The synthesis, crystal structure and characterization of a cubane type tetranuclear molybdenum cluster compound containing two kinds of bidentate ligands {[$Mo_4S_4(\mu$-OAc$)_2$(dtp$)_4\cdot$H]$(CH_3)_2CO$} (4)

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(Received January 29, 1990)

Abstract

The tetranuclear molybdenum cluster {[$Mo_4S_4(\mu$-OAc$)_2$(dtp$)_4\cdot$H]$(CH_3)_2CO$} (**4**) (dtp = $S_2P(OEt)_2$) was obtained by the reaction of [Mo_3S_4(dtp$)_4(H_2O)$] with $Mo(CO)_6$ in HOAc/Ac_2O medium and then by recrystallization from acetone. The crystal belongs to the space group C_{2h}^{4}-$P2/n$ with two molecules in a unit cell whose dimensions are $a = 17.271(3)$, $b = 11.985(3)$, $c = 13.061(2)$ Å and $\beta = 105.94(1)°$, $V = 2599(2)$ Å^3, $D_c = 1.826$ g/cm^3. On the basis of 3613 independent reflections with $I \geqslant 3\sigma(I)$, the structure was refined to $R = 0.040$, $R_w = 0.055$. The cluster anion [$Mo_4S_4(\mu$-OAc$)_2$(dtp$)_4]^-$ contains a $[Mo_4S_4]^{5+}$ cubane type core. This formulation is supported by XPS, ESR and ^{1}H NMR measurements of **4**. There are 11 electrons which make up six Mo–Mo bonds.

Introduction

During the past several years, a series of tetranuclear molybdenum cluster compounds with the $[Mo_4S_4]^{n+}$ ($n = 4, 5, 6$) core has been reported [1–6]. We have also succeeded in synthesizing the cluster {$Mo_4S_4(\mu$-dtp$)_2$(dtp$)_4$} (**1**) [7] from the reaction of the Mo(III) compound ($MoCl_3\cdot 3H_2O$) with P_2S_5 first and then the neutral cluster {$Mo_4S_4(\mu$-OAc$)_2$(dtp$)_4$} (**2**) [8] by the ligand substitution of **1**. Recently, we have tried an alternative synthetic route according to $[Mo_3S_4]^{4+}$ + $Mo(CO)_6$ + HOAc → $[Mo_4S_4]^{n+}$, i.e. a [3 + 1] reaction mode. Two tetranuclear Mo cluster compounds **3** [9] and **4** have been obtained, which have the same cluster anion geometry. In this paper, the crystal structure of **4** is reported and a comparison is made concerning the important structure details, XPS, ESR, ^{1}H NMR and cyclic voltammograms data for **4** and **2** to reveal the difference in bonding parameters and electronic structures of both the tetranuclear cluster compounds, obtained from different synthetic routes.

Experimental and results

Preparation

A mixture of 360 mg (0.3 mmol) of [Mo_3S_4(dtp$)_4(H_2O)$] [10] and 80 mg (0.3 mmol) of $Mo(CO)_6$ dissolved in 10 ml HOAc and 5 ml Ac_2O was refluxed for 1 h. After standing for three days, the mother liquid was removed. The residual fine black crystals were washed with EtOH and then dissolved in a solution of the correct amount of acetone and ethanol under reflux. After standing for two weeks, 80 mg of the black pillar-like crystals were obtained. The IR spectra of the product show the stretching vibration of the coordinated bridging carboxyl group RCO_2^- at 1425 and 1600 cm^{-1} and the solvent acetone at 1215 and 1710 cm^{-1} [11].

X-ray structure analysis

A brownish-black crystal of dimensions 0.6 × 0.4 × 0.2 mm was mounted on the end of a thin glass fiber with epoxy glue and then on an Enraf–Nonius CAD–4 diffractometer. All X-ray measurements were made using graphite monochromated Mo Kα radiation, ω–2θ scan technique and variable scan speeds. A total of 25 reflections in the range of $15° \leqslant \theta \leqslant 16°$ was used as input to the automatic centering, autoindexing and least-squares routines of the instrument to achieve a set of the lattice parameters.

