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Syntheses and structures of two complexes with incomplete cuboidal $Mo_3Te_4{}^{4+}$ and $Mo_3(\mu_3\text{-}S)Te_3{}^{4+}$ cluster cores

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Abstract

The reaction of tributylphosphine, benzoic acid and $Mo_3Te_7(S_2P(OPr^i)_2)_3I$ produced a new compound with triangular cluster skeleton $Mo_3Te_4{}^{4+}$, $Mo_3Te_4[S_2P(OPr^i)_2]_3(\mu\text{-}PhCO_2)PBu_3$ (**1**). An unexpected compound including an $Mo_3Te_3S^{4+}$ skeleton, $Mo_3(\mu_3\text{-}S)Te_3[S_2P(OPr^i)_2]_3(\mu\text{-}PhNH_2CO_2)PBu_3$ (**2**), was obtained using aminobenzoic acid instead of benzoic acid. X-ray crystallographic analysis revealed that these complexes belong to the $Mo_3E_4{}^{4+}$ (E = S, Se, Te) incomplete cuboidal cluster family and are dimeric through the Te···Te interaction. ^1H and ^{31}P NMR and IR spectroscopic data were also used to characterize these compounds. ©2000 Elsevier Science Ltd All rights reserved.

Keywords: Cluster compounds; Molybdenum complexes; Tellurium-rich compounds; De-tellurium reaction; Crystal structures

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1. Introduction

Intensive studies have been carried out on molybdenum/tungsten chalcogenide clusters since 1985 [1–5]. Compared with sulfides and selenides, the chemistry of tellurido complexes of molybdenum and tungsten is much less developed because many traditional reagents applicable to Mo/W–S/Se systems are not simply transferable to the Mo/W–Te system, and limited progress has been made in the exploration of effective reagents or starting materials [6]. Until recently, only a few such Mo/W–Te clusters, including the triangular cluster complex $Cs_{4.5}[Mo_3Te_7(CN)_6]I_{2.5}\cdot 3H_2O$ [7] with an $Mo_3(\mu_3\text{-}Te)(\mu\text{-}Te_2)_3{}^{4+}$ core, the tetrahedral clusters $K_7[Mo_4Te_4(CN)_{12}]\cdot H_2O$ and $K_6[W_4Te_4(CN)_{12}]\cdot 5H_2O$ containing the $M_4(\mu_3\text{-}Te)_4{}^{n+}$ ($n = 5, 6$) cuboidal core [8–10], and the octahedral cluster $[Na(Py)_6]^+[W_6Te_8(Py)_6]^-\cdot Py$ and $W_6Te_8(PiP)_6\cdot 6PiP$ with a W_6Te_8 core [11], have been reported. However, the absence of the Mo_3Te_4 type cluster, of which the sulfide and selenide analogues have been well studied, has drawn our attention to conversion of the Mo_3Te_7 cluster core to Mo_3Te_4. In comparison with those compounds containing Mo_3Te_7, Mo_4Te_4 or W_6Te_8 cores, the compound with an Mo_3Te_4 core has higher reactivity since it possesses a vacant subsite and three μ-Te ligands, making it potentially a good precursor for other tellurido cluster compounds.

A convenient route to the $M_3(\mu_3\text{-}E)(\mu\text{-}E)_3{}^{4+}$ (M = Mo, W; E = S, Se) cluster by reaction of $M_3(\mu_3\text{-}E)(\mu\text{-}E_2)_3{}^{4+}$ cluster compounds with phosphine or cyanide has been reported [12–15]. Saito and co-workers considered that the $Mo_3Te_7{}^{4+}$ fragment has an extraordinary stability in aqueous cyanide or in CH_3OH with PEt_3 [7]. However, our experiments showed that the $Mo_3Te_7{}^{4+}$ cluster core is stable in CH_2Cl_2 with PPh_3, and the reaction of $Mo_3Te_7[S_2P(OPr^i)_2]_3I$ with tributylphosphine leads to transformation of the $Mo_3Te_7{}^{4+}$ core to the $Mo_3Te_4{}^{4+}$ core. Another very interesting result in our experiments is that aromatic acids might have different effects on the transformation of the $Mo_3Te_7{}^{4+}$ cluster core to produce a Te-capping or S-capping triangular cluster core, which has never been observed in previous studies in this field. Herein we report the syntheses and molecular structures of two cluster compounds containing $Mo_3Te_4{}^{4+}$ and $Mo_3(\mu_3\text{-}S)Te_3{}^{4+}$ cores.

