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Telluride Clusters of Molybdenum: Synthesis, Structures, and NMR Spectra

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Abstract—High-temperature reactions of Mo, chalcogen (S or Se), Te, and Br_2 in molar ratio Mo : S/Se : Te : Br = 3 : 1 : 6 : 4 were carried out. The reaction products were subjected to mechanochemical activation with K(Dtp) (Dtp = $(EtO)_2PS_2$) in a vibrational mill, resulting in the formation of new compounds $[Mo_3(\mu_3\text{-}Q)_{0.5}(\mu_3\text{-}O)_{0.5}(\mu_2\text{-}Te_2)_3(Dtp)_3](Dtp)$ (Q = Se (**I**) and S (**II**)). The structure of compound **I** has been established by X-ray diffraction analysis. Solutions of compounds **I** and **II** contain mixtures of $[Mo_3(\mu_3\text{-}Q)(\mu_2\text{-}Te_2)_3(Dtp)_3]^+$ and $[Mo_3(\mu_3\text{-}O)(\mu_2\text{-}Te_2)_3(Dtp)_3]^+$, which is confirmed by mass spectrometry and ^{31}P, ^{77}Se, and ^{125}Te NMR spectroscopy. Quantum-chemical calculations of the ^{125}Te NMR chemical shifts were performed. The compounds are also characterized by IR spectroscopy, Raman spectroscopy, and elemental analysis. Structure **I** contains short nonvalent contacts between the sulfur atom of the out-of-sphere Dtp anion and the axial tellurium atoms of the cluster.

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Chalcogenide clusters containing the stable cluster group $\{M_3Q_7\}^{4+}$ (M = Mo, W; Q = S, Se, Te) represent a vast and well studied family of coordination compounds and find use in advanced materials [1]. The sulfide and selenide anionic complexes with dithiolates, $[Mo_3Q_7(dithiolate)_3]^{2-}$, are capable of oxidizing to form neutral complexes $[Mo_3Q_7(dithiolate)_3]$, which can be used in molecular electronics as new one-component molecular conductors [2–5]. Short nonvalent chalcogen–chalcogen contacts between $[Mo_3Q_7(dithiolate)_3]$ play an important role in electron transport in these conducting cluster systems. The sulfide complexes with bromide, dithiolate, and oxalate ligands are interesting for the production of materials with nonlinear optical properties [6].

The telluride clusters $M_3Te_7^{4+}$ are the least studied representatives of this family of compounds [7]. Due to the large size and diffuse orbitals, tellurium is an attractive ligand favoring cluster formation [8–11]. The chemical properties of the telluride clusters often differ drastically from those of the selenide clusters resembling, to a considerable extent, the sulfide analogs [9, 12]. On the one hand, the increased tendency of tellurium to participate in nonvalent intermolecular interactions, which manifests itself already in the structure of elementary Te, evokes interest from the viewpoint of using tellurium-containing building blocks in supramolecular chemistry [13].

On the other hand, the M–Te bond is weak, and the replacement of tellurium by bridging atoms of other chalcogens becomes possible. For example, cluster chalcogenides $W_3Te_7Br_4$ and $Mo_3Te_7I_4$ react with a KNCSe melt to form chalcogen-mixed clusters $W_3(\mu_3\text{-}Te)(\mu\text{-}TeSe)_3(CN)_6]^{2-}$ and $[W_3(\mu_3\text{-}Te)(\mu\text{-}Se)_3(CN)_9]^{5-}$ [14]. In the first reaction the bridging ligand $\mu_2\text{-}Te_2^{2-}$ is transformed into $\mu_2\text{-}TeSe^{2-}$. It is known that the reactivity of the disulfide and diselenide ligands in the clusters $M_3Q_7^{4+}$ differs sharply from that of the ditelluride ligands. For example, the telluride clusters, unlike the sulfide and selenide analogs, can interact with electrophilic agents of the Br_2 or S_2Cl_2 type resulting in the formation of complexes with the $\mu_2\text{-}TeS^{2-}$ ligand [15]. The above listed examples demonstrate the possibility of selective preparation of chalcogenide-mixed complexes in which chalcogen atoms of various nature occupy well defined positions.

In this work we continued studies on the synthesis of chalcogenide-mixed complexes. New dithiophosphate complexes $[Mo_3(\mu_3\text{-}Q)(\mu_2\text{-}Te_2)_3(Dtp)_3]^+$ (Dtp = $(EtO)_2PS_2$) crystallized in the form of $[Mo_3(\mu_3\text{-}Q)_{0.5}(\mu_3\text{-}O)_{0.5}(\mu_2\text{-}Te_2)_3(Dtp)_3](Dtp)$ (Q = Se (**I**) and S (**II**)) and containing ligands $\mu_2\text{-}Te_2^{2-}$, and sulfur or selenium and oxygen atoms in the μ_3 position were obtained by high-temperature synthesis in a sealed ampule followed by mechanochemical treatment. The NMR spectra, including the ^{125}Te NMR

spectra, of the synthesized compounds are discussed in detail.

