Synthesis, Structural Characterization and Reactivity of Two New Triangular Molybdenum Cluster Compounds: Mo_3Te_7-$[S_2CN(CH_2CH_2OH)_2]_3I$ and $Mo_3Te_4Y_3[S_2P(^iPrO)_2]_3I$ ($Y_3 = 1.43Te + 1.57S$)

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Two triangular molybdenum-tellurium clusters, Mo_3Te_7-$[S_2CN(CH_2CH_2OH)_2]_3I$ (1) and $Mo_3Te_4Y_3[S_2P(^iPrO)_2]_3I$ ($Y_3 = 1.43Te + 1.57S$) (2), were obtained from the reaction of K · HOdtc [HOdtc = $S_2CN(CH_2CH_2OH)_2$] or K·$^iPr_2dtp$ ($^iPr_2dtp$ = $S_2P[OCH(CH_3)_2]_2$) with a mixed product of elements Mo, Te(S) and I_2 at high temperature. The structures of the two compounds were determined by X-ray crystallography study. Crystal data are, (1): monoclinic, $P2_1/n$, $a = 1.6256(3)$, $b = 1.3264(2)$, $c = 1.8808(4)$ nm, $\beta = 96.923°$, $V = 4.025.9(14)$ nm³, $D_{cal} = 3.050$ g·cm⁻³, $Z = 4$, and (2): monoclinic, $P2_1/n$, $a = 1.4564(2)$, $b = 2.3917(4)$, $c = 1.5094(3)$ nm, $\beta = 114.35(2)°$, $V = 4.0259(14)$ nm³, $D_{cal} = 2.449$ g·cm⁻³ and $Z = 4$. Single crystal analyses show that 1 consists of discrete $Mo_3Te_7[S_2CN(CH_2CH_2OH)_2]_3I$ connected into three-dimensional framework via hydrogen bonds, while 2 forms a linear chain via Te(S)—I interaction.

Keywords   triangle molybdenum-tellurium clusters, synthesis, crystal structure, reactivity

Introduction

In the last two decades intensive studies have been carried out on the molybdenum (tungsten) chalcogenide clusters, resulting in the discovery of series of monomeric, polynuclear Mo(W)- and Mo(W)-heterometallic complexes. Triangular, cubane, octahedral as well as hex-

nuclear raft-type frameworks are typical in the known Mo (W)-S(Se) clusters. These entities are relevant in a number of areas ranging from the bioinorganic chemistry of Mo(W)-S(Se) containing enzyme[1-2] to the synthesis of highly dispersed/amorphous metal chalcogenides, which are important catalysts for hydrogenation/dehydrogenation reactions as well as C—S bond hydrogenation, i.e., crude-oil hydrodesulfurization (HAD) processes,[3-4] and structural relations to Chevrel phase[5-7] and nonlinear optical properties.[8] Compared to the extensively studied Mo (W)-S(Se) clusters, the corresponding telluride chemistry has been rather undeveloped owing to the fact that many traditional reagents applicable to Mo(W)-S(Se) systems are not simply transferable to the Mo(W)-Te system.[9] Up to date, only a few such compounds have been reported, including the first triangular cluster complex $Mo_3Te_7(TeI_3)_3I$ synthesized directly from the high temperature solid state reaction,[10] then $Cs_{4.5}[Mo_3Te_7-(CN)_6]I_{2.5}$ · $3H_2O$ reported by Fedin in 1995,[11] K_7-$[Mo_4Te_4(CN)_{12}]$ · H_2O and $K_6[W_4Te_4(CN)_{12}]$ · $5H_2O$ containing a cuboidal-type $M_4(\mu_3-Te)_4^{n+}$ ($n = 5, 6$) core,[12-13] and $[Na(Py)_6]^+[W_6Te_8(Py)_6]^-$ · Py and $W_6Te_8(PiP)_6$ · 6PiP with a W_6Te_8 core.[14] Recently, we have been paying much attention to the synthesis of new

Mo(W)/Te compounds by the combinational method of high temperature solid state reaction followed by the treatment of its product in solution to afford several triangle $\{M_3Te_7[(RO)_2PS_2]_3\}I$ (M = Mo, W; R = Et, ^iPr) clusters and two incomplete cubane complexes with $[Mo_3Te_4]^{4+}$ core.[15-17] Here, we report two new triangular molybdenum clusters containing telluride.

Experimental

Preparation of $K \cdot S_2CN(CH_2CH_2OH)_2(K \cdot HOdtc)$

CS_2(25 mL) was added into a solution of $NH(CH_2CH_2OH)_2$(35 mL) in MeOH (60 mL). The reaction mixture was stirred for 20 min, heated up to 40 °C, then 60 mL of KOH solution (40%) of MeOH was added. The precipitate was filtered, washed with MeOH and dried in air. $K \cdot {}^iPr_2dtp$ ($^iPr_2dtp = S_2P[OCH(CH_3)_2]_2$) was prepared by dissolve P_2S_5(99%) in isopropanol followed by neutralization with KOH and precipitated in diethyl ether.[15-17]

Synthesis of the compound $Mo_3Te_7(HOdtc)_3I$ [HOdtc = $S_2CN(CH_2CH_2OH)_2$] (1)

A well-ground mixture of $K \cdot HOdtc$ (0.4 g) and the solid precursor (1.0 g) containing $Mo_3Te_7(TeI_3)_3I$, which was prepared directly from solid state reaction of Mo, Te and I_2 powder,[10] was placed in a schlenk flask with 30 mL of pyridine, and heated for 10 h with stirring under nitrogen atmosphere. After filtration, the solvent (pyridine) was removed under vacuum. The black residue was extracted with hot THF (100 mL) and filtered again. The deep brown extract was vaporized under an IR lamp to afford dark-brown crystals 1 after one day (0.12 g). IR (KBr, cm^{-1}): 3332 (br), ν(O—H); 1483 (s), ν(C=N); 1213(s), ν(C—S). Anal. calcd for $Mo_3Te_7[S_2CN(CH_2CH_2OH)_2]I$: C 9.74, H 1.62, N 2.27, Mo 15.57, S 10.39, Te 48.31; found C 9.86, H 1.68, N 2.52, Mo 15.65, S 10.43, Te 48.28.