2. Experimental

All manipulations were carried out under dinitrogen atmosphere using standard Schlenk techniques. The solvents were degassed prior to use. Other materials were reagent-grade purity and used without further purification. The ^{31}P NMR

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Table 1
Crystallographic data for $Mo_3Te_4[S_2P(OPr^i)_2]_3(\mu\text{-}PhCO_2)PBu_3$ and $Mo_3(\mu_3\text{-}S)Te_3[S_2P(OPr^i)_2]_3(\mu\text{-}PhNH_2CO_2)PBu_3$

Formula	$Mo_3Te_4S_6P_4O_8C_{37}H_{74}$	$Mo_3Te_3S_7P_4O_8C_{37}NH_{75}$
FW	1762.42	1680.9
Space group	$C2/c$	$P\bar{1}$
a (Å)	29.8261(3)	15.9465(2)
b (Å)	16.4363(3)	16.0576(1)
c (Å)	26.6482(6)	16.3111(3)
α (°)	90	103.508(1)
β (°)	96.218(1)	115.859(1)
γ (°)	90	100.141(1)
V (Å^3)	12986.9(6)	3465.19(8)
Z	8	2
D_{calc} (g cm^{-3})	1.803	1.611
μ (mm^{-1})	2.664	2.112
R_1, wR_2 (%) [a]	7.95, 17.24	8.66, 20.24
Weighting scheme [b]	$w^{-1}=\sigma^2(F_o^2)+(0.0858P)^2+82.0874P$	$w^{-1}=\sigma^2(F_o^2)+(0.1149P)^2$

[a] $wR_2=\sqrt{\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2}$.
[b] $P=(F_o^2+2F_c^2)/3$.

spectra were obtained on a Varian Unity-500 spectrometer in CH_2Cl_2 solutions with 80% H_3PO_4 as external standard in a $^{31}P\{^1H\}$ mode. UV–Vis spectra were recorded on a Varian Cary-2390 spectrophotometer in CH_2Cl_2 solutions. IR spectra were recorded on a Nicolet Magna 750 FT-IR spectrophotometer using KBr pellets (4000–500 cm^{-1}) and CsI pellets (600–120 cm^{-1}). Element analyses were carried out by the Elemental Analysis Laboratory in our institute.

Preparation of $Mo_3Te_4S_6P_4O_8C_{37}H_{74}$ (**1**): 0.195 g (0.1 mmol) $Mo_3Te_7(S_2P(OPr^i)_2)_3I$, which was prepared according to the literature [16], 0.018 g (0.15 mmol) benzoic acid and 0.3 ml tributylphosphine were heated in 30 ml mixed-solvent of CH_2Cl_2–C_2H_5OH at 40°C for 3 h. The black crystals were isolated after the solution was allowed to stand for 4 days (0.072 g, yield 41%). *Anal*. Calc. for $Mo_3Te_4[S_2P(OPr^i)_2]_3(\mu\text{-}PhCO_2)PBu_3$: C, 25.23; H, 4.23. Found: C, 25.05; H, 4.29%. IR (KBr pellet, cm^{-1}): ν 1600, 1510 (CO), 716, 677 (C_6H_5). UV–Vis (CH_2Cl_2, nm): λ 370, 620. ^{31}P NMR (200 MHz, CH_2Cl_2, H_3PO_4): δ 111.7, 85.2, 22.3.

The preparation procedure of $Mo_3Te_3S_7P_4O_8C_{37}NH_{75}$ (**2**) was the same as for complex **1** except that 2-aminobenzoic acid was used instead of benzoic acid (0.053 g, yield 32%). *Anal*. Calc. for $Mo_3(\mu_3\text{-}S)Te_3[S_2P(OPr^i)_2]_3(\mu\text{-}PhNH_2\text{-}CO_2)PBu_3$: C, 26.44; H, 4.5; N, 0.83. Found: C, 26.62; H, 4.91; N, 0.88%. IR (KBr pellet, cm^{-1}): ν 1614, 1498 (CO), 3361 (NH_2), 667 (C_6H_5), 414 (Mo–(μ_3-S)). UV–Vis (CH_2Cl_2, nm): λ 337, 580. ^{31}P NMR (200 MHz, CH_2Cl_2, H_3PO_4): δ 106.0, 85.6, 17.8.