EXPERIMENTAL

All procedures, except for the high-temperature reactions, were carried out in air. Starting materials from commercial sources were used are received, and KDtp was synthesized from $[Ni(Dtp)_2]$ according to a described procedure [16]. Solvents were purified using standard procedures.

Synthesis of compound I. Molybdenum (1.44 g, 15 mmol), Te (3.83 g, 30 mmol), Se (0.39 g, 5 mmol), and Br_2 (1.6 g, 10 mmol) were heated at 350°C in an evacuated sealed ampule for 4 days. After mechanochemical activation of a mixture of the reaction product (1.9 g) and KDtp (0.80 g, 0.36 mmol), the final product was extracted with $CHCl_3$ (20 mL) and filtered. A double volume of ethanol was added to a dark brown extract, and the obtained mixture was left to evaporate for several days. A black crystalline substance was filtered off, washed with ethanol and ether, and dried in air. The yield was 0.44 g (18%).

For $C_{16}H_{40}Mo_3O_{8.5}P_4Se_{0.5}S_8Te_6$		
anal. calcd. (%):	C, 10.43;	H, 2.19.
Found (%):	C, 10.77;	H, 2.57.

IR, ν, cm^{-1}: 3439 w, 2974 w, 2928 w, 2891 w, 2861 w, 1470 w, 1437 w, 1384 w, 1288 w, 1157 m, 1097 w, 1027 sh, 1011 s, 960 s, 945 sh, 809 sh, 790 sh, 771 s, 638 s, 545 m, 449 w. Raman, ν, cm^{-1}: 639 w, 543 w, 516 w, 217 m, 195 w, 122 m, 98 m. ^{31}P NMR ($CHCl_3$; 25°C; δ, ppm): 92.91, 98.93. ^{77}Se NMR: 617.18. ^{125}Te NMR: 144 (Te_{ax} from Mo_3OTe_6), −53 (Te_{ax} from Mo_3Te_6O), −856 (Te_{eq1} from Mo_3OTe_6), −862 (Te_{eq2} from Mo_3OTe_6), −875 (Te_{eq1} from Mo_3SeTe_6), −880 (Te_{eq2} from $Mo_{3S}eTe_6$). MS ($CHCl_3$), *m/z*, **I**, %: $[MoSeTe_{6(}Dtp)_3]^+$ 1689 (100), $[Mo_3OTe_6(Dtp)_3]^+$ 1627 (70).

Synthesis of compound II. Molybdenum (1.44 g, 15 mmol), Te (3.83 g, 30 mmol), S (0.16 g, 5 mmol), and Br_2 (1.6 g) were heated at 350°C in an evacuated sealed ampule for 4 days. After mechanochemical activation of a mixture of the polymer (2.0 g) and KDtp (0.90 g, 0.40 mmol), the final product was extracted with $CHCl_3$ (30 mL) and filtered. A double volume of ethanol was layered on a dark brown extract and cooled at 5°C for 2 days. A black crystalline substance was filtered off, washed with ethanol and ether, and dried in air. The yield was 0.26 g (10%).

For $C_{16}H_{43}Mo_3O_{10}P_4S_{8.5}Te_6$		
anal. calcd. (%):	C, 10.45;	H, 2.18.
Found (%):	C, 10.13;	H, 2.23.

IR, ν, cm^{-1}: 3453 w, 2974 w, 2930 w, 2891 w, 1470 w, 1438 w, 1384 m, 1287 w, 1158 m, 1096 w, 1030 s, 1010 s, 947 s, 771 s, 650 s, 636 s, 543 m, 512 w, 449 w. Raman, ν, cm^{-1}: 218 m, 141 s, 124 s, 99 s. ^{125}Te NMR ($CHCl_3$; 25°C; δ, ppm): 76 (Te_{ax} from Mo_3STe_6), −52 (Te_{ax} from Mo_3Te_6O), −856 (Te_{eq1} from Mo_3OTe_6), −883 (Te_{eq1} from Mo_3STe_6). ^{31}P NMR: 92.86, 96.90. MS ($CHCl_3$), *m/z* (*I*, %)): $[Mo_3STe_6(Dtp)_3]^+$ 1644 (100), $[Mo_3OTe_6(Dtp)_3]^+$ 1627 (100).

Vibrational spectra in the range from 4000 to 400 cm^{-1} were recorded in KBr pellets on a Scimitar FTS 2000 instrument with a resolution of 1 cm^{-1}. Raman spectra were measured on a Triplimate SPEX spectrometer using a He–Ne laser (632.8 nm) for excitation. ^{125}Te NMR spectra were obtained on an MSL300 spectrometer (Bruker) at ambient temperature in chloroform using a saturated aqueous solution H_6TeO_6 as an external standard. Electrospray ionization mass spectra (ESI-MS) were recorded on a Quattro LC (quadrupole–hexapole–quadrupole) mass spectrometer (Micromass, Manchester, UK) [17]. Analyses for C, H, and N were carried out on a EuroEA3000 analyzer.