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0020-1693/90/$3.50

Table 1 summarizes the data pertaining to the crystallographic measurements and refinement.

During the data collection three intensity standards were collected every hour. No decay in intensity was observed. The crystal orientation was rechecked every 200 reflections indicating that the change from the setting angle was less than 0.12°. Data reduction included Lorentz–polarization corrections and empirical absorption correction in terms of the ψ scan technique. The structure was solved by a combination of Patterson and direct methods (MULTAN 11/82 [12]) and refined by the full matrix least-squares method. The non-hydrogen atoms were assigned by the anisotropic thermal parameters with the exception of those belonging to the solvent acetone, of which the isotropic thermal vibrations were assumed. Hydrogen atoms were not located. All the calculations were performed on a VAX-785 computer with the VAXSDP program package [13].

Table 2 gives the coordinates and equivalent isotropic thermal parameters of all the non-hydrogen atoms. The important bond lengths and angles are listed in Tables 3 and 4, respectively. The geometry of the $[Mo_4S_4(\mu\text{-OAc})_2(dtp)_4]^-$ cluster anion is shown in Fig. 1. (Note: atoms generated by the two-fold axis are labelled by the corresponding atom number but without parentheses.) The packing of the $[Mo_4S_4(\mu\text{-OAc})_2(dtp)_4 \cdot H]$ and $(CH_3)_2CO$ molecules in the unit cell is depicted in Fig. 2.

X-ray photoelectron spectroscopy (XPS) (see Fig. 3)

Instrument: NP-3G XPS Spectrometer made in Shenyang Scientific Instrument Factory, Chinese Academy of Sciences.

Radiation source: Mg Kα (1253.6 eV), 15 kV, 5 mA.

Sample preparation: the sample was powdered and dusted on to metal Ga on a Ni trough, which was put in a Mo holder.

All the measurements were performed with the Ag(3d) lines (373.89, 367.9 eV) as reference. the resolution was ±0.1 eV and the relative binding energies can be precisely measured to ±0.05 eV. The electron binding energies of $[Mo_3S_4(dtp)_4 \cdot (H_2O)]$ (here Mo was +4 oxidation state) are also presented for comparison. The analysis was carried out by Dr Lu Qingbin and Mr. Huang Zhenwu, Department of Physics, Fuzhou University. Results are given in Table 5.

Electron spin resonance spectra (ESR)

The powder spectra were measured on an ER-420 spectrometer (X-band), 100 kHz small modulation magnetic field) at room temperature and 77 K. Results are given in Table 6.

Nuclear magnetic resonance (^1H NMR)

The ^1H NMR spectra (see Fig. 4) were recorded on a VARIAN FT-80A spectrometer. The peak of active hydrogen disappears after the exchange by

TABLE 1. Crystal and intensity collection data for $\{[Mo_4S_4(\mu\text{-OAc})_2(dtp)_4 \cdot H](CH_3)_2CO\}$ (4)

Formula	$\{[Mo_4S_4(\mu\text{-OAc})_2(dtp)_4 \cdot H](CH_3)_2CO\}$
Molecular weight	1430.09
Space group	$P2/n$
Systematic absences	$(h0l)$ $h+l=2n+1$
a, b, c (Å)	17.271(3), 11.985(3), 13.061(2)
β (°)	105.94(1)
V (Å^3), Z	2599(2), 2
D_c (g/cm^3)	1.826
Crystal size (mm)	0.6×0.4×0.2
μ (Mo Kα) (cm^{-1})	15.535
Radiation monochromated λ_α (Å)	Mo Kα (0.71073)
Orientation reflection: no., range (θ) (°)	25, 15–16
Temperature (K)	296
Scan method	ω–2θ
Data collection range (θ) (°)	1–26 $-21 \leqslant h \leqslant 21$, $-14 \leqslant k \leqslant 0$, $-16 \leqslant l \leqslant 0$
Transmission factors (%)	99.73–88.62
No. unique data, total with $I \geqslant 3\sigma(I)$	5104, 3613
No. parameters refined	243
R, R_w (%)	4, 5.3
Quality-of-fit indicator	1.385
Largest shift/e.s.d., final cycle	0.12
Largest peak (e/Å^3)	0.624

$R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$; $R_w=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; Quality-of-fit$=[\Sigma w(|F_o|-|F_c|)^2/(N_{obs}-N_{param})]^{1/2}$.