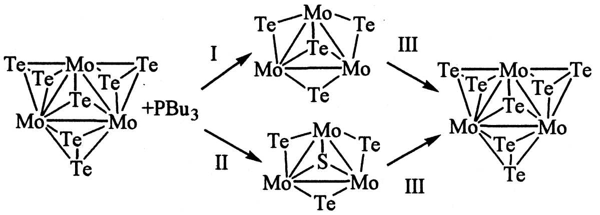
2.1. X-ray crystallography

The crystal data of complexes **1** and **2** were collected on a Siemens SMART CCD area detector diffractometer using graphite-monochromated Mo Kα radiation ($\lambda=0.71073$ Å) at 293 K, and empirical absorption correction by SADABS [17] was applied to the intensity data. Structure solution and refinement were performed on a SGI INDY workstation using the SHELXTL-5 program package [18]. The crystallographic data and refinement parameters are listed in Table 1.

3. Discussion

3.1. Synthesis

The preparation of complex **1**, $Mo_3Te_4[S_2P(OPr^i)_2]_3(\mu\text{-}PhCO_2)PBu_3$, using the abstraction of tellurium from an $Mo_3Te_7^{4+}$ cluster core to generate $Mo_3Te_4^{4+}$, is very similar to the preparation of the sulfide and selenide analogues, in which the bridging ligand is benzoic acid. This reaction can be completed at ambient temperature within a few hours. The preparation of complex **2**, $Mo_3(\mu_3\text{-}S)Te_3[S_2P(OPr^i)_2]_3(\mu\text{-}PhNH_2CO_2)PBu_3$, is similar to that of **1**, except that 2-aminobenzoic acid was employed instead of benzoic acid, and the capping tellurium atom of the cluster core was substituted by sulfur in complex **2**, which might originate from the decomposition of the DTP (dialkyldithiophosphinate) ligand. It seems plausible that there is ‘competition’ between sulfur and tellurium to occupy the cap site in solution, and the nature of the bridging ligand might affect the structure of the final product. We found that the formation of the $Mo_3Te_3S^{4+}$ skeleton was not an incidental event since we could repeat this experiment very well. Furthermore, by using 4-aminobenzoic acid instead of 2-aminobenzoic acid, a similar product can be obtained, in which the position of 2-aminobenzoic acid was replaced by 4-aminobenzoic acid but the cluster core was still $Mo_3Te_3S^{4+}$ [19]. These compounds are mildly air sensitive, and when their solutions were exposed in air for several days, a tellurium mirror at the bottom of the receptacles was found along with some dark-brown crystals, which proved to be $Mo_3Te_7[S_2P(OPr^i)_2]_3I$ by IR spectra and X-ray diffraction experiments. The reaction scheme can be represented as shown in Scheme 1.



I benzoic acid; II 2(4)-aminobenzoic acid; III O_2, decomposition

Scheme 1.

3.2. Structure

The structures of cluster molecules **1** and **2** are shown in Fig. 1, and selected bond distances and angles are listed in Tables 2 and 3, respectively.