Synthesis of $Mo_3Te_4Y_3(^iPr_2dtp)_3I$ [$^iPr_2dtp = S_2P(^iPrO)_2$, $Y_3 = 1.43Te + 1.57S$] (2)

The precursor was prepared by a method similar to that just described in literature.[10] A mixture of molybdenum powder (0.288 g, 3 mmol), sulfur powder (0.16 g,

5 mmol), tellurium (0.51 g, 4 mmol) and I_2 (1.27 g, 5 mmol) was ground, pressed and sealed in an evacuated quartz tube, then heated for 4 d at the range of temperature from 375 °C to 385 °C. After being cooled to room temperature, the mixed solid was ground into powder, washed with ethanol and dried in air. The resulting amorphous powder was well ground together with 0.4 g of $K \cdot S_2P[OCH(CH_3)_2]$ and heated at 110 °C for 12 h in a reaction tube under nitrogen atmosphere. The product was extracted with 30 mL of CH_2Cl_2 and filtered, and then 10 mL of ethanol was added into the filtrate. The brown-yellow filtrate was vaporized at room atmosphere, and dark-brown crystals of compound 2 were precipitated after several days (yield, 10% based on Mo powder). IR (KBr, cm^{-1}): 989 (vs), 966 (vs), ν(P—O); 648 (m), 636 (m), 553 (m), ν(P—S). Anal. calcd for $Mo_3Te_4Y_3[S_2P-(^iPrO)_2]_3I$: C 12.02, H 2.34, Mo 16.02, S 13.48, Te 38.56; found C 12.14, H 2.19, Mo 15.97, S 13.57, Te 38.43.

Crystal structure determination

Crystals of 1 and 2 were mounted on a glass fiber with epoxy resin, and used for data collection on a Simens SMART CCD diffractometer with graphite monochromated Mo K_α radiation ($\lambda = 0.071073$ nm) at room temperature. The reflections were corrected by LP factor and by SADABS empirical absorption. All calculations were carried out with a 586 computer with the SHELXTL-5 program package.[18] A total of 19099 ($1.57° \leqslant \theta \leqslant 25.05°$) and 22417 ($1.64° \leqslant \theta \leqslant 25.05°$) reflections were collected respectively, of which independent reflections 7024 [$R_{int} = 0.0698$] for 1 and 8266 [$R_{int} = 0.0485$] for 2 were used in the structure analysis. Other crystallographic data and structure determination parameters are given in Table 1.

Structures of 1 and 2 were solved by direct methods, successive Fourier difference synthesis, and refined by the full matrix least-squares minimization of $\sum w(F_o - F_c)^2$ with anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen atoms riding on carbon atoms were added during calculation, and refine isotropically, giving rise to final convergence $R_1 = 0.0504$, $wR_2 = 0.1081$ [$I > 2\sigma(I)$] with 370 parameters, $(\Delta/\sigma)_{max} = 0.004$ and

$S = 1.077$ for **1**, and $R_1 = 0.0564$, $wR_2 = 0.1121$ [$I > 2\sigma(I)$] with 400 parameters, $(\Delta/\sigma)_{max} = 0.001$ and $S = 1.059$ for **2**, respectively. Final atomic coordinates and displacement parameters for non-hydrogen atoms, important bond lengths and angles are listed in Tables 2, 3 and 4, respectively.

Table 1   Crystallographic data of **1** and **2**

Formula	$Mo_3Te_7[S_2CN(CH_2CH_2OH)_2]_3I$ (**1**)	$Mo_3Te_4Y_3[S_2P(^iPrO)_2]_3I$ (**2**) $(Y_3 = 1.43Te + 1.57S)$
M_w	1848.8	1796.7
Crystal size (mm)	$0.14 \times 0.14 \times 0.08$	$0.21 \times 0.25 \times 0.12$
Space group	$P2_1/n$	$P2_1/n$
Unit cell parameters	$a = 1.6256(3)$ nm	$a = 1.4564(2)$ nm
	$b = 1.3264(2)$ nm	$b = 2.3917(4)$ nm
	$c = 1.8808(4)$ nm	$c = 1.5094(3)$ nm
	$\beta = 96.923°$	$\beta = 114.35(2)°$
V (nm^3)	4.0259(14)	4.790(2)
Z	4	4
$F(000)$	3312	3251
$D_{cal}(g \cdot cm^{-3})$	3.050	2.449
μ-Mo K_α(mm^{-1})	7.003	4.972
Scan type	ω	ω
Difractometer	Smart CCD	Smart CCD
Radiation (nm)	0.071073	0.071073
Temperature (K)	293	293
Absorption correction	SADABS	SADABS
θ range	$1.57°$ to $25.05°$	$1.64°$ to $25.05°$
h, k, l range	$-19 \leqslant h \leqslant 15$	$-13 \leqslant h \leqslant 17$
	$-15 \leqslant k \leqslant 14$	$-27 \leqslant k \leqslant 28$
	$-22 \leqslant l \leqslant 22$	$-17 \leqslant l \leqslant 17$
Reflection collected	19099	22417
Independent reflections [R_{int}]	7024 (0.0698)	8266 (0.0485)
Number of observed data with $I > 2\sigma(I)$	5502	5840
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
variables	370	400
R_1	0.0504	0.0564
$wR_2(I > 2\sigma(I))^a$	0.1081	0.1121
Weighting scheme (w^{-1})^b	$\sigma^2(F_o^2) + (0.0382P)^2 + 21.1700P$	$\sigma^2(F_o^2) + (0.0385P)^2 + 26.2046P$
Max. shift (Δ/σ) in final cycle	0.004	0.001
Goodness of fit: S	1.077	1.059
Largest diff. peak and hole (e$\cdot$nm^{-3})	1220/ $-$ 1265	1042/ $-$ 977