TABLE 2. Positional parameters and their e.s.d.s

Atom	x	y	z	B (Å^2)[a]
Mo(1)	0.16692(3)	0.21775(4)	0.72348(4)	3.49(1)
Mo(2)	0.23022(3)	0.38983(4)	0.64058(4)	3.74(1)
S(1)	0.25519(8)	0.1985(1)	0.8967(1)	3.96(3)
S(2)	0.13914(9)	0.4089(1)	0.7425(1)	4.19(3)
S(3)	0.05264(9)	0.1897(2)	0.8101(1)	4.87(4)
S(4)	0.14261(9)	0.0124(1)	0.7019(1)	4.77(4)
S(5)	0.2154(1)	0.5955(2)	0.6120(2)	5.70(5)
S(6)	0.2963(1)	0.4215(2)	0.4902(1)	5.56(4)
P(1)	0.05608(9)	0.0292(2)	0.7767(1)	4.72(4)
P(2)	0.2700(1)	0.5812(2)	0.4971(2)	5.71(5)
O(1)	0.0683(2)	0.2328(3)	0.5795(3)	4.43(9)
O(2)	0.1223(2)	0.3764(4)	0.5103(3)	4.7(1)
O(3)	0.0679(3)	−0.0493(4)	0.8760(4)	6.2(1)
O(4)	−0.0267(2)	−0.0208(4)	0.7101(4)	6.0(1)
O(5)	0.3456(3)	0.6604(4)	0.5132(4)	7.1(1)
O(6)	0.2184(3)	0.6316(4)	0.3902(4)	7.3(1)
C(1)	0.0674(4)	0.3042(6)	0.5061(5)	4.8(1)
C(2)	−0.0038(4)	0.3054(7)	0.4080(5)	6.5(2)
C(3)	0.1397(5)	−0.0381(8)	0.9674(6)	8.4(2)
C(4)	−0.0663(4)	0.0222(7)	0.6016(6)	7.1(2)
C(5)	0.4154(5)	0.6481(8)	0.6065(7)	9.5(3)
C(6)	0.1313(6)	0.5946(9)	0.3436(7)	11.2(3)
C(7)	0.1186(6)	−0.0665(9)	1.0633(7)	9.5(3)
C(8)	−0.1444(6)	0.0670(9)	0.6017(8)	9.9(3)
C(9)	0.4879(6)	0.659(1)	0.5769(9)	12.8(4)
C(10)	0.1143(7)	0.596(1)	0.2337(9)	12.5(4)
O(01)	0.2500(0)	0.103(4)	0.2500(0)	67(3)*
C(01)	0.2500(0)	0.183(2)	0.2500(0)	22(1)*
O(02)	0.1741(8)	0.237(1)	0.260(1)	16.4(5)*

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2b(1,1)+b^2b(2,2)+c^2b(3,3)+ab(\cos\gamma)b(1,2)+ac(\cos\beta)b(1,3)+bc(\cos\alpha)b(2,3)]$.

TABLE 3. Bond distances (Å)[a]

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Mo(1)	Mo(1)	2.7612(9)	S(6)	P(2)	1.976(3)
Mo(1)	Mo(2)	2.6964(7)	P(1)	O(3)	1.570(4)
Mo(1)	Mo(2)	2.9715(7)	P(1)	O(4)	1.575(4)
Mo(2)	Mo(2)	2.750(1)	P(2)	O(5)	1.580(6)
Mo(1)	S(1)	2.367(1)	P(2)	O(6)	1.558(6)
Mo(1)	S(1)	2.342(1)	O(1)	C(1)	1.282(8)
Mo(1)	S(2)	2.367(1)	O(2)	C(1)	1.275(8)
Mo(1)	S(3)	2.553(1)	O(3)	C(3)	1.472(8)
Mo(1)	S(4)	2.500(2)	O(4)	C(4)	1.487(7)
Mo(1)	O(1)	2.170(3)	O(5)	C(5)	1.468(9)
Mo(2)	S(1)	2.372(1)	O(6)	C(6)	1.52(2)
Mo(2)	S(2)	2.334(1)	C(1)	C(2)	1.513(7)
Mo(2)	S(2)	2.363(1)	C(3)	C(7)	1.44(2)
Mo(2)	S(5)	2.497(2)	C(4)	C(8)	1.46(2)
Mo(2)	S(6)	2.557(2)	C(5)	C(9)	1.41(1)
Mo(2)	O(2)	2.157(4)	C(6)	C(10)	1.38(1)
S(3)	P(1)	1.976(2)	O(01)	C(01)	0.97(4)
S(4)	P(1)	2.008(3)	C(01)	C(02)	1.50(2)
S(5)	P(2)	1.987(3)			

