2C**) in 2 M HCl —·—.

Controlled potential electrolysis of **2B** in 2 M Hpts at −0.12 V (versus SCE) gives the reduced form, $[Mo_4S_4(H_2O)_{12}]^{4+}$ (**2C**), whereas oxidation of **2B** at 0.8 V (versus SCE) produces a mixture of several oxidation products including the $[Mo_3S_4(H_2O)_9]^{4+}$ aqua ion [2, 6c]. If we use 2 M HCl instead of 2 M Hpts, controlled potential electrolysis of **2B** at +0.60 V (versus SCE, Pt) gave the oxidized form. However, overelectrolysis beyond one coulometric equivalent ($e/Mo_4 = 1$) caused decomposition of the oxidized form, which could be estimated from the decrease of absorption peak at *c.* 575 nm. Electronic spectra of **2A**, **2B** and **2C** are shown in Fig. 2(b). Electronic spectral data of **1A**, **1B**, **1C**, **2A**, **2B** and **2C** are given in Table 7.

The purple cluster $[Mo_4S_4(NCS)_{12}]^{6-}$ (**3A**) was obtained from the aqua ion **2B** and NCS^- in air [2, 7]. If the procedure was performed under a dinitrogen atmosphere, the color of the solution remained brown after mixing of **2B** and NCS^-, and precipitation of a brown powder occurred. The core charge of Mo_4S_4 in **2B** is +5, and that in **3A** is +6, therefore, coordination of NCS^- to **2B** seems to induce air oxidation. The

TABLE 7 Electronic spectral data[a] for $[Mo_4S_4(edta)_2]^{n-}$ ($n = 2, 3, 4$) and $[Mo_4S_4(H_2O)_{12}]^{n+}$ ($n = 4, 5, 6$)

Compound	λ_{max} (nm) (ϵ(M^{-1} cm^{-1}))	Solvent	Reference
$[Mo_4S_4(edta)_2]^{2-}$ (**1A**)	572(816), 945(666)	water	2
$[Mo_4S_4(edta)_2]^{3-}$ (**1B**)	450sh(750), 636(630), 900sh(86), 1150(260)	water	1
$[Mo_4S_4(edta)_2]^{4-}$ (**1C**)	391(2450), 430sh(1120)	water	2
$[Mo_4S_4(H_2O)_{12}]^{6+}$ (**2A**)	575(460), 990(150)	2 M HCl	[b]
$[Mo_4S_4(H_2O)_{12}]^{5+}$ (**2B**)	370sh(1008), 643(445), 1100(128)	2 M Hpts	2
$[Mo_4S_4(H_2O)_{12}]^{5+}$ (**2B**)	300sh(4380), 380sh(1140), 647(444), 1116(120)	2 M HCl	[b]
$[Mo_4S_4(H_2O)_{12}]^{4+}$ (**2C**)	378(1090)	2 M Hpts	2
$[Mo_4S_4(H_2O)_{12}]^{4+}$ (**2C**)	375(1120)	2 M HCl	[b]

[a] ϵ values per tetramer [b] This work

color change from brown to purple was accelerated by the addition of methanol in air.

Addition of concentrated ammonia–water to the aqua ion **2B** gave $[Mo_4S_4(NH_3)_{12}]Cl_4 \cdot 7H_2O$ (**4C′**), the structure of which has been determined [5]. Coordination of ammonia to molybdenum also induced a change of the oxidation state of molybdenum. The color of the crystals **4C′** turned green on exposure to air. Dissolution of the crystals in acids gives the aqua ion **2B**. The electronic spectrum of **4C′** in concentrated ammonia–water has no absorption peak in the visible region.

No absorption peaks appear in the visible region of the electronic spectra of **1C**, **2C** and **4C**, that is the feature of the clusters in which the mean oxidation states of molybdenum is 3.00.

The chemistry of the dinitrogen complexes of molybdenum, including an X-ray structure determination, has been studied extensively to understand the chemistry of the nitrogen-fixing system, and it is known that ammonia can be liberated from some of the complexes by the action of acids [16]. Although syntheses and properties have been described [17], only one report has appeared so far on the X-ray structure determination of molybdenum complexes with ammonia as a ligand [18].

*Structures of $Na_2[Mo_4S_4(edta)_2] \cdot 6H_2O$ (**Na1A**), $Ca_{1.5}[Mo_4S_4(edta)_2] \cdot 13H_2O$ (**Ca1B**), $Mg_2[Mo_4S_4(edta)_2] \cdot 20H_2O$ (**Mg1C**), $[Mo_4S_4(H_2O)_{12}](CH_3C_6H_4SO_3)_5 \cdot 14H_2O$ (**2Bpts**) and $[Mo_4S_4(NH_3)_{12}]Cl_4 \cdot 7H_2O$ (**4C′**) and electronic structures of 2A, 2B and 2C*

No crystallographically imposed symmetry exists in **Na1A**, **Ca1B**, **2Bpts** and **4C′**, while the anion of **Mg1C** has a mirror plane, which introduces disorder in the ethylenediamine moiety of $edta^{4-}$ in **Mg1C**. Some waters of crystallization have high B_{eq} values in **Ca1B**, **Mg1C** and **2Bpts**, and each number of water crystallization was determined according to the results of the elemental analyses (nitrogen, carbon and hydrogen for **Ca1B** and **Mg1C**; carbon and hydrogen for **2Bpts**) and the density measurements.