In complex **1**, the three molybdenum atoms define an approximate isosceles triangle with Mo–Mo distances of 2.940(2), 2.970(2) and 2.832(2) Å, respectively, of which the shortest side is bridged by a $PhCO_2^-$ ligand. The average Mo–Mo distance of 2.914 Å is slightly longer than the value of 2.891 Å in $Cs_{4.5}[Mo_3Te_7(CN)_6]I_{2.5}\cdot 3H_2O$ [7] and 2.889 Å in $Mo_3Te_7[S_2P(OPr^i)_2]_3I$ [16]. One μ_3-Te atom and three μ-Te atoms are located above and below the Mo_3 plane, respectively, to form an incomplete cuboidal cluster skeleton. The Mo–(μ-Te) distances range from 2.597(2) to 2.649(2) Å. The average Mo–(μ_3-Te) distance of 2.650 Å is comparable to those found in $Mo_3Te_{10}I_{10}$ (2.661 Å) [20], $[Mo_3Te_7(CN)_6]^{3-}$ (2.696 Å) and $[Mo_4Te_4(CN)_{12}]^{7-}$ (2.676 Å) [8–10]. In addition to the $PhCO_2^-$ ligand that bridges two Mo atoms and one PBu_3 molecule coordinated to the third Mo atom, there is a terminal $S_2P(OPr^i)_2^-$ ligand chelating to each Mo atom. As a result, each Mo atom has a distorted octahedral coordination geometry. The Mo–P distance of 2.615(5) Å is comparable to those of other complexes containing the Mo_3S_4 cluster core and PPh_3 ligand [21,22].

Table 2
Selected interatomic distances (Å) and angles (°) in $Mo_3Te_4[S_2P(OPr^i)_2]_3(\mu\text{-}PhCO_2)PBu_3$ (**1**)

Mo(1)–Te(2)	2.606(2)	Mo(2)–Te(1)	2.608(2)
Mo(1)–Te(1)	2.612(2)	Mo(2)–Te(4)	2.637(2)
Mo(1)–P(4)	2.615(5)	Mo(2)–Te(3)	2.639(2)
Mo(1)–S(1)	2.630(5)	Mo(2)–Mo(3)	2.831(2)
Mo(1)–S(2)	2.636(5)	Mo(3)–O(8)	2.207(10)
Mo(1)–Te(4)	2.663(2)	Mo(3)–S(6)	2.529(5)
Mo(1)–Mo(3)	2.946(2)	Mo(3)–S(5)	2.577(5)
Mo(1)–Mo(2)	2.972(2)	Mo(3)–Te(2)	2.597(2)
Mo(2)–O(7)	2.216(11)	Mo(3)–Te(4)	2.648(2)
Mo(2)–S(3)	2.540(5)	Mo(3)–Te(3)	2.649(2)
Mo(2)–S(4)	2.576(5)	Te(3)–Te(3)#1 [a]	3.103(2)
Te(2)–Mo(1)–P(4)	81.26(13)	S(4)–Mo(2)–Te(4)	155.66(13)
Te(2)–Mo(1)–Te(1)	100.68(6)	Te(1)–Mo(2)–Te(4)	108.42(6)
P(4)–Mo(1)–Te(1)	82.91(14)	O(7)–Mo(2)–Te(3)	84.9(3)
Te(2)–Mo(1)–S(1)	91.68(12)	S(3)–Mo(2)–Te(3)	157.22(13)
P(4)–Mo(1)–S(1)	84.3(2)	S(4)–Mo(2)–Te(3)	81.76(13)
Te(1)–Mo(1)–S(1)	160.58(14)	Te(1)–Mo(2)–Te(3)	91.25(6)
Te(2)–Mo(1)–S(2)	161.03(14)	Te(4)–Mo(2)–Te(3)	115.25(7)
P(4)–Mo(1)–S(2)	83.8(2)	O(8)–Mo(3)–S(6)	83.7(3)
Te(1)–Mo(1)–S(2)	88.99(13)	O(8)–Mo(3)–S(5)	82.8(3)
S(1)–Mo(1)–S(2)	75.2(2)	S(6)–Mo(3)–S(5)	77.0(2)
Te(2)–Mo(1)–Te(4)	108.98(7)	O(8)–Mo(3)–Te(2)	168.0(3)
P(4)–Mo(1)–Te(4)	163.17(14)	S(6)–Mo(3)–Te(2)	98.17(13)
Te(1)–Mo(1)–Te(4)	107.41(6)	S(5)–Mo(3)–Te(2)	86.11(13)
S(1)–Mo(1)–Te(4)	82.17(13)	O(8)–Mo(3)–Te(4)	82.2(3)
S(2)–Mo(1)–Te(4)	83.13(14)	S(6)–Mo(3)–Te(4)	81.93(14)
O(7)–Mo(2)–S(3)	82.7(3)	S(5)–Mo(3)–Te(4)	155.27(14)
O(7)–Mo(2)–S(4)	83.5(3)	Te(2)–Mo(3)–Te(4)	109.73(7)
S(3)–Mo(2)–S(4)	77.9(2)	O(8)–Mo(3)–Te(3)	84.0(3)
O(7)–Mo(2)–Te(1)	170.6(3)	S(6)–Mo(3)–Te(3)	157.8(2)
S(3)–Mo(2)–Te(1)	97.94(13)	S(5)–Mo(3)–Te(3)	83.23(14)
S(4)–Mo(2)–Te(1)	87.41(13)	Te(2)–Mo(3)–Te(3)	90.28(6)
O(7)–Mo(2)–Te(4)	81.0(3)	Te(4)–Mo(3)–Te(3)	114.53(7)
S(3)–Mo(2)–Te(4)	81.58(12)		