$^a wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$; $^b P = (F_o^2 + 2F_c^2)/3$

Table 2   Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$nm^2 \times 10$] for **1** and **2**

Continued

Mo$_3$Te$_7$[S$_2$CN(CH$_2$CH$_2$OH)$_2$]$_3$I (**1**)				Mo$_3$Te$_4$Y$_3$[S$_2$P(^{i}PrO)$_2$]$_3$I (Y$_3$ = 1.43Te + 1.57S) (**2**)			
Atoms	x	y	z	U_{eq}	Atoms	x	y	z	U_{eq}
Mo(1)	8096(1)	− 6160(1)	3276(1)	33(1)	Mo(1)	10739(1)	1703(1)	1687(1)	51(1)
Mo(2)	6528(1)	− 6159(1)	3837(1)	33(1)	Mo(2)	10841(1)	2532(1)	353(1)	48(1)
Mo(3)	7777(1)	− 4717(1)	4351(1)	31(1)	Mo(3)	11416(1)	1412(1)	210(1)	52(1)
Te(1)	6757(1)	− 7323(1)	2629(1)	48(1)	Te(1)	12494(1)	2069(1)	1729(1)	57(1)
Te(2)	6148(1)	− 4565(1)	4725(1)	50(1)	Te(2)	9925(1)	1928(1)	− 1323(1)	57(1)
Te(3)	9185(1)	− 4531(1)	3620(1)	47(1)	Te(3)	9808(1)	886(1)	338(1)	59(1)
Te(4)	7517(1)	− 7848(1)	3913(1)	43(1)	Te(4)	9084(1)	2311(1)	522(1)	57(1)
Te(5)	9097(1)	− 6028(1)	4560(1)	39(1)	Y(1)	10506(1)	2830(1)	1990(1)	62(1)
Te(6)	7142(1)	− 6051(1)	5266(1)	43(1)	Y(2)	11603(1)	658(1)	1626(1)	75(1)
Te(7)	6989(1)	− 4662(1)	3011(1)	38(1)	Y(3)	11733(2)	2247(1)	− 837(1)	77(1)
I	8564(1)	− 7936(1)	5634(1)	84(1)	I(1)	7798(1)	1471(1)	− 1386(1)	89(1)
S(1)	8372(2)	− 5782(3)	2022(2)	55(1)	S(1)	9523(2)	1404(2)	2454(2)	72(1)
S(2)	9204(2)	− 7308(3)	2890(2)	55(1)	S(2)	11839(2)	1665(2)	3522(2)	71(1)
S(3)	8499(2)	− 3775(2)	5429(1)	40(1)	S(3)	13221(2)	1131(2)	546(3)	80(1)
S(4)	7661(2)	− 2852(2)	4186(2)	46(1)	S(4)	11215(2)	627(1)	− 1048(2)	73(1)
S(5)	5392(2)	− 7292(3)	4189(2)	60(1)	S(5)	9797(2)	3341(1)	− 725(2)	66(1)
S(6)	5157(2)	− 5749(3)	3136(2)	53(1)	S(6)	12077(2)	3349(1)	786(2)	58(1)
N(1)	9563(7)	− 6940(11)	1543(6)	71(4)	P(1)	1o664(2)	1395(2)	3763(2)	70(1)
N(2)	8628(6)	− 1780(7)	5171(5)	45(2)	P(2)	12684(3)	712(2)	− 702(3)	75(1)
N(3)	3926(8)	− 7020(12)	3346(9)	107(6)	P(3)	10993(2)	3836(1)	− 142(2)	59(1)
C(1)	9111(7)	− 6701(11)	2081(6)	53(3)	O(1)	12924(8)	1051(5)	− 1468(9)	127(4)
C(2)	10162(9)	− 7804(15)	1651(9)	94(6)	O(2)	10483(7)	1736(4)	4570(6)	88(3)
C(3)	9366(11)	− 6409(17)	851(8)	96(6)	O(3)	13249(6)	148(4)	− 660(6)	79(2)
C(4)	9801(16)	− 5481(28)	869(14)	169(13)	O(4)	10818(7)	808(4)	4272(6)	83(3)
C(5)	11112(15)	− 7753(26)	1968(18)	214(19)	O(5)	10809(6)	4381(3)	345(6)	68(2)
C(6)	8288(7)	− 2670(9)	4961(6)	44(3)	O(6)	11281(6)	4132(3)	− 921(6)	70(2)
C(7)	8443(8)	− 870(9)	4695(7)	58(4)	C(1)	12540(30)	759(19)	− 2965(23)	297(22)
C(8)	9279(18)	− 602(14)	4351(12)	201(19)	C(2)	9390(20)	2338(12)	4913(29)	269(19)
C(9)	9285(9)	− 1673(9)	5787(7)	58(3)	C(3)	10996(18)	2656(9)	5063(20)	182(10)
C(10)	9061(11)	− 844(13)	6323(8)	84(5)	C(4)	11916(16)	55(10)	4387(19)	175(9)
C(11)	4709(8)	− 6722(10)	3544(7)	59(3)	C(5)	10693(15)	3918(11)	− 2607(12)	169(10)
C(12)	3406(9)	− 6533(16)	2698(10)	92(5)	C(6)	10109(18)	− 92(8)	3687(16)	161(8)
C(13)	3002(13)	− 5683(20)	3042(10)	122(8)	C(7)	10142(16)	2315(8)	4472(13)	122(6)
C(14)	3536(16)	− 7836(27)	3830(20)	223(20)	C(8)	12378(16)	1157(11)	− 2430(13)	140(8)
C(15)	3505(25)	− 8862(34)	3769(18)	515(73)	C(9)	9575(13)	4384(7)	1029(13)	114(6)
O(1)	10647(16)	− 5573(21)	774(14)	249(12)	C(10)	12534(13)	3959(9)	− 1529(13)	128(7)
O(2)	11241(15)	− 6816(25)	1976(25)	382(27)	C(12)	12814(14)	− 826(8)	− 702(12)	121(6)
O(3)	9231(12)	− 1224(22)	3842(10)	272(16)	C(13)	10963(13)	305(7)	3787(11)	93(5)
O(4)	8326(10)	− 1035(15)	6576(8)	164(8)	C(14)	10683(13)	4361(6)	1282(10)	94(5)
O(5)	2507(12)	− 5279(18)	2503(11)	201(9)	C(15)	14248(11)	− 419(8)	702(12)	117(6)
O(6)	3190(22)	− 9299(27)	4288(24)	324(21)	C(16)	11508(12)	3795(6)	− 1623(10)	92(4)
					C(17)	13208(10)	− 318(5)	− 42(9)	70(3)
					C(18)	12959(39)	1610(16)	− 2694(28)	334(24)