As described in 'Experimental', **Ca1B** was prepared from **Na1B** through cation replacement of three sodium ions with two calcium ions. Both the two calcium ions (Ca1 and Ca2) occupy general positions, and one (Ca2) of the ions should have the occupancy factor of 0.5. The calcium ion Ca1 is surrounded by seven atoms (three oxygen atoms of three carboxylate groups and four waters of crystallization), and Ca2 is surrounded by seven waters of crystallization. In **Mg1C**, six waters of crystallization reside on a mirror plane, and seven waters of crystallization occupy general positions; as a result, each $Mg_2[Mo_4S_4(edta)_2]$ accompanies twenty waters of crystallization.

ORTEP figures of $[Mo_4S_4(edta)_2]^{3-}$ in **Ca1B**, $[Mo_4S_4(H_2O)_{12}]^{5+}$ in **2Bpts**, and $[Mo_4S_4(NH_3)_{12}]^{4+}$ in **4C′** are shown in Figs. 3–5, respectively, and the selected interatomic distances and angles for **Na1A**, **Ca1B**, **Mg1C**, **2Bpts** and **4C′** are listed in Tables 8–12, respectively.

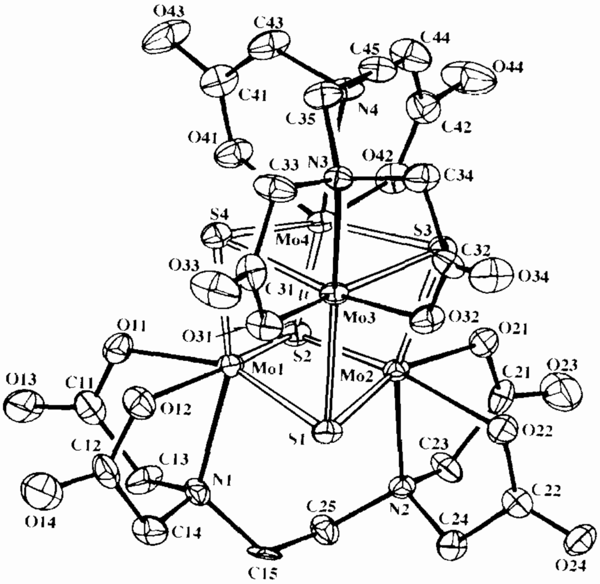

Fig 3 Perspective view of $[Mo_4S_4(edta)_2]^{3-}$ (the anion of **Ca1B**) showing the atom-labeling scheme. In Figs. 3–5 the 50% probability vibrational ellipsoids are shown.

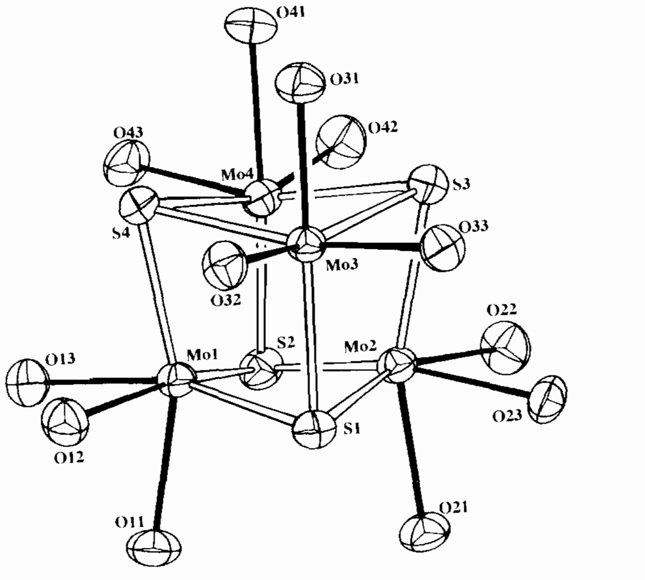

Fig 4. Perspective view of $[Mo_4S_4(H_2O)_{12}]^{5+}$ (the cation of **2Bpts**) showing the atom-labeling scheme.

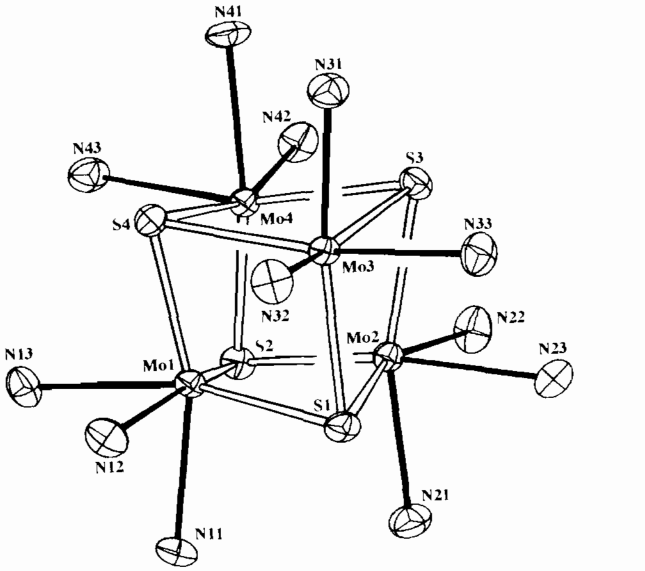

Fig 5. Perspective view of $[Mo_4S_4(NH_3)_{12}]^{4+}$ (the cation of **4C′**) showing the atom-labeling scheme.