[a] Symmetry transformations used to generate equivalent atoms: #1: $-x-1/2$, $-y-1/2$, $-z+1$.

Table 3
Selected interatomic distances (Å) and and angles (°) in $Mo_3(\mu_3\text{-}S)Te_3[S_2P(OPr^i)_2]_3(\mu\text{-}PhNH_2CO_2)PBu_3$ (**2**)

Mo(1)–S(7)	2.384(4)	Mo(2)–S(4)	2.623(5)
Mo(1)–Te(2)	2.633(2)	Mo(2)–Te(1)	2.647(2)
Mo(1)–Te(1)	2.646(2)	Mo(2)–Te(3)	2.687(2)
Mo(1)–S(2)	2.657(5)	Mo(2)–Mo(3)	2.822(2)
Mo(1)–S(1)	2.659(5)	Mo(3)–O(7)	2.232(10)
Mo(1)–P(4)	2.675(5)	Mo(3)–S(7)	2.364(4)
Mo(1)–Mo(3)	2.900(2)	Mo(3)–S(6)	2.562(4)
Mo(1)–Mo(2)	2.921(2)	Mo(3)–S(5)	2.641(5)
Mo(2)–O(8)	2.261(11)	Mo(3)–Te(2)	2.644(2)
Mo(2)–S(7)	2.358(4)	Mo(3)–Te(3)	2.679(2)
Mo(2)–S(3)	2.571(4)	Te(3)–Te(3)#1 [a]	3.140(2)
S(7)–Mo(1)–Te(2)	107.57(12)	S(3)–Mo(2)–Te(1)	97.77(12)
S(7)–Mo(1)–Te(1)	106.38(11)	S(4)–Mo(2)–Te(1)	88.24(12)
Te(2)–Mo(1)–Te(1)	97.71(6)	O(8)–Mo(2)–Te(3)	83.5(3)
S(7)–Mo(1)–S(2)	83.5(2)	S(7)–Mo(2)–Te(3)	111.31(11)
Te(2)–Mo(1)–S(2)	162.87(13)	S(3)–Mo(2)–Te(3)	159.37(12)
Te(1)–Mo(1)–S(2)	91.41(12)	S(4)–Mo(2)–Te(3)	84.77(11)
S(7)–Mo(1)–S(1)	82.4(2)	Te(1)–Mo(2)–Te(3)	91.56(5)
Te(2)–Mo(1)–S(1)	93.10(12)	O(7)–Mo(3)–S(7)	82.7(3)
Te(1)–Mo(1)–S(1)	163.15(13)	O(7)–Mo(3)–S(6)	84.5(3)
S(2)–Mo(1)–S(1)	75.1(2)	S(7)–Mo(3)–S(6)	83.9(2)
S(7)–Mo(1)–P(4)	164.1(2)	O(7)–Mo(3)–S(5)	81.5(3)
Te(2)–Mo(1)–P(4)	82.12(14)	S(7)–Mo(3)–S(5)	156.8(2)
Te(1)–Mo(1)–P(4)	84.1(2)	S(6)–Mo(3)–S(5)	77.7(2)
S(2)–Mo(1)–P(4)	84.4(2)	O(7)–Mo(3)–Te(2)	169.5(3)
S(1)–Mo(1)–P(4)	84.6(2)	S(7)–Mo(3)–Te(2)	107.82(11)
O(8)–Mo(2)–S(7)	82.9(3)	S(6)–Mo(3)–Te(2)	97.08(12)
O(8)–Mo(2)–S(3)	84.3(3)	S(5)–Mo(3)–Te(2)	88.58(11)
S(7)–Mo(2)–S(3)	83.5(2)	O(7)–Mo(3)–Te(3)	84.9(3)
O(8)–Mo(2)–S(4)	82.6(3)	S(7)–Mo(3)–Te(3)	111.38(11)
S(7)–Mo(2)–S(4)	156.9(2)	S(6)–Mo(3)–Te(3)	160.06(13)
S(3)–Mo(2)–S(4)	77.2(2)	S(5)–Mo(3)–Te(3)	84.12(11)
O(8)–Mo(2)–Te(1)	169.9(3)	Te(2)–Mo(3)–Te(3)	90.45(5)
S(7)–Mo(2)–Te(1)	107.11(11)		