[a] Numbers in parentheses are e.s.d.s. in the least significant digits.

TABLE 4. Bond angles (°)[a]

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
Mo(1)	Mo(1)	Mo(2)	65.96(2)	Mo(2)	S(2)	Mo(2)	71.68(4)
Mo(1)	Mo(1)	Mo(2)	55.97(1)	Mo(1)	S(3)	P(1)	87.51(7)
Mo(2)	Mo(1)	Mo(2)	57.81(2)	Mo(1)	S(4)	P(1)	88.33(7)
Mo(1)	Mo(2)	Mo(1)	58.06(2)	Mo(2)	S(5)	P(2)	88.69(8)
Mo(1)	Mo(2)	Mo(2)	66.12(2)	Mo(2)	S(6)	P(2)	87.22(8)
Mo(1)	Mo(2)	Mo(2)	56.07(1)	S(3)	P(1)	S(4)	106.06(9)
Mo(1)	Mo(1)	O(1)	137.0(1)	S(3)	P(1)	O(3)	113.9(2)
Mo(2)	Mo(1)	O(1)	84.1(1)	S(3)	P(1)	O(4)	114.5(2)
Mo(2)	Mo(1)	O(1)	131.2(1)	S(4)	P(1)	O(3)	113.4(2)
S(1)	Mo(1)	S(1)	107.04(4)	S(4)	P(1)	O(4)	112.2(2)
S(1)	Mo(1)	S(2)	95.17(5)	O(3)	P(1)	O(4)	96.9(2)
S(1)	Mo(1)	O(1)	169.3(2)	S(5)	P(2)	S(6)	106.3(1)
S(1)	Mo(1)	S(2)	109.63(5)	S(5)	P(2)	O(5)	113.2(2)
S(1)	Mo(1)	S(3)	160.12(5)	S(5)	P(2)	O(6)	111.7(2)
S(1)	Mo(1)	O(1)	83.5(1)	S(6)	P(2)	O(5)	113.3(2)
S(2)	Mo(1)	S(4)	158.74(5)	S(6)	P(2)	O(6)	114.6(2)
S(2)	Mo(1)	O(1)	82.9(2)	O(5)	P(2)	O(6)	97.7(3)
Mo(1)	Mo(2)	O(2)	84.4(2)	Mo(1)	O(1)	C(1)	123.3(3)
Mo(1)	Mo(2)	O(2)	131.7(2)	Mo(2)	O(2)	C(1)	123.8(3)
Mo(2)	Mo(2)	O(2)	137.2(2)	P(1)	O(3)	C(3)	120.3(4)
S(1)	Mo(2)	S(2)	109.74(5)	P(1)	O(4)	C(4)	120.3(4)
S(1)	Mo(2)	S(2)	95.14(5)	P(2)	O(5)	C(5)	120.7(4)
S(1)	Mo(2)	S(5)	159.48(6)	P(2)	O(6)	C(6)	120.3(5)
S(1)	Mo(2)	O(2)	83.3(2)	O(1)	C(1)	O(2)	124.4(5)
S(2)	Mo(2)	S(2)	107.18(4)	O(1)	C(1)	C(2)	118.7(5)
S(2)	Mo(2)	S(6)	159.48(6)	O(2)	C(1)	C(2)	116.9(6)
S(2)	Mo(2)	O(2)	83.4(2)	O(3)	C(3)	C(7)	109.0(6)
S(2)	Mo(2)	O(2)	169.1(2)	O(4)	C(4)	C(8)	108.2(6)
Mo(1)	S(1)	Mo(1)	71.80(4)	O(5)	C(5)	C(9)	110.6(8)
Mo(1)	S(1)	Mo(2)	77.66(4)	O(6)	C(6)	C(10)	108.5(9)
Mo(1)	S(1)	Mo(2)	66.77(5)	O(01)	C(01)	C(02)	115(2)
Mo(1)	S(2)	Mo(2)	70.00(4)	O(01)	C(01)	C(02)	115(2)
Mo(1)	S(2)	Mo(2)	77.84(4)	O(02)	C(01)	C(02)	130(3)