TABLE 8. Selected interatomic distances (Å) and angles (°) in $Na_2[Mo_4S_4(edta)_2]\cdot 6H_2O$ (**Na1A**)

Mo1–Mo2	2.872(1)	C11–C13	1.536(14)
Mo1–Mo3	2.740(1)	C12–C14	1.524(14)
Mo1–Mo4	2.780(1)	C21–C23	1.524(15)
Mo2–Mo3	2.842(1)	C22–C24	1.496(14)
Mo2–Mo4	2.853(1)	C31–C33	1.521(14)
Mo3–Mo4	2.870(1)	C32–C34	1.509(15)
mean	2.826[54]	C41–C43	1.511(13)
		C42–C44	1.516(13)
Mo1–S1	2.355(2)	mean	1.517[12]
Mo1–S2	2.382(3)		
Mo1–S4	2.339(2)	C15–C25	1.538(14)
Mo2–S1	2.388(3)	C35–C45	1.528(13)
Mo2–S2	2.332(2)	mean	1.533[7]
Mo2–S3	2.330(2)		
Mo3–S1	2.350(3)	Mo2–Mo1–Mo3	60.81(3)
Mo3–S3	2.340(3)	Mo2–Mo1–Mo4	60.61(3)
Mo3–S4	2.386(2)	Mo3–Mo1–Mo4	62.64(3)
Mo4–S2	2.324(2)	Mo1–Mo2–Mo3	57.31(3)
Mo4–S3	2.380(2)	Mo1–Mo2–Mo4	58.10(3)
Mo4–S4	2.351(3)	Mo3–Mo2–Mo4	60.52(3)
mean	2.355[23]	Mo1–Mo3–Mo2	61.88(3)
		Mo1–Mo3–Mo4	59.35(3)
Mo1–O11	2.105(6)	Mo2–Mo3–Mo4	59.92(3)
Mo1–O12	2.103(7)	Mo1–Mo4–Mo2	61.29(3)
Mo2–O21	2.081(7)	Mo1–Mo4–Mo3	58.01(3)
Mo2–O22	2.095(7)	Mo2–Mo4–Mo3	59.56(3)
Mo3–O31	2.100(7)	mean	60.0[16]
Mo3–O32	2.092(6)		
Mo4–O41	2.081(6)	S1–Mo1–S2	102.1(1)
Mo4–O42	2.104(7)	S1–Mo1–S4	107.9(1)
mean	2.095[10]	S2–Mo1–S4	104.8(1)
		S1–Mo2–S2	102.6(1)
Mo1–N1	2.276(7)	S1–Mo2–S3	103.3(1)
Mo2–N2	2.257(8)	S2–Mo2–S3	104.0(1)
Mo3–N3	2.272(7)	S1–Mo3–S3	104.1(1)
Mo4–N4	2.282(8)	S1–Mo3–S4	106.5(1)
mean	2.272[11]	S3–Mo3–S4	102.6(1)
		S2–Mo4–S3	102.7(1)
O11–C11	1.282(11)	S2–Mo4–S4	106.3(1)
O12–C12	1.309(11)	S3–Mo4–S4	102.4(1)
O21–C21	1.289(12)	mean	104.1[19]
O22–C22	1.293(13)		
O31–C31	1.287(11)	O11–Mo1–O12	79.1(3)
O32–C32	1.274(11)	O21–Mo2–O22	79.1(3)
O41–C41	1.287(13)	O31–Mo3–O32	80.1(2)
O42–C42	1.290(12)	O41–Mo4–O42	79.0(3)
mean	1.289[10]	mean	79.3[5]
O13–C11	1.226(11)	O11–Mo1–N1	77.3(2)
O14–C12	1.221(12)	O12–Mo1–N1	78.4(3)
O23–C21	1.220(13)	O21–Mo2–N2	78.9(3)
O24–C22	1.229(13)	O22–Mo2–N2	76.8(3)
O33–C31	1.224(12)	O31–Mo3–N3	76.9(3)
O34–C32	1.244(11)	O32–Mo3–N3	78.7(3)
O43–C41	1.229(13)	O41–Mo4–N4	79.0(3)
O44–C42	1.233(13)	O42–Mo4–N4	77.1(3)
mean	1.228[8]	mean	77.9[10]
N1–C13	1.513(11)	Mo1–S1–Mo2	74.5(1)
N1–C14	1.503(13)	Mo1–S1–Mo3	71.2(1)
N1–C15	1.525(11)	Mo2–S1–Mo3	73.7(1)
N2–C23	1.516(14)	Mo1–S2–Mo2	75.0(1)
N2–C24	1.516(13)	Mo1–S2–Mo4	72.4(1)
N2–C25	1.555(11)	Mo2–S2–Mo4	75.6(1)
N3–C33	1.514(13)	Mo2–S3–Mo3	75.0(1)
N3–C34	1.502(12)	Mo2–S3–Mo4	74.5(1)
N3–C35	1.547(13)	Mo3–S3–Mo4	74.9(1)
N4–C43	1.519(12)	Mo1–S4–Mo3	70.9(1)
N4–C44	1.517(12)	Mo1–S4–Mo4	72.7(1)
N4–C45	1.503(11)	Mo3–S4–Mo4	74.6(1)
mean	1.519[17]	mean	73.8[16]

Mean values of bond distances and angles in $CH_3C_6H_4SO_3^-$ of **2Bpts** are listed in Table 13.