[a] Symmetry transformations used to generate equivalent atoms: #1: $-x+1$, $-y+1$, $-z+1$.

In comparison, the structure of complex **2** is similar to that of complex **1** with the (μ_3-Te) and bridging $PhCO_2^-$ ligand replaced by the (μ_3-S) and 2-aminobenzoic acid group. The average Mo–Mo distance of **2** is slightly shorter (ca. 0.01–

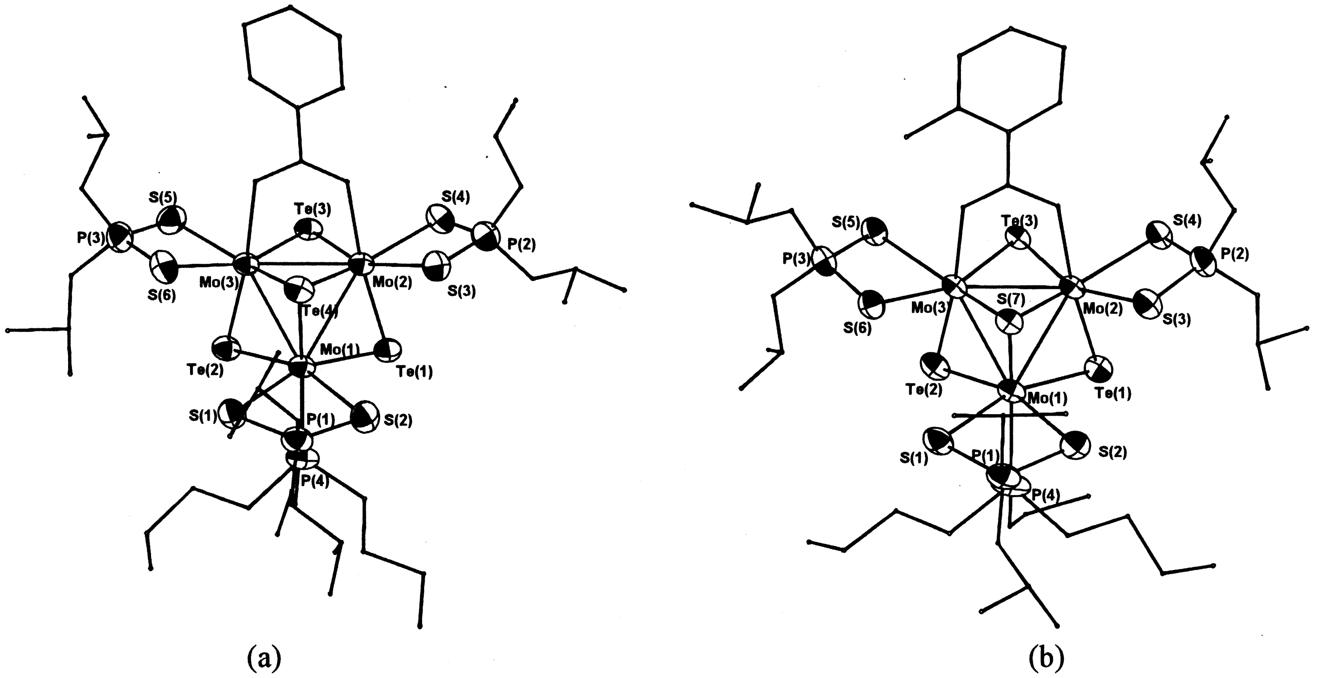


Fig. 1. Molecular drawings of (a) $Mo_3Te_4[S_2P(OPr^i)_2]_3(\mu\text{-}PhCO_2)PBu_3$ (**1**) and (b) $Mo_3(\mu_3\text{-}S)Te_3[S_2P(OPr^i)_2]_3(\mu\text{-}PhNH_2CO_2)PBu_3$ (**2**). The labels for carbon and oxygen atoms have been omitted for clarity.