Table 3   Selected bond lengths [nm] for **1** and **2**^{a}

Compound 1					
Mo(1)—S(1)	0.2505(3)	Mo(1)—S(2)	0.2530(3)	Mo(1)—Te(7)	0.26867(12)
Mo(1)—Te(5)	0.27499(12)	Mo(1)—Te(4)	0.27576(13)	Mo(1)—Te(3)	0.28189(13)
Mo(1)—Te(1)	0.28215(12)	Mo(1)—Mo(2)	0.28746(14)	Mo(1)—Mo(3)	0.28757(13)
Mo(2)—S(6)	0.2508(3)	Mo(2)—S(5)	0.2530(3)	Mo(2)—Te(7)	0.26838(12)
Mo(2)—Te(4)	0.27519(12)	Mo(2)—Te(6)	0.27543(13)	Mo(2)—Te(2)	0.28086(12)
Mo(2)—Te(1)	0.28101(12)	Mo(2)—Mo(3)	0.28701(13)	Mo(3)—S(4)	0.2497(3)
Mo(3)—S(3)	0.2547(3)	Mo(3)—Te(7)	0.26869(12)	Mo(3)—Te(5)	0.27532(12)
Mo(3)—Te(6)	0.27540(12)	Mo(3)—Te(3)	0.28203(13)	Mo(3)—Te(2)	0.28271(13)
Te(1)—Te(4)	0.26694(12)	Te(2)—Te(6)	0.26711(12)	Te(3)—Te(5)	0.26745(11)
Te(4)—I	0.3473(2)	Te(5)—I	0.34140(14)	Te(6)—I	0.34190(14)
O(1)—O(6) #1	0.255(5)	O(4)—O(6) #2	0.282(5)	O(5)—O(4) #3	0.290(3)
Compound 2					
Mo(1)—S(2)	0.2568(3)	Mo(1)—S(1)	0.2584(3)	Mo(1)—Te(1)	0.26781(12)
Mo(1)—Te(3)	0.27418(13)	Mo(1)—Te(4)	0.275419(12)	Mo(1)—Y(1)	0.2778(2)
Mo(1)—Y(2)	0.2817(2)	Mo(1)—Mo(2)	0.28736(14)	Mo(1)—Mo(3)	0.28706(14)
Mo(2)—S(3)	0.2552(3)	Mo(2)—S(4)	0.2581(3)	Mo(2)—Te(1)	0.26859(12)
Mo(2)—Y(3)	0.2702(2)	Mo(2)—Te(4)	0.27270(12)	Mo(2)—Te(2)	0.27360(12)
Mo(2)—Y(1)	0.2802(2)	Mo(2)—Mo(3)	0.28410(14)	Mo(3)—S(5)	0.2553(3)
Mo(3)—S(6)	0.2599(3)	Mo(3)—Te(1)	0.26882(13)	Mo(3)—Y(3)	0.2701(2)
Mo(3)—Y(2)	0.2724(2)	Mo(3)—Te(2)	0.27298(12)	Mo(3)—Te(3)	0.27343(13)
Te(2)—I(1)	0.32490(13)	Te(3)—Y(2)	0.2592(2)	Te(3)—I(1)	0.33191(13)
Te(4)—Y(1)	0.26370(14)	Te(4)—I(1)	0.33759(13)	Y(1)—I(1) #1	0.3634(2)
S(1)—P(1)	0.1989(4)	S(2)—P(1)	0.1998(5)	S(3)—P(2)	0.1997(4)
S(4)—P(2)	0.1987(4)	S(5)—P(3)	0.1986(5)	S(6)—P(3)	0.1991(5)
P(1)—O(1)	0.1577(9)	P(1)—O(2)	0.1570(9)	P(2)—O(3)	0.1574(8)
P(2)—O(4)	0.1570(8)	P(3)—O(5)	0.1565(11)	P(3)—O(6)	0.1568(9)
O(1)—C(1)	0.146(2)	O(2)—C(4)	0.147(2)	O(3)—C(7)	0.1500(14)
O(4)—C(10)	0.148(2)	O(5)—C(13)	0.136(2)	O(6)—C(16)	0.1471(14)
C(1)—C(2)	0.150(3)	C(1)—C(3)	0.145(3)	C(4)—C(5)	0.152(2)
C(4)—C(6)	0.144(2)	C(7)—C(8)	0.152(2)	C(7)—C(9)	0.150(2)
C(10)—C(11)	0.149(4)	C(10)—C(12)	0.150(2)	C(13)—C(14)	0.153(4)
C(13)—C(15)	0.133(4)	C(16)—C(17)	0.149(2)	C(16)—C(18)	0.153(2)

^{a} Symmetry transformations used to generate equivalent atoms: #1 $-x + 3/2$, $y + 1/2$, $-z + 1/2$; #2 $-x + 1$, $-y - 1$, $-z + 1$; #3 $x - 1/2$, $-y - 1/2$, $z - 1/2$.

Results and discussion

Synthesis

Compound **1** is readily soluble in DMF, DMSO and pyridine, and has certain solubility in THF and Et-OH, but insoluble in CH_3CN and CH_2Cl_2. During the synthesis of **1**, if CH_3CN was used to extract the dark residue instead of hot THF, red product was obtained, which had been proved to be Te(HOdtc)$_2$[19] by X-ray analysis.