The presence of cubane-type Mo_4S_4 cores in all the clusters has been confirmed. As indicated in the Tables, the Mo–Mo bond distances in the clusters are distributed in relatively narrow ranges, and each Mo_4 tetrahedron has an approximate symmetry of T_d. The structures of the three complex anions **1A**, **1B** and **1C** are very similar to each other. Some notable differences, however, can be found if bond distances and volumes of the tetrahedra consisting of four Mos are compared among these three complex anions (Table 14). The mean values for the

TABLE 9. Selected interatomic distances (Å) and angles (°) in $Ca_{1.5}[Mo_4S_4(edta)_2]\cdot 13H_2O$ (**Ca1B**)

Mo1–Mo2	2.776(2)	C11–C13	1.505(19)
Mo1–Mo3	2.794(2)	C12–C14	1.490(22)
Mo1–Mo4	2.881(2)	C21–C23	1.487(15)
Mo2–Mo3	2.845(2)	C22–C24	1.516(16)
Mo2–Mo4	2.755(2)	C31–C33	1.483(18)
Mo3–Mo4	2.797(2)	C32–C34	1.537(18)
mean	2.808[47]	C41–C43	1.526(21)
		C42–C44	1.505(25)
Mo1–S1	2.352(3)	mean	1.506[19]
Mo1–S2	2.366(5)		
Mo1–S4	2.356(4)	C15–C25	1.518(22)
Mo2–S1	2.370(5)	C35–C45	1.528(24)
Mo2–S2	2.362(4)	mean	1.523[7]
Mo2–S3	2.352(3)		
Mo3–S1	2.350(3)	Mo2–Mo1–Mo3	61.4(1)
Mo3–S3	2.359(4)	Mo2–Mo1–Mo4	58.3(1)
Mo3–S4	2.355(3)	Mo3–Mo1–Mo4	59.01(5)
Mo4–S2	2.354(4)	Mo1–Mo2–Mo3	59.6(1)
Mo4–S3	2.354(3)	Mo1–Mo2–Mo4	62.79(4)
Mo4–S4	2.363(5)	Mo3–Mo2–Mo4	59.89(5)
mean	2.358[6]	Mo1–Mo3–Mo2	59.0(1)
		Mo1–Mo3–Mo4	62.0(1)
Mo1–O11	2.145(8)	Mo2–Mo3–Mo4	58.5(1)
Mo1–O12	2.143(11)	Mo1–Mo4–Mo2	58.96(5)
Mo2–O21	2.119(10)	Mo1–Mo4–Mo3	58.9(1)
Mo2–O22	2.152(8)	Mo2–Mo4–Mo3	61.65(5)
Mo3–O31	2.132(11)	mean	60.0[15]
Mo3–O32	2.153(9)		
Mo4–O41	2.138(9)	S1–Mo1–S2	106.6(1)
Mo4–O42	2.130(11)	S1–Mo1–S4	105.4(1)
mean	2.139[12]	S2–Mo1–S4	101.0(1)
		S1–Mo2–S2	106.1(1)
Mo1–N1	2.285(10)	S1–Mo2–S3	102.0(1)
Mo2–N2	2.281(10)	S2–Mo2–S3	106.7(1)
Mo3–N3	2.297(11)	S1–Mo3–S3	102.3(1)
Mo4–N4	2.292(10)	S1–Mo3–S4	105.5(1)
mean	2.289[7]	S3–Mo3–S4	105.6(1)
		S2–Mo4–S3	106.9(1)
O11–C11	1.282(16)	S2–Mo4–S4	101.1(1)
O12–C12	1.273(14)	S3–Mo4–S4	105.5(1)
O21–C21	1.267(19)	mean	104.6[23]
O22–C22	1.288(16)		
O31–C31	1.260(19)	O11–Mo1–O12	76.3(4)
O32–C32	1.258(17)	O21–Mo2–O22	77.8(4)
O41–C41	1.267(17)	O31–Mo3–O32	77.7(4)
O42–C42	1.263(14)	O41–Mo4–O42	79.0(4)
mean	1.270[11]	mean	77.7[11]
O13–C11	1.228(14)	O11–Mo1–N1	76.2(3)
O14–C12	1.218(16)	O12–Mo1–N1	77.1(4)
O23–C21	1.271(19)	O21–Mo2–N2	77.6(4)
O24–C22	1.236(14)	O22–Mo2–N2	75.9(3)
O33–C31	1.242(22)	O31–Mo3–N3	76.9(4)
O34–C32	1.232(18)	O32–Mo3–N3	76.5(3)
O43–C41	1.252(16)	O41–Mo4–N4	75.7(3)
O44–C42	1.269(21)	O42–Mo4–N4	76.9(4)
mean	1.244[19]	mean	76.6[6]
N1–C13	1.508(18)	Mo1–S1–Mo2	72.0(1)
N1–C14	1.491(20)	Mo1–S1–Mo3	72.9(1)
N1–C15	1.536(17)	Mo2–S1–Mo3	74.1(1)
N2–C23	1.498(21)	Mo1–S2–Mo2	71.9(1)
N2–C24	1.486(16)	Mo1–S2–Mo4	75.2(1)
N2–C25	1.542(12)	Mo2–S2–Mo4	71.5(1)
N3–C33	1.494(21)	Mo2–S3–Mo3	74.3(1)
N3–C34	1.512(14)	Mo2–S3–Mo4	71.7(1)
N3–C35	1.522(17)	Mo3–S3–Mo4	72.8(1)
N4–C43	1.484(15)	Mo1–S4–Mo3	72.8(1)
N4–C44	1.510(20)	Mo1–S4–Mo4	75.3(1)
N4–C45	1.563(21)	Mo3–S4–Mo4	72.7(1)
mean	1.512[25]	mean	73.1[13]