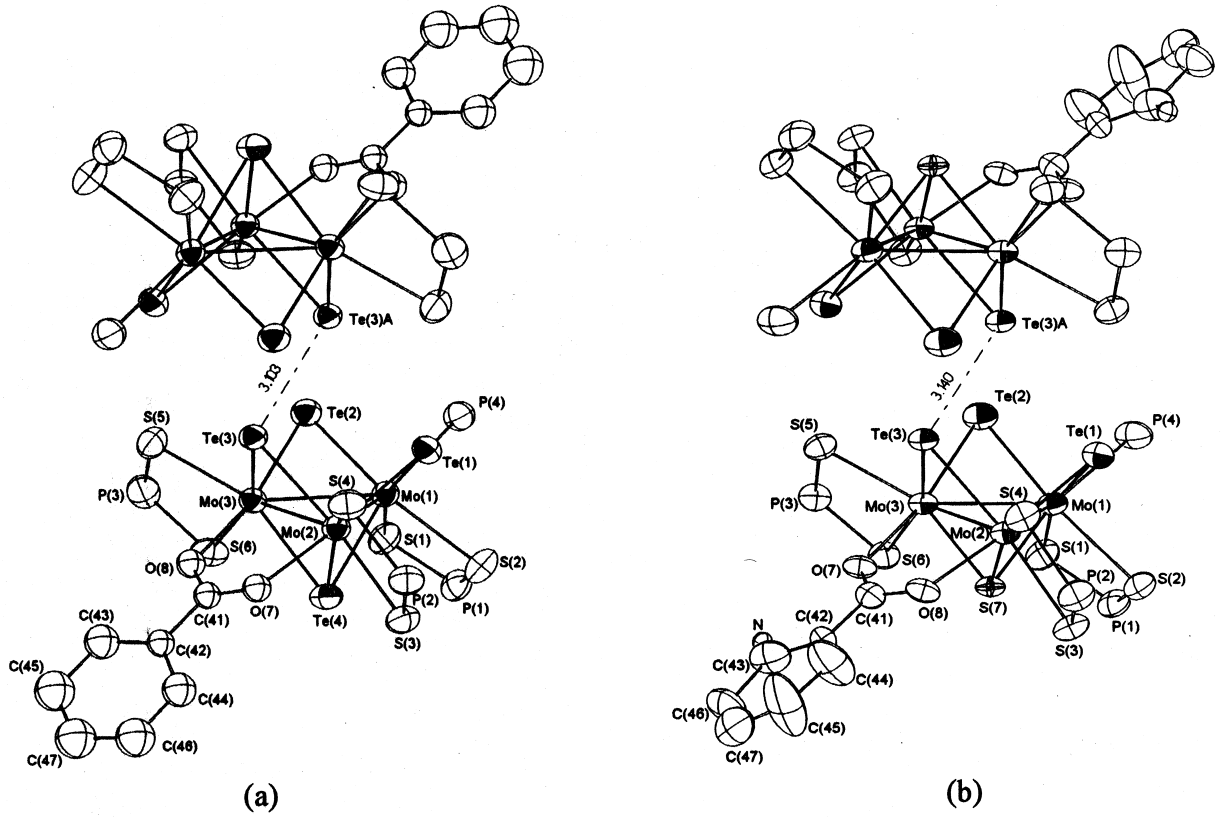


Fig. 2. ORTEP drawings of (a) $Mo_3Te_4[S_2P(OPr^i)_2]_3(\mu\text{-}PhCO_2)PBu_3$ (**1**) and (b) $Mo_3(\mu_3\text{-}S)Te_3[S_2P(OPr^i)_2]_3(\mu\text{-}PhNH_2CO_2)PBu_3$ (**2**) dimers showing the atom labelling scheme at 30% probability of thermal ellipsoids. The butyl and isopropoxy groups have been omitted for clarity.