[a] Numbers in parentheses are e.s.d.s in the least significant digits.

deuterium. At first, the peak may overlap that of CH_3 of the (dtp) ligands. However, it shifts to low field owing to the rapid proton exchange of active hydrogen with OH in the air or in the solvent.

Cyclic voltammograms (see Fig. 5)

The instrument used consists of a CV-1B Cyclic voltammograph and an X–Y recorder. The reaction cell includes three compartments: a platinum auxiliary electrode, SCE reference electrode and a Pt working electrode.

Discussion

Obviously, the cluster configuration of **4** is very similar to those of **2** and **3**, all of which are of cubane structure. However, from the important crystallographic data including the distances and angles of these three tetranuclear Mo clusters (see Table 7), some significant differences can still be seen. First, the average Mo–Mo bond lengths of **3** (2.811 Å) and **4** (2.808 Å) are notably longer than that of **2** (2.764 Å) (*c.* 0.04–0.05 Å). This may be related to differences in the synthetic routes of **2**, **3** and **4** as shown below.

(i) The ligand substitution reaction of a known cluster compound

$$\underset{\mathbf{1}}{\{Mo_4S_4(\mu\text{-dtp})_2(dtp)_4\}} + HOAc + Ac_2O \longrightarrow \underset{\mathbf{2}}{\{Mo_4S_4(\mu\text{-OAc})_4(dtp)_4\}}$$

(ii) [3+1] reaction mode

$$\{Mo_3S_4(\mu\text{-dtp})(dtp)_3 \cdot H_2O\} + Mo(CO)_6 + HOAc + Ac_2O \longrightarrow \mathbf{3} \text{ and } \mathbf{4}$$

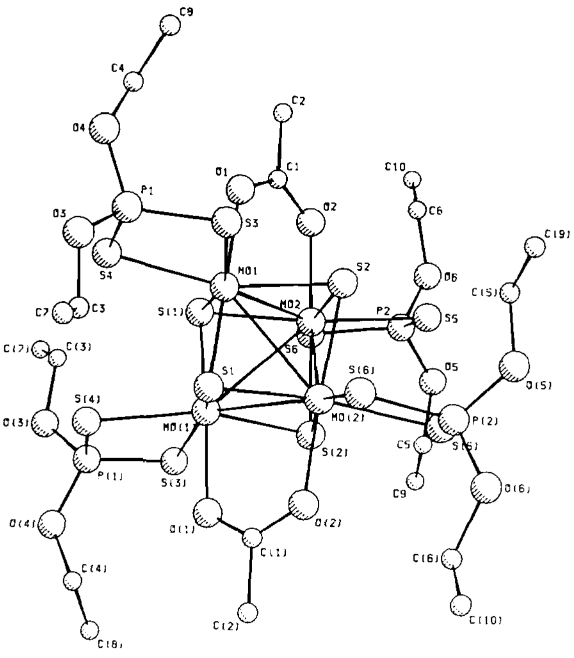

Fig. 1. The geometry of the $[\mathrm{Mo_4S_4(\mu\text{-}OAc)_2(dtp)_4}]^-$ cluster anion.

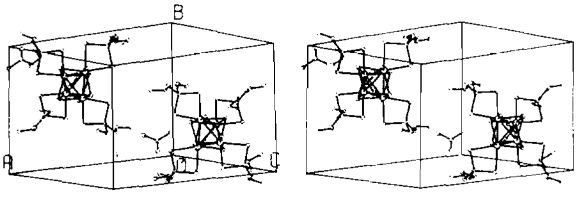

Fig. 2. The packing of 4 in the unit cell.