Therefore, the reaction of $Mo_3Te_7(TeI_3)_3I$ with K·dtcOH can be described as equation:

$$Mo_3Te_7(TeI_3)_3I \xrightarrow{\text{HOdtc}^-} Mo_3Te_7(HOdtc)_3I + Te(HOdtc)_2$$
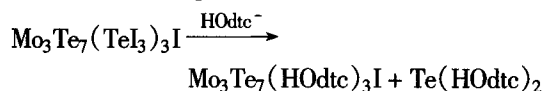
As for the $[Mo_3Te_4Y_3]^{4+}$ core in **2**, it has been formed in solid state reaction, of which the products might be $Mo_3Te_4Y_3(TeI_3)_3I$ or $Mo_3Te_4Y_3I_4$, of which three TeI_3^- or I^- ligands are replaced by three $^iPr_2dtp^-$ ligands in the subsequent low-temperature (110 ℃) solid

Table 4   Selected bond angles [°] for **1** and **2**

Mo$_3$Te$_7$[S$_2$CN(CH$_2$CH$_2$OH)$_2$]$_3$I (**1**)

S(1)-Mo(1)-S(2)	68.65(12)	S(6)-Mo(2)-S(5)	68.67(11)	S(4)-Mo(3)-S(3)	68.49(9)
S(1)-Mo(1)-Te(7)	82.47(9)	S(6)-Mo(2)-Te(7)	80.06(8)	S(4)-Mo(3)-Te(7)	80.59(7)
S(1)-Mo(1)-Te(5)	131.32(9)	S(5)-Mo(2)-Te(7)	148.72(9)	S(3)-Mo(3)-Te(7)	148.87(7)
S(2)-Mo(1)-Te(5)	85.64(8)	Te(7)-Mo(2)-Te(4)	115.45(4)	S(4)-Mo(3)-Te(5)	133.54(8)
Te(7)-Mo(1)-Te(5)	115.36(4)	S(6)-Mo(2)-Te(6)	134.14(9)	S(3)-Mo(3)-Te(5)	85.36(7)
S(1)-Mo(1)-Te(4)	132.89(9)	S(5)-Mo(2)-Te(6)	88.06(9)	Te(7)-Mo(3)-Te(5)	115.24(4)
Te(7)-Mo(1)-Te(4)	115.16(4)	Te(7)-Mo(2)-Te(6)	115.66(4)	S(4)-Mo(3)-Te(6)	133.32(8)
Te(5)-Mo(1)-Te(4)	82.36(3)	Te(4)-Mo(2)-Te(6)	81.42(3)	S(3)-Mo(3)-Te(6)	89.38(7)
S(1)-Mo(1)-Te(3)	83.33(9)	S(6)-Mo(2)-Te(2)	84.53(9)	Te(7)-Mo(3)-Te(6)	115.57(4)
Te(7)-Mo(1)-Te(3)	82.19(4)	S(5)-Mo(2)-Te(2)	94.15(10)	Te(5)-Mo(3)-Te(6)	81.30(4)
Te(5)-Mo(1)-Te(3)	57.39(3)	Te(7)-Mo(2)-Te(2)	83.37(4)	S(4)-Mo(3)-Te(3)	84.60(8)
Te(4)-Mo(1)-Te(3)	139.52(4)	Te(4)-Mo(2)-Te(2)	138.70(4)	S(3)-Mo(3)-Te(3)	91.23(8)
S(1)-Mo(1)-Te(1)	85.37(8)	Te(6)-Mo(2)-Te(2)	57.38(3)	Te(7)-Mo(3)-Te(3)	82.16(4)
S(2)-Mo(1)-Te(1)	94.91(9)	S(6)-Mo(2)-Te(1)	83.67(9)	Te(6)-Mo(3)-Te(3)	138.42(4)
Te(7)-Mo(1)-Te(1)	81.92(4)	S(5)-Mo(2)-Te(1)	93.28(10)	S(4)-Mo(3)-Te(2)	84.36(8)
Te(5)-Mo(1)-Te(1)	139.26(4)	Te(7)-Mo(2)-Te(1)	82.18(4)	S(3)-Mo(3)-Te(2)	97.02(8)
Te(4)-Mo(1)-Te(1)	57.16(3)	Te(4)-Mo(2)-Te(1)	57.35(3)	Te(7)-Mo(3)-Te(2)	82.96(4)
Te(3)-Mo(1)-Te(1)	161.56(4)	Te(6)-Mo(2)-Te(1)	138.55(4)	Te(5)-Mo(3)-Te(2)	138.28(4)
Mo(2)-Mo(1)-Mo(3)	59.88(3)	Te(2)-Mo(2)-Te(1)	162.71(4)	Te(3)-Mo(3)-Te(2)	162.72(4)
		Mo(3)-Mo(2)-Mo(1)	60.08(3)	Mo(2)-Mo(3)-Mo(1)	60.04(3)

Mo$_3$Te$_4$Y$_3$[S$_2$P(^{i}PrO)$_2$]$_3$I (Y$_3$ = 1.43Te + 1.57S) (**2**)