0.05 Å) than that of **1** because the capping sulfur atom has a smaller covalent radius than tellurium. On the other hand, the Mo–(μ-Te) and the Mo–P distances are significantly elongated (ca. 0.02–0.03 Å for Mo–Te and 0.06 Å for Mo–P).

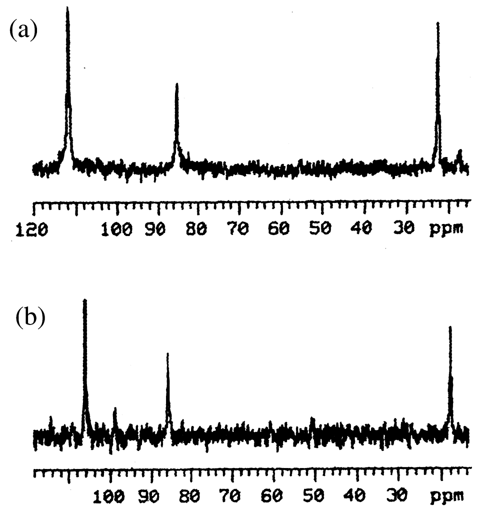


Fig. 3. ^{31}P spectra of (a) $Mo_3Te_4[S_2P(OPr^i)_2]_3(\mu\text{-}PhCO_2)PBu_3$ (**1**) and (b) $Mo_3(\mu_3\text{-}S)Te_3[S_2P(OPr^i)_2]_3(\mu\text{-}PhNH_2CO_2)PBu_3$ (**2**).

It is interesting that there is a short contact between Te(3) and Te(3A) of an adjacent molecule in both complexes (3.103(2) Å in **1** and 3.140(2) Å in **2**), leading to the formation of a dimer (Fig. 2). Consequently, the distances of Te(3) and Mo are elongated (ca. 0.03–0.05 Å) and the coordination environment of Te(3) is somewhat like that of the μ_3-Te (the distances Te(3)–Mo are comparable with Te(4)–Mo). EHMO calculation also attested that there is a weak bond between two Te(3) atoms [1][23]. Although there are some examples of longer Te···Te interactions in existing tellurium-rich tellurides [24,25] (e.g. 3.07–3.17 Å in $LnTe_n$ ($n > 1.75$), 3.16 Å in $NaTe_3$), to our knowledge no example of dimerization of two triangular $Mo_3E_4^{4+}$ ($E = S$, Se) clusters through bonding interaction has been found, although the weaker dimerization through Se···Se interaction (3.415 Å) was reported in the $[M_3Se_4(CN)_9]^{5-}$ ($M = Mo$, W) [14] anion before.

The ^{31}P NMR spectra of complexes **1** and **2** are shown in Fig. 3. The chemical shift of P_1 of the DTP ligand is at 85.2 ppm for complex **1** (85.6 ppm for complex **2**). The peak at 111.8 ppm for complex **1** (106.0 ppm for complex **2**) with twice integration can be assigned to P_2 and P_3 of the DTP ligands, which coordinate symmetrically to Mo_2 and Mo_3, and the chemical shift of PBu_3 is at 22.3 ppm for complex **1** (17.8 ppm for complex **2**). Compared to their counterparts, δ_{P1} has no significant shift and $\delta_{P2,}$ δ_{P3} and δ_{PBu3} for complex **2** have shifted to high field. The substitution of capping-Te (in complex **1**) by capping-S (in complex **2**) in the cluster core should be mainly responsible for these shifts.

Supplementary data

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk) and are available on request quoting the deposition numbers 135939 and 135940.

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[1] Molecular orbital reduced overlap populations (MP) between Te(3) and Te(3A) are 0.052 for complex **1** and 0.027 for complex **2**. The EHMO calculations are based on the position of the atoms obtained from the X-ray structure analysis. Standard atomic parameters of the program were used. When we used a different atomic orbital parameter for tellurium (5s: −20.5, 2.57; 5p: −12.9, 2.16) [26], the MP between Te(3) and Te(3A) was 0.193 for complex **1** and 0.168 for complex **2**.