From the structural analysis and IR spectra, it is deduced that the cluster core of 3 and 4 is $[\mathrm{Mo_4S_4(\mu\text{-}OAc)_2(dtp)_4}]^{n-}$, where n awaits definition.

Secondly, so far $[\mathrm{Mo_4S_4(\eta\text{-}C_5H_4Pr^i)_4}]^{n+}$ ($n=0$, 1, 2) [2] and $[\mathrm{Mo_4S_4(edta)_2}]^{n-}$ ($n=2$, 3, 4) [1] have been reported in the literature. They have almost the same cubane type structure but different oxidation states of Mo. The notable feature is that the Mo–Mo distances vary regularly with the oxidation state of Mo as shown in Table 8.

The Mo–Mo distances in $[\mathrm{Mo_4S_4(edta)_2}]^{n-}$ shorten as the electron numbers in $\{\mathrm{Mo_4}\}$ increase (10, 11, 12), i.e. the average oxidation state of Mo decreases (3.50, 3.25, 3.00), whereas in $[\mathrm{Mo_4S_4(\eta\text{-}C_5H_4Pr^i)_4}]^{n+}$, the Mo–Mo bond lengths increase. It is reasonable to deduce from the Mo–Mo distances given in Table 8 that the same oxidation states of Mo in 3 and 4 are different from that in 2. Meanwhile, since the oxidation state of Mo in 2 is 3.50 as stated earlier, we can further infer that the oxidation states of Mo in 3 and 4 are 3.25, that means $\{\mathrm{Mo_4}\}$ may be regarded as an 11 electron system and the formula

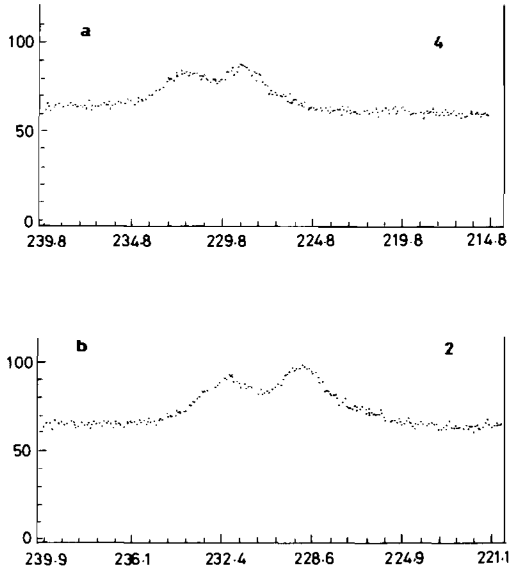

Fig. 3. XPS spectrum of the core electron: (a) in $[\mathrm{Mo_4S_4(OAc)_2(dtp)_4 \cdot H}]$ (4), i.e. $[\mathrm{Mo_4S_4}]^{5+}$; (b) in $[\mathrm{Mo_4S_4(OAc)_2(dtp)_4}]$ (2), i.e. $[\mathrm{Mo_4S_4}]^{6+}$.

for the corresponding cluster molecule as $[\mathrm{Mo_4S_4(\mu\text{-}OAc)_2(dtp)_4}]^-$.

On account of the absence of the non-hydrogen cation peak in the electron density map of the X-ray structural analysis, we therefore suppose the cation to be hydrogen and thus the complete formula for cluster molecules of 3 and 4 is $[\mathrm{Mo_4S_4(\mu\text{-}OAc)_2(dtp)_4 \cdot H}]$ (4 has an additional interstitial solvent acetone molecule). This is supported by the ^{1}H NMR study, which indicates that there is actually an active hydrogen in 4, and it can be rapidly exchanged by deuterium, while there is no such hydrogen in 2.

The scc-EHMO molecular orbital method has been used to study the electronic structures of a series of Mo cluster compounds [14]. It is shown that at C_{2v} or C_{3v} symmetry, owing to the distortion of the cluster configuration deviated from T_d and the nature of the ligands, the ten electrons of the $\{\mathrm{Mo_4}\}$ fragment can stabilize the $\mathrm{Mo_4S_4}$ core to form six Mo–Mo bonds. In $[\mathrm{Mo_4S_4}]^{5+}$ obtained from the [3 + 1] mode, however, due to the increase of the metal–ligand interaction, the addition of one electron to the frontier region has resulted in a weaker and accordingly longer Mo–Mo bond length [15].