TABLE 10 Selected interatomic distances (Å) and angles (°) in $Mg_2[Mo_4S_4(edta)_2]\cdot 20H_2O$ (**Mg1C**)

Mo1–Mo2	2.769(2)	C11–C13	1.468(18)
Mo1–Mo3	2.790(1)	C21–C23	1.528(13)
Mo2–Mo3	2.789(1)	C31–C33	1.495(18)
Mo3–Mo3′	2.766(1)	C32–C34	1.503(12)
mean	2.779[13]	mean	1.499[25]
Mo1–S1	2.360(2)	C15–C25	1.527(23)
Mo1–S4	2.354(3)	C35A–C35B	1.515(22)
Mo2–S1	2.356(2)	mean	1.521[8]
Mo2–S3	2.346(3)		
Mo3–S1	2.357(2)	Mo2–Mo1–Mo3	60.22(3)
Mo3–S3	2.361(2)	Mo3–Mo1–Mo3′	59.45(4)
Mo3–S4	2.354(2)	Mo1–Mo2–Mo3	60.25(3)
mean	2.355[5]	Mo3–Mo2–Mo3′	59.47(4)
		Mo1–Mo3–Mo2	59.52(4)
Mo1–O11	2.174(6)	Mo1–Mo3–Mo3′	60.28(2)
Mo2–O21	2.184(6)	Mo2–Mo3–Mo3′	60.27(2)
Mo3–O31	2.194(6)	mean	59.92[42]
Mo3–O32	2.203(5)		
mean	2.189[13]	S1–Mo1–S1′	105.8(1)
		S1–Mo1–S4	104.7(1)
Mo1–N1	2.286(10)	S1–Mo2–S1′	106.0(1)
Mo2–N2	2.302(9)	S1–Mo2–S3	104.9(1)
Mo3–N3	2.284(7)	S1–Mo3–S3	104.4(1)
mean	2.291[10]	S1–Mo3–S4	104.8(1)
		S3–Mo3–S4	106.1(1)
O11–C11	1.282(14)	mean	105.2[7]
O21–C21	1.247(11)		
O31–C31	1.315(17)	O11–Mo1–O11′	76.9(3)
O32–C32	1.284(9)	O21–Mo2–O21′	77.2(3)
mean	1.282[28]	O31–Mo3–O32	75.8(2)
		mean	76.6[7]
O13–C11	1.245(16)		
O23–C21	1.219(14)	O11–Mo1–N1	76.5(3)
O33–C31	1.265(15)	O21–Mo2–N2	76.8(2)
O34–C32	1.249(9)	O31–Mo3–N3	76.3(3)
mean	1.245[19]	O32–Mo3–N3	76.2(2)
		mean	76.5[3]
N1–C13	1.488(13)		
N1–C15	1.591(21)	Mo1–S1–Mo2	71.9(1)
N2–C23	1.501(11)	Mo1–S1–Mo3	72.5(1)
N2–C25	1.505(16)	Mo2–S1–Mo3	72.6(1)
N3–C33	1.441(15)	Mo2–S3–Mo3	72.7(1)
N3–C34	1.483(12)	Mo3–S3–Mo3′	71.7(1)
N3–C35B	1.682(17)	Mo1–S4–Mo3	72.7(1)
N3′–C35A	1.435(18)	Mo3–S4–Mo3′	72.0(1)
mean	1.516[82]	mean	72.3[4]

Mo–Mo bond lengths and volumes of Mo_4 decrease in the order of **1A**, **1B** and **1C**. The Mo–O (edta) bond lengths, on the contrary, increase in the order of **1A**, **1B** and **1C**; the latter tendency agrees with the general tendency that the lower is the oxidation state of metal, the longer is the metal–ligating atom distance. The Mo–S and Mo–N bond lengths show no distinct tendency of becoming shorter or longer in the order of **1A**, **1B** and **1C**. The average Mo–N distance in **4C** is longer than the other metal–nitrogen (NH_3) distances (e.g. $[Ru_2(NH_3)_{10}N_2]^{4+}$ (2.12 Å)) [19].