S(2)-Mo(1)-S(1)	75.18(10)	S(3)-Mo(2)-S(4)	76.00(10)	S(5)-Mo(3)-S(6)	75.60(11)
S(2)-Mo(1)-Te(1)	79.66(8)	S(3)-Mo(2)-Te(1)	78.76(7)	S(5)-Mo(3)-Te(1)	78.07(9)
S(1)-Mo(1)-Te(1)	154.57(8)	S(4)-Mo(2)-Te(1)	154.70(8)	S(6)-Mo(3)-Te(1)	153.60(8)
S(2)-Mo(1)-Te(3)	132.33(9)	S(3)-Mo(2)-Y(3)	95.17(9)	S(5)-MO93)-Y(3)	84.32(10)
S(1)-Mo(1)-Te(3)	85.18(8)	S(4)-Mo(2)-Y(3)	83.52(5)	S(6)-Mo(3)-Y(3)	95.82(9)
Te(1)-Mo(1)-Te(3)	115.19(4)	S(3)-Mo(2)-Te(4)	135.63(8)	Te(1)-Mo(3)-Y(3)	83.49(5)
S(2)-Mo(1)-Te(4)	134.67(9)	S(4)-Mo(2)-Te(4)	82.67(8)	S(5)-Mo(3)-Y(2)	84.71(10)
S(1)-Mo(1)-Te(4)	81.41(8)	Te(1)-Mo(2)-Te(4)	115.08(4)	S(6)-Mo(3)-Y(2)	92.29(9)
Te(1)-Mo(1)-Te(4)	114.84(4)	Y(3)-Mo(2)-Te(4)	137.75(6)	Te(1)-Mo(3)-Y(2)	83.29(4)
Te(3)-Mo(1)-Te(4)	82.37(4)	S(3)-Mo(2)-Te(2)	131.65(8)	S(5)-Mo(3)-Te(2)	132.99(109)
S(2)-Mo(1)-Y(1)	85.45(9)	S(4)-Mo(2)-Te(2)	82.90(8)	S(6)-Mo(3)-Te(2)	84.07(8)
S(1)-Mo(1)-Y(1)	92.36(9)	Te(1)-Mo(2)-Te(2)	115.96(4)	Te(1)-Mo(3)-Te(2)	116.10(4)
Te(1)-Mo(1)-Y(1)	81.90(4)	Y(3)-Mo(2)-Te(2)	55.74(5)	Te(1)-Mo(3)-Te(2)	116.10(4)
Te(3)-Mo(1)-Y(1)	139.19(4)	Te(4)-Mo(2)-Te(2)	82.25(4)	Y(2)-Mo(3)-Te(2)	138.75(5)
Te(4)-Mo(1)-Y(1)	57.07(3)	S(3)-Mo(2)-Y(1)	86.62(8)	S(5)-MO(3)-Te(3)	134.92(10)
S(2)-Mo(1)-Y(2)	85.13(9)	S(4)-Mo(2)-Y(1)	95.38(8)	S(6)-Mo(3)-Te(3)	82.99(8)
S(1)-Mo(1)-Y(2)	99.62(10)	Te(1)-Mo(2)-Y(1)	81.32(4)	Te(1)-Mo(3)-Te(3)	115.10(4)
Te(1)-Mo(1)-Y(2)	81.72(4)	Te(4)-Mo(2)-Y(1)	56.95(3)	Y(3)-Mo(3)-Te(3)	137.67(6)
Te(3)-Mo(1)-Y(2)	55.57(4)	Te(2)-Mo(2)-Y(1)	138.91(4)	Y(2)-Mo(3)-Te(3)	56.70(4)
Te(4)-Mo(1)-Y(2)	137.41(5)	Mo(3)-Mo(2)-Mo(1)	60.13(3)	Te(2)-Mo(3)-Te(3)	82.10(4)

reaction with K·^{i}Pr$_2$dtp, and the Mo$_3$Te$_4$Y$_3$ are left intact. The resulting title complex **2** is readily soluble in DMF, DMSO and CH$_2$Cl$_2$, and isolated easily from the solid residue. Compounds **1** and **2** are quite stable in air as crystal solid and in solution, suggesting it is possible to use them as convenient starting materials for the synthesis

of other molybdenum telluride clusters.

Crystal structure description

The molecular structure of **1** is shown in Fig. 1 and the packing diagram of unit cell in Fig. 2. The structures of **1** and **2** are in general similar to that of $Mo_3Te_7(dtp)_3I$ reported in the previous papers.[15] Three molybdenum atoms define an approximate isosceles triangle capped by an apical μ_3-Te atom with the average Mo—Te(μ_3) bond length of 0.2686 nm in **1** and 0.2684 nm in **2**. Each Mo—Mo edge is bridged by a Te_2 in **1** or TeY group in **2** in a slant mode, so that three equatorial Te [Te(1), Te(2), Te(3)] atoms lie approximately on the Mo_3 plane, while the other three axial Te [Te(4), Te(5), Te(6)] atoms in **1** and Y centers [Y(1), Y(2), Y(3)] in **2** lie on the side of Mo_3 plane opposite to the μ_3-Te atom. The three equatorial Y centers in **2** are statistically occupied by Te and S atoms [Y(1) = 0.643Te + 0.357S, Y(2) = 0.526Te + 0.474S and Y(3) = 0.266Te + 0.734S]. The bidentate sulfur dtcOH⁻ or $^iPr_2dtp^-$ ligand chelates to each Mo atom to complete the coordination sphere (distorted pentagonal bipyramid) of metal atoms.
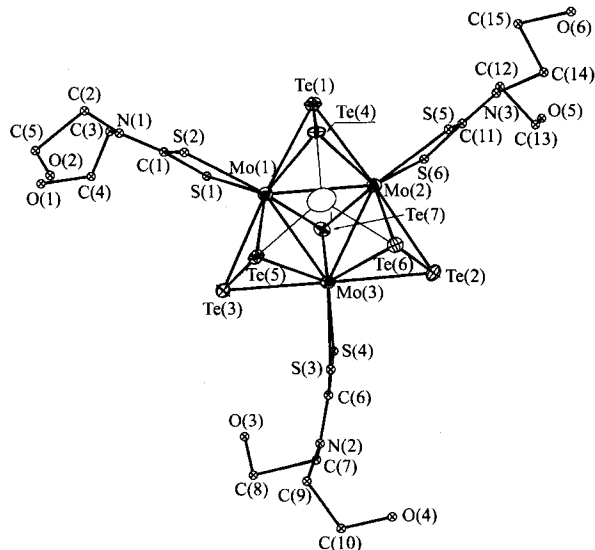

Fig. 1 Molecular structure of **1**.