Let us now compare the XPS spectra and the electrochemical behavior of 4 and 2. The values of the observed binding energies of 4 are somewhat less than those of 2 (for $3d_{3/2}$ and $3d_{5/2}$). This suggests that the oxidation state of Mo of 4 is lower than that of 2. In addition, both the cyclic voltammograms of 4 and 2 have two quasi-reversible waves. The E_p

TABLE 5. Binding energies (eV)

Sample	$[Mo_3S_4]^a$	$[Mo_4S_4]$ (**2**)	$[Mo_4S_4]$ (**4**)
$3d_{3/2}$	233.65	232.21	232.04
$3d_{5/2}$	230.95	229.05	228.84
Mo oxidation state	+4.00	+3.50	+3.25

[a]Reference sample.

TABLE 6. Parameters of the ESR spectra

Specimen	Temperature (K)	g
2	289	$g_1=2.79$, $g_2=2.29$, $g_3\sim1.98$
	77	$g_1=2.37$, $g_2=2.14$, $g_3=1.98$
4	289	$g_1=2.15$, $g_2=1.97$
	77	$g_1=2.00$, $g_2=1.95$, $g_3=1.92$

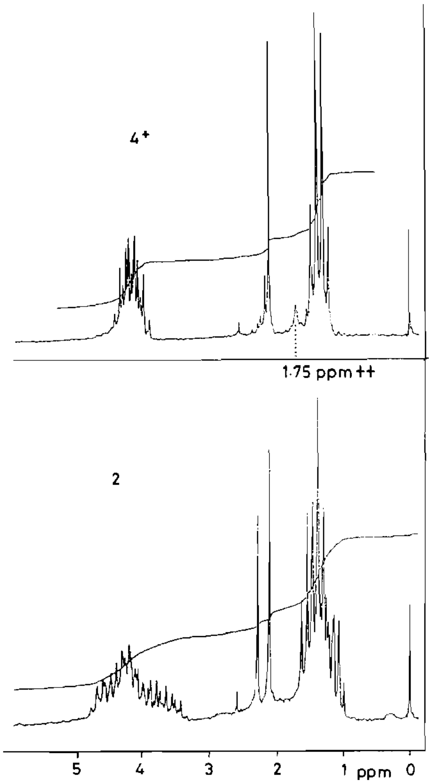

Fig. 4. ^1H NMR spectrum of **2** and **4** in $CDCl_3$ together with the peak integrals. $^+$The measurement was performed after the product was left standing for 1/2 h. $^{++}$Peak of active hydrogen.

values of **4** have shifted to more positive values than those of **2**, indicating that **4** is more readily reduced than **2**. These studies give further support to the inference that the formula of **3** and **4** is $[Mo_4S_4(\mu\text{-}OAc)_2(dtp)_4\cdot H]$. Moreover, the formation of $[Mo_4S_4]^{5+}$ may be attributed to the reducing atmosphere of $Mo(CO)_6$.

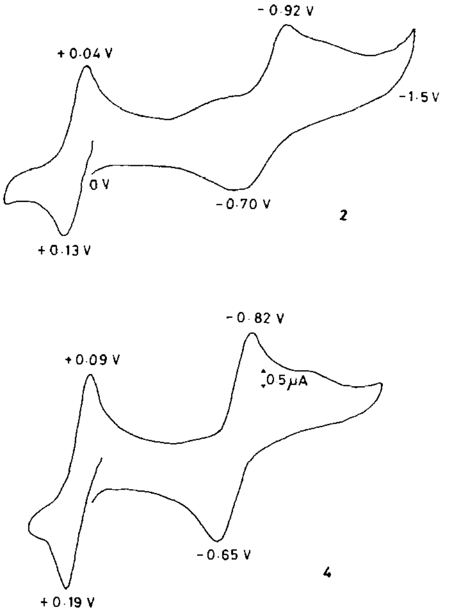

Fig. 5. Cyclic voltammograms (100 mV/s) of $[Mo_4S_4]^{6+}$ (**2**) and $[Mo_4S_4]^{5+}$ (**4**) (2 mM) in DMF solution containing 0.1 M Bu_4NClO_4 as the supporting electrolyte; peak potential vs. SCE.