Magnetic measurement of $Mg[Mo_4S_4(edta)_2]\cdot 12H_2O$ (**Mg1A**), $Na_3[Mo_4S_4(edta)_2]\cdot 10H_2O$ (**Na1B**) and

TABLE 11. Selected interatomic distances (Å) and angles (°) in $[Mo_4S_4(H_2O)_{12}](CH_3C_6H_4SO_3)_5$ $14H_2O$ (**2Bpts**)

Mo1–Mo2	2 827(1)	S1–Mo1–S2	103.6(1)
Mo1–Mo3	2 820(1)	S1–Mo1–S4	103 7(1)
Mo1–Mo4	2.785(1)	S2–Mo1–S4	105 7(1)
Mo2–Mo3	2.785(1)	S1–Mo2–S2	103 4(1)
Mo2–Mo4	2.800(1)	S1–Mo2–S3	105.3(1)
Mo3–Mo4	2.794(1)	S2–Mo2–S3	104.6(1)
mean	2.802[18]	S1–Mo3–S3	105.7(1)
		S1–Mo3–S4	103.6(1)
Mo1–S1	2.349(2)	S3–Mo3–S4	104.8(1)
Mo1–S2	2.346(2)	S2–Mo4–S3	104.4(1)
Mo1–S4	2.344(2)	S2–Mo4–S4	105.2(1)
Mo2–S1	2.356(2)	S3–Mo4–S4	104.4(1)
Mo2–S2	2.345(2)	mean	104.5[8]
Mo2–S3	2.354(2)		
Mo3–S1	2.351(2)	O11–Mo1–O12	78.5(2)
Mo3–S3	2.346(2)	O11–Mo1–O13	77.4(2)
Mo3–S4	2.346(2)	O12–Mo1–O13	80.1(2)
Mo4–S2	2 352(2)	O21–Mo2–O22	79.7(2)
Mo4–S3	2.351(2)	O21–Mo2–O23	76 7(2)
Mo4–S4	2 354(2)	O22–Mo2–O23	79.6(2)
mean	2.350[4]	O31–Mo3–O32	77.4(2)
		O31–Mo3–O33	80.0(2)
Mo1–O11	2 178(4)	O32–Mo3–O33	79.0(2)
Mo1–O12	2.195(5)	O41–Mo4–O42	77.8(2)
Mo1–O13	2.197(4)	O41–Mo4–O43	79.2(2)
Mo2–O21	2.197(4)	O42–Mo4–O43	78.8(2)
Mo2–O22	2.184(5)	mean	78.7[11]
Mo2–O23	2 173(4)		
Mo3–O31	2.181(4)	Mo1–S1–Mo2	73.9(1)
Mo3–O32	2 208(5)	Mo1–S1–Mo3	73.7(1)
Mo3–O33	2.202(4)	Mo2–S1–Mo3	72.6(1)
Mo4–O41	2.201(4)	Mo1–S2–Mo2	74.1(1)
Mo4–O42	2.183(5)	Mo1–S2–Mo4	72 7(1)
Mo4–O43	2.178(4)	Mo2–S2–Mo4	73.2(1)
mean	2.190[11]	Mo2–S3–Mo3	72.7(1)
		Mo2–S3–Mo4	73.0(1)
Mo2–Mo1–Mo3	59.10(3)	Mo3–S3–Mo4	73.0(1)
Mo2–Mo1–Mo4	59 86(3)	Mo1–S4–Mo3	73.9(1)
Mo3–Mo1–Mo4	59.80(3)	Mo1–S4–Mo4	72.7(1)
Mo1–Mo2–Mo3	60.31(3)	Mo3–S4–Mo4	73.0(1)
Mo1–Mo2–Mo4	59.32(3)	mean	73.2[5]
Mo3–Mo2–Mo4	60.03(3)		
Mo1–Mo3–Mo2	60.58(3)		
Mo1–Mo3–Mo4	59.47(3)		
Mo2–Mo3–Mo4	60.25(3)		
Mo1–Mo4–Mo2	60.83(3)		
Mo1–Mo4–Mo3	60.72(3)		
Mo2–Mo4–Mo3	59.72(3)		
mean	60.00[56]		

TABLE 12. Selected interatomic distances (Å) and angles (°) in $[Mo_4S_4(NH_3)_{12}]Cl_4$ $7H_2O$ (**4C′**)