A summary of important bond lengths of **1** and **2** as well as several analogues was presented in Table 5 for further understanding the cluster structure-ligands relationship. It is shown from the data that: Firstly, the average Mo—Mo distances of 0.2873 nm for **1** and 0.2862 nm for **2** are apparently longer than those in the corresponding S/

Se compounds {0.2782 nm in $[Mo_3S_7(TDT)_3]^{2-}$, TDT = $CH_3(C_6H_3)S_2$,[20] and 0.2714 nm in $Mo_3S_7(dtc)_3I$, dtc = Et_2NCS_2}[21] due to larger size of Te atom. Secondly, the average Mo—S_L(0.2520 nm) distance of **1** is shorter than those of $Mo_3Te_7(dtp)_3I$ (0.2895 and 0.2581 nm) and $Mo_3Te_7(^iPr_2dtp)_3I$ (0.2889 and 0.2571 nm), owing to stronger electron donor capability of HOdtc⁻ ligands. Similar phenomena have been observed on analogous $[Mo_3S_7]^{4+}$ clusters.[20-21] Finally, the Mo—Mo, Mo—(μ_2-Y) and Te—Y distances of the $[Mo_3Te_4Y_3]^{4+}$ core in **2** are certainly shorter than those of $[Mo_3Te_7]^{4+}$. In other word, the $Mo_3E_7^{4+}$ cluster core is constricted, when part of Te atoms are replaced by smaller S atoms.
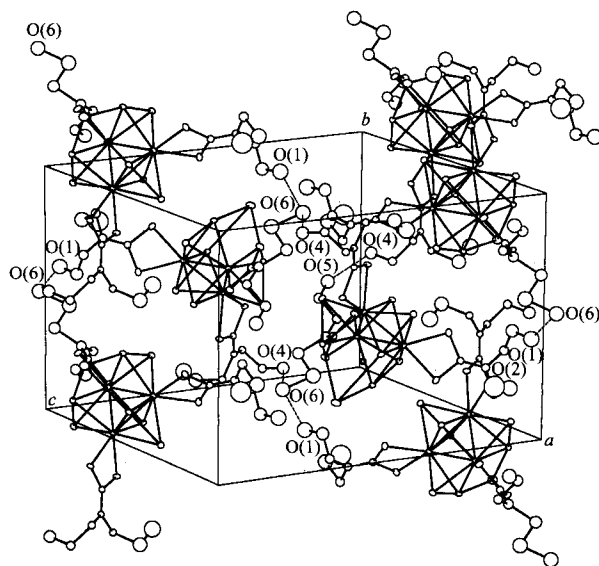

Fig. 2 View of hydrogen-bonded network of **1**.

Moreover, three apical Te atoms bond to an iodine atom forming a Te_3I tetrahedron. The average Te—I distance is 0.343 nm in **1** and 0.331 nm in **2**, which are remarkably shorter than the sum of van der Waals radii of Te and I (0.435 nm), showing an obvious bonding interaction. In addition, another short Y(1)—I contact in **2** takes place between two neighboring cluster molecules [Y(1)—I = 0.3634(2) nm, Y(1) = 0.643Te + 0.357S], thus leading to the formation of linear Te-Y(1)-I-Te-Y(1)-I⋯ chain along the diagonal of ac-plane (Fig. 4). Compared to **2** and several analogues compounds containing $[Mo_3E_7]^{4+}$ (E = S, Se and Te), cluster **1** contains no Te_2 ⋯I⋯Te_2 interaction, however, there exists hydrogen bonding

Table 5   Selected important bond length [nm] of some M_2-type Mo_3 clusters.

Compounds	Mo—Mo	Mo—(μ_3-X)	Mo—(μ_2-X) (out-plane)	Mo—(μ_2-X) (in-plane)	μ_2(X—X)	Mo—S_L
$Mo_3Te_7(HOdtc)_3I$ (**1**)	0.2873	0.2686	0.2753	0.2818	0.2672	0.2520
$Mo_3Te_4Y_3($ *iso*-$Pr_2dtp)_3I$ (**2**)	0.2862	0.2684	0.2735	0.2754	0.2590	0.2573
$Mo_3Te_7(dtp)_3I$ [15]	0.2895	0.2673	0.2740	0.2811	0.2671	0.2582
$Mo_3Te_7($ *iso*-$Pr_2dtp)_3I$ [15]	0.2889	0.2677	0.2742	0.2817	0.2652	0.2571
$[Mo_3S_7(TDT)_3]^{2-}$ [20]	0.2782	0.2370	0.2416	0.2511	2.029	0.2465
$Mo_3S_7(dtc)_3I$ [21]	0.2714	0.2372	0.2414	0.2481	2.053	0.2491
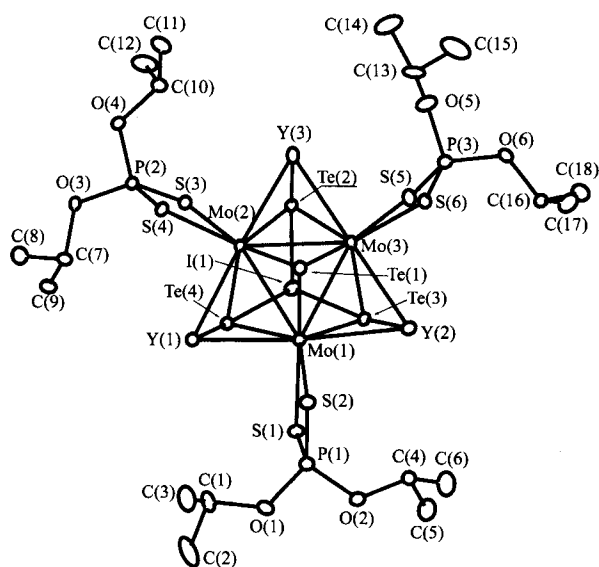
Fig. 3   Molecular structure of $Mo_3Te_4Y_3$ [$S_2P($ $^iPrO)_2$]$_3I$
(Y$_3$ = 1.43Te + 1.57S).
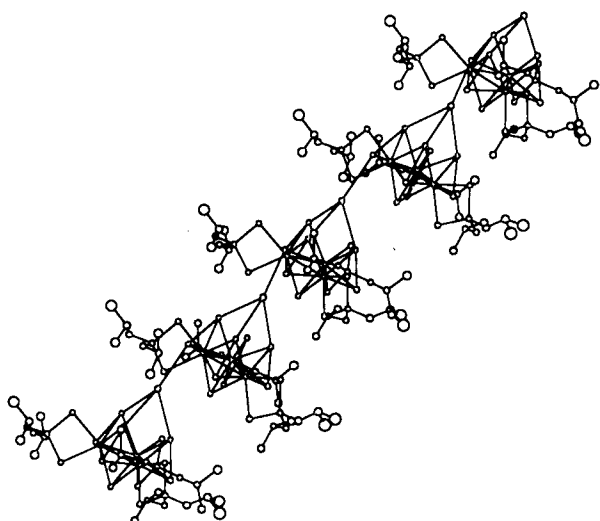
**Fig. 4**   Representation of the Te-Y(1)-I-Te-Y(1)-I··· linear
chain in **2**.