Finally, as to what form the active hydrogen atom takes in the cluster structure, from the present experimental results, it can be seen that there is little possibility of its existence as a free cation. It is highly probable that it exists as (SH) or (OH) statistically distributed in the ligands. Furthermore, it is interesting to note that the ^1H NMR and ESR spectra of **4** and **2** are significantly different from each other; **4** and **2** are both paramagnetic, indicating that they may have novel magnetic behavior [16]. This still needs further study.

Supplementary material

A list of the observed and calculated structure factors may be obtained from the authors.

TABLE 7. Important crystallographic data and bonding parameters of $[Mo_4S_4(\mu\text{-}OAc)_2(dtp)_4]^{n-}$ (n = 0, 1)

	2	3	4
Formula	$Mo_4S_4(\mu\text{-}OAc)_2(dtp)_4$	$[Mo_4S_4(\mu\text{-}OAc)_2(dtp)_4 \cdot H]$	$[Mo_4S_4(\mu\text{-}OAc)_2(dtp)_4 \cdot H] \cdot OC(CH_3)_2$
Space group	*P2/c*	*Pcab*	*P2/n*
Cell parameters			
a (Å)	13.176(4)	18.90(2)	17.271(3)
b (Å)	11.699(3)	21.678(4)	11.985(3)
c (Å)	18.526(4)	24.491(4)	13.061(2)
β (°)	116.11(3)		105.94(1)
V (Å³)	2564(3)	10031(7)	2599(2)
Z (Å³)	2	8	2
D_c (g cm^{-3})	1.776	1.818	1.826
R factor	0.085	0.069	0.040
Mo–Mo (Å)	2.665(2) (2×) 2.748(2) 2.739(2) 2.879(2) (2×) av. = 2.764	2.685(1) 2.707(1) 2.765(1) 2.772(1) 2.969(1) 2.969(1) av. = 2.811	2.696(1) (2×) 2.750(1) 2.761(1) 2.972(1) (2×) av. = 2.808
Mo–S (dtp) (Å)	2.517(4) 2.508(4) 2.543(4) 2.542(4) av. = 2.528	2.481(2) 2.495(2) 2.550(2) 2.563(2) 2.495(2) 2.498(2) 2.557(2) 2.564(2) av. = 2.525	2.500(2) 2.497(2) 2.553(1) 2.557(2) av. = 2.527
Mo–O (OAc) (Å)	2.170(8) 2.145(8) av. = 2.158	2.181(5) 2.170(5) 2.193(4) 2.208(5) av. = 2.188	2.170(3) 2.157(4) av. = 2.163
S–Mo–S (°) (S:μ_3-S)	93.3(1)–109.6(1)	94.85(7)–110.11(7)	95.14(5)–109.74(5)

TABLE 8. Mo oxidation states and Mo–Mo bond lengths

Compounds	*n*	Electrons of {Mo_4}	Mo oxidation states	Mo–Mo bond length
$[Mo_4S_4(edta)_2]^{n-}$	4	12	+3.00	2.783
	3	11	+3.25	2.807
	2	10	+3.50	2.826
$[Mo_4S_4(\eta\text{-}C_5H_4Pr^i)_4]^{n+}$	0	12	+3.00	2.887
	1	11	+3.25	2.856
	2	10	+3.50	2.749
$[Mo_4S_4(\mu\text{-}OAc)_2(dtp)_4]^{n-}$	0	10	+3.50	2.811 (in **3**) 2.808 (in **4**) 2.764 (in **2**)

Acknowledgements

The authors thank the Fuzhou Laboratory of Structural Chemistry for financial support. Thanks are also due to the IR group for the measurement of IR spectra, Professor Gao Huairong of Fuzhou University for helpful discussions about XPS and Professor Fang Yixiong for his careful examination of the manuscript.

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