Mo1–Mo2	2.808(1)	S1–Mo1–S2	104.8(1)
Mo1–Mo3	2.807(1)	S1–Mo1–S4	104.8(1)
Mo1–Mo4	2.793(1)	S2–Mo1–S4	105.4(1)
Mo2–Mo3	2.802(1)	S1–Mo2–S2	104.6(1)
Mo2–Mo4	2.807(1)	S1–Mo2–S3	105.1(1)
Mo3–Mo4	2.801(1)	S2–Mo2–S3	104.8(1)
mean	2 803[6]	S1–Mo3–S3	105.4(1)
		S1–Mo3–S4	104.5(1)
Mo1–S1	2.363(1)	S3–Mo3–S4	105.0(1)
Mo1–S2	2.364(2)	S2–Mo4–S3	104.8(1)
Mo1–S4	2.360(1)	S2–Mo4–S4	105.2(1)
Mo2–S1	2.369(2)	S3–Mo4–S4	105.1(1)
Mo2–S2	2.363(1)	mean	105.0[3]
Mo2–S3	2.373(2)		
Mo3–S1	2.364(2)	N11–Mo1–N12	80.4(2)
Mo3–S3	2 370(2)	N11–Mo1–N13	80.9(2)
Mo3–S4	2.369(2)	N12–Mo1–N13	79.1(2)
Mo4–S2	2 367(1)	N21–Mo2–N22	80.7(2)
Mo4–S3	2 370(2)	N21–Mo2–N23	80.9(2)
Mo4–S4	2.364(2)	N22–Mo2–N23	79.1(2)
mean	2.366[4]	N31–Mo3–N32	79.8(2)
		N31–Mo3–N33	79.9(2)
Mo1–N11	2 295(4)	N32–Mo3–N33	79.4(2)
Mo1–N12	2 294(7)	N41–Mo4–N42	79.3(2)
Mo1–N13	2.311(5)	N41–Mo4–N43	79.9(2)
Mo2–N21	2.301(4)	N42–Mo4–N43	80.5(2)
Mo2–N22	2.295(7)	mean	80.0[7]
Mo2–N23	2.294(5)		
Mo3–N31	2.294(4)	Mo1–S1–Mo2	72.80(5)
Mo3–N32	2.304(6)	Mo1–S1–Mo3	72.85(5)
Mo3–N33	2.309(5)	Mo2–S1–Mo3	72.6(1)
Mo4–N41	2.275(4)	Mo1–S2–Mo2	72.90(5)
Mo4–N42	2 287(6)	Mo1–S2–Mo4	72.38(5)
Mo4–N43	2 309(5)	Mo2–S2–Mo4	72.82(4)
mean	2 297[10]	Mo2–S3–Mo3	72.4(1)
		Mo2–S3–Mo4	72.59(5)
Mo2–Mo1–Mo3	59.86(3)	Mo3–S3–Mo4	72.5(1)
Mo2–Mo1–Mo4	60.15(3)	Mo1–S4–Mo3	72.82(5)
Mo3–Mo1–Mo4	60.03(3)	Mo1–S4–Mo4	72.49(5)
Mo1–Mo2–Mo3	60.05(3)	Mo3–S4–Mo4	72.6(1)
Mo1–Mo2–Mo4	59.66(3)	mean	72.65[18]
Mo3–Mo2–Mo4	59.93(3)		
Mo1–Mo3–Mo2	60.09(3)		
Mo1–Mo3–Mo4	59.75(3)		
Mo2–Mo3–Mo4	60 14(3)		
Mo1–Mo4–Mo2	60.19(3)		
Mo1–Mo4–Mo3	60.23(3)		
Mo2–Mo4–Mo3	59.94(3)		
mean	60.00[18]		

$Mg_2[Mo_4S_4(edta)_2]\cdot 20H_2O$ (**Mg1C**) made clear that **1A** and **1C** are essentially diamagnetic, whereas **1B** is in the paramagnetic $S=1/2$ ground state [20]. Although the ligands are different in the two groups **1A**–**1C** and **2A**–**2C**, electronic structures of **1A** and **2A**, **1B** and **2B**, and **1C** and **2C** will not change much, and **2A** and **2C** is expected to be diamagnetic

Qualitatively, under T_d symmetry six bonding orbitals, (a_1+e+t_2) [21] are filled with twelve 4d-electrons from four Mo(III)s in **1C**, and removal of one or two electrons

TABLE 13. Mean values of bond distances (Å) and angles (°) in $CH_3C_6H_4SO_3^-$

S–O	1.444[17]	O–S–O	112.0[10]
S–C	1.761[11]	O–S–C	106.8[8]
		S–C–C	119.5[10]
O–C[a]	1.395[21]	C–C–C[a]	120.0[12]
O–C[b]	1.528[11]	C–C–C[b]	120.5[7]

[a] Carbon atoms in a phenylene group. [b] Carbon atoms in methyl and phenylene groups.

TABLE 14. Summary of volume and bond distances of $Na_2[Mo_4S_4(edta)_2]$ $6H_2O$ (**Na1A**), $Ca_{1.5}[Mo_4S_4(edta)_2]$ $13H_2O$ (**Ca1B**), $Mg_2[Mo_4S_4(edta)_2]$ $20H_2O$ (**Mg1C**), $[Mo_4S_4(H_2O)_{12}](CH_3C_6H_4SO_3)_5$ $14H_2O$ (**2Bpts**) and $[Mo_4S_4(NH_3)_{12}]Cl_4$ $7H_2O$ (**4C′**)

	Na1A	**Ca1B**	**Mg1C**	**2Bpts**	**4C′**
Oxidation state of molybdenum	3.50	3.25	3.00	3.25	3.00
Volume (Å^3)					
Mo_4	2.654(3)	2.602(3)	2.540(3)	2.592(3)	2.594(2)
Bond distance (Å)[a]					
Mo–Mo	2.826[54]	2.808[47]	2.779[13]	2.802[18]	2.803[6]
Mo–S	2.355[23]	2.358[6]	2.355[5]	2.350[4]	2.366[4]
Mo–N	2.272[11]	2.289[7]	2.291[10]		2.297[10]
Mo–O	2.095[10]	2.139[12]	2.189[13]	2.190[11]	

[a] Mean value. The estimated deviation in brackets is calculated as being equal to $[\Sigma_i(x_i-x)^2/(n-1)]^{1/2}$, in which x is the mean of n values

from the bonding orbitals in **1C** will afford **1B** and **1A**, respectively, resulting in weaker, accordingly longer Mo–Mo bond length and larger Mo_4 volume.