between OH groups of HOdtc⁻ ligands. Fig. 2 shows how
the structure is built up through hydrogen bonds. Each
cluster molecule of **1** is linked to four neighboring cluster
molecules by hydrogen bonds toward different directions to
form a three-dimensional network structure [O(6)—O(1)
0.255(5) nm, O(6)—O(4) 0.282(5) nm and O(5)—
O(4) 0.290(3) nm].

Reactivity

Previous studies showed that [Mo_3Te_7]$^{4+}$ fragment
is rather stable in aqueous cyanide or in CH_3OH with
PEt_3,[11] and the reaction of Mo_3Te_7[$S_2P(OPr^i)_2$]$_3I$ with
tributylphosphine leads to the transformation of the
[Mo_3Te_7]$^{4+}$ core to the [Mo_3Te_4]$^{4+}$ core.[17] We had
been attempting to synthesize new incomplete cuboidal
skeleton cluster with [Mo_3Te_4]$^{4+}$ core from Mo_3Te_7
(HOdtc)$_3I$ using a similar synthetic route that reported by
Lin *et al*.[17] When tributylphosphine was added into the
DMF or DMSO solution of Mo_3Te_7 (HOdtc)$_3I$ and Ph-
COOH under N_2 atmosphere, powder product was precipi-
tated in several hours, which proved to be Mo_3Te_4
(HOdtc)$_3$ (μ-PhCO$_2$) PBu$_3$ by elemental analyses. The
treatment of **2** with tributylphosphine in the presence of
PhCOOH leads to the transformation of the [Mo_3Te_7]$^{4+}$
core to the [Mo_3Te_4]$^{4+}$ core, yielding the reported
Mo_3Te_4[$S_2P(OPr^i)_2$]$_3$(μ-PhCO$_2$) PBu$_3$. The reactions of
[Mo_3S_4]$^+$ clusters with heterometallic atoms (*i.e*. Fe,
Co, Ni, Sn, Sb, Pb and Hg) have been extensively in-
vestigated, leading to the discovery of a series of het-
erometal-containing cuboidal clusters. Considering that
[Mo_3Te_4]$^{4+}$ core is sensitive in air,[17] a one-pot reaction
using [Mo_3Te_7]$^+$ clusters, $SbCl_3$/PbI_3^- ligands and trib-
utylphosphine as starting materials to synthesize het-
erometal-containing cuboidal complexes has been carried
out several times under N_2 atmosphere. Although no ex-
pected products were obtained, the immediate color

change (from brown to deep green) of the reaction solution indicated that an unidentified cluster compound, which might be a heterometal-containing cuboidal complex, was formed. Moreover, when the resulting solutions were exposed to air for several minutes, a tellurium mirror at the bottom was found along with the colour change of the solution from deep green to brown immediately. The reaction scheme maybe presented as Scheme 1.

Scheme 1
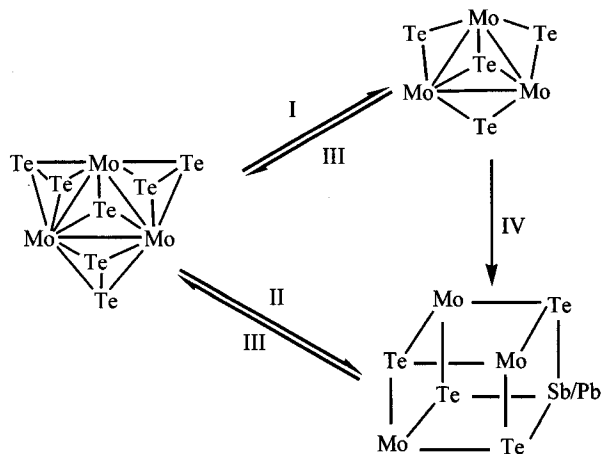
(I) benzoic acid, PBu_3; (II) PBu_3, $SbCl_3$ or PbI_3^-; (III) O_2; (IV) [3 + 1] reaction may take place under suitable conditions.

Conclusions

The solid precursors containing $Mo_3Te_7(TeI_3)_3I$ or $Mo_3Te_7I_4$, $Mo_3Te_4Y_3(TeI_3)_3I$ or $Mo_3Te_4Y_3I$ were obtained from elements via high temperature solid-state reaction, and then soluble triangular molybdenum cluster $Mo_3Te_7(HOdtc)_3I$ (1) and $Mo_3Te_4Y_3(^iPr_2dtp)_3I$ (2) were synthesized from the solid precursors by ligand-replacing reaction. Both clusters have a similar structural core compared to that of $[Mo_3X_7]^{4+}$ (X = S, Se or Te). The hydrogen-bonded network exists in the crystal structure of 1, while 2 possesses linear Te-Y(1)-I-Te-Y(1)-I ··· chains [Y(1) = 0.643Te + 0.357S].

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