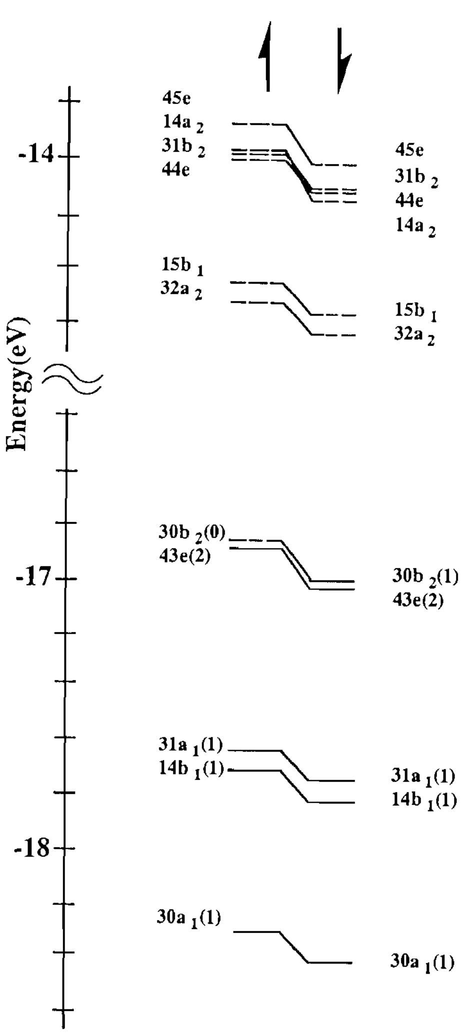

Fig 6. Electronic energy levels of $[Mo_4S_4(H_2O)_{12}]^{5+}$ (**2B**) near HOMO Occupied levels are indicated by solid lines and unoccupied ones by dotted lines. Levels with up- and down-spin are indicated by ↑ and ↓, respectively. The number of electron(s) in each orbital is indicated in parentheses

The electronic structures of **2A**, **2B** and **2C** were investigated by the spin-polarized discrete variational (DV)-Xα method [22] Both T_d and D_{2d} symmetries were applied. In T_d symmetry, all the HOMOs of **2A**, **2B** and **2C** are t_2 orbitals, which indicates that **2A** and **2B** are paramagnetic and **2C** is diamagnetic: there is discrepancy between the observation and the calculation in the case of **2A**. Then D_{2d} symmetry was adopted to **2A**, **2B** and **2C** (t_2 orbital in T_d symmetry splits into b_2 and e orbitals in D_{2d} symmetry). Spin polarization occurred in the case of **2B** only. The HOMOs of **2A**, **2B** and **2C** are e (occupied), e up (occupied), and b_2 (occupied), respectively, which agrees with the experimental results. Electronic energy levels of **2B** near HOMO are shown in Fig. 6.

XPS measurements on some of the above cubane-type clusters gave Mo3d$_{3/2}$ and Mo3d$_{5/2}$ binding energies, which are listed in Table 15 together with those of incomplete cubane-type compounds for comparison. As expected, the binding energy of **Na1A** is larger than those of **Na1B** and **Na1C**, however, the binding energies of **Na1B** and **Na1C** are identical. Further investigation is necessary to explain this result. As seen in the Table, the binding energies depend not only on the oxidation state of the metals but also on the nature of ligands. Compounds with negatively-charged ligands show lower binding energies than those of the compounds with neutral ones.

Supplementary material

Listing of crystallographic details, atomic coordinates and thermal parameters, bond distances and angles of **Na1A**, **Ca1B**, **Mg1C**, **2Bpts** and **4C′**; Tables of F_o and F_c values; Figures of **Na1A** and **Mg1C** are available from the authors on request.

TABLE 15. Mo3d$_{3/2}$ and Mo3d$_{5/2}$ binding energies

Compound	Ox[a]	Mo3d$_{3/2}$	Mo3d$_{5/2}$	Ref.
$Na_2[Mo_4S_4(edta)_2]$ $6H_2O$ (**NaIA**)	3.50	232.7	229.7	[b]
$Na_3[Mo_4S_4(edta)_2]\cdot 10H_2O$ (**NaIB**)	3.25	232.1	229.0	[b]
$Na_4[Mo_4S_4(edta)_2]\cdot 19H_2O$ (**NaIC**)	3.00	232.1	229.0	[b]
$[Mo_4S_4(H_2O)_{12}](pts)_5\cdot 14H_2O$ (**2Bpts**)	3.25	233.0	230.0	[b]
$[Mo_4S_4(NH_3)_{12}]Cl_4$ $7H_2O$ (**4C′**)	3.00	232.1	228.9	[b]
$[Mo_3S_4(H_2O)_9](pts)_4\cdot 9H_2O$	4.00	233.8	230.8	[b]
$(pyH)_4[Mo_3S_4(NCS)_8(H_2O)]$ $4H_2O$	4.00	232.2	229.2	23

[a]Mean oxidation state of molybdenum [b]This work

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