The mechanochemical activation method using a vibrational mill, whose construction was described [18], was applied to the syntheses of compounds **I** and **II**. The reactions were carried out in a titanium cylindrical reactor (volume 100 mL, height 50 mm). Carbidotungsten balls 10 mm in diameter (weight 320 g) and the starting substances were loaded into a reactor in such a way that the degree of filling with the balls was 65%. Mechanical activation was carried out subjecting the reactor to vibration with a frequency of 25 Hz and an amplitude of 1 cm for 12 h.

Quantum-chemical calculations were performed by the density functional theory in the ADF2010 program package [19]. The full geometry optimization was carried out with the VWN + BP86 functional in the full-electron basis set consisting of triply split singly polarized zeta functions [20]. Spin-orbital relativistic effects were applied using the ZORA method [21]. The GIAO method was used for the calculation of NMR shifts [22].

X-ray diffraction analysis. Diffraction data for compound **I** were obtained on a Bruker X8Apex four-circle automated diffractometer equipped with a CCD detector [23, 24] (MoK_α radiation, graphite monochromator). The crystallographic characteristics and details of diffraction experiments are given in Table 1. The relative occupancy factors of the μ_3-Se and μ_3-O positions equal to 50% were preliminarily confirmed during the refinement in the isotropic (for these atoms) approximation with the fixation of U_{iso} = 0.05 $Å^{-2}$. The positions of the μ_3-O and μ_3-Se ligands were separated in the final refinement by equalizing to each other anisotropic parameters of atomic shifts of the oxygen and selenium atoms. The O(7)···Se(7) distance (~0.77 Å) is substantially longer than the half of

the wavelength and, in our opinion, allows one to claim the correctness of the structural model in combination with reasonable Mo–O and Mo–Se bond lengths.

Selected bond lengths are listed in Table 2. The full information on the studied structure of compound **I** was deposited with the Cambridge Crystallographic Data Centre (no. 870551; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

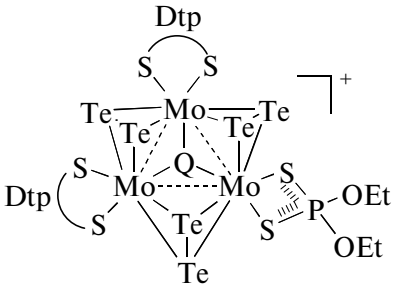
RESULTS AND DISCUSSION

One of the methods for the synthesis of telluride complexes with the cluster core $\{M_3Te_7\}^{4+}$ (M = Mo, W) is the solid-phase interaction of inorganic coordination polymers $Mo_3Te_7I_4$ or $W_3Te_7Br_4$ with an appropriate compound that can act as a ligand in a vibrational mill. Although no reactions with KNCS, $K_2C_2O_4$, Na(Acac), and Na(Dtc) were observed under these conditions, the reactions with KDtp result in cutting off of the M_3Te_7 cluster fragment and formation of discrete complexes $[Mo_3(\mu_3\text{-}Te)(\mu_2\text{-}Te_2)_3(Dtp)_3]I$ [25] and $[W_3(\mu_3\text{-}Te)(\mu_2\text{-}Te_2)_3(Dtp)_3]Br$ [26] in a yield of 15–20%.

$$M_3Te_7X_4 + 3KDtp \rightarrow [M_3Te_7(Dtp)_3]X + 3KX.$$

A similar approach was used in the present work for the synthesis of chalcogen-mixed clusters. The reaction of Mo, Te, Q (Q = S, Se), and Br_2 in a molar ratio of 3 : 6 : 1 : 2 gave the products with a presumable composition of $Mo_3QTe_6Br_4$. The mechanochemical reaction of these products with KDtp afforded complexes $[Mo_3(\mu_3\text{-}Q)(\mu_2\text{-}Te_2)_3(Dtp)_3]^+$ containing the sulfur or selenium atom in the μ_3 position

$$3Mo + 6Te + Q + 2Br_2 \rightarrow \text{“}Mo_3QTe_6Br_4\text{”},$$
$$\text{“}Mo_3QTe_6Br_4\text{”} + 4KDtp$$
$$\rightarrow [Mo_3QTe_6(Dtp)_3](Dtp) + 4KBr \ (Q = S; Se).$$



$[Mo_3QTe_6(Dtp)_3]^+$

It is most likely that the incorporation of the smaller chalcogen atom into the cluster core with the occupation of the maximum binding position is a general regularity. For instance, the sulfur atoms occupy exclusively the μ_3 position in the triangular complexes $[Mo_3(\mu_3\text{-}S)_{0.65}(\mu_3\text{-}Se)_{0.35}(\mu_2\text{-}Se_2)_3(Dtp)_3]^+$ [27] and $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}Se_2)_3Br_6]^{2-}$ [28] simultaneously containing the sulfide and selenide bridging ligands, and the sulfur atoms occupy exclusively the μ_3 position. Tantalum chalcohalide $Ta_4S_{1.54}Se_{7.46}I_8$ contains only the sulfur atoms in the μ_4 position [29].

Table 1. Main crystallographic characteristics and details of X-ray diffraction experiments for compound **I**

Parameter	Value
FW	1841.74
Crystal system	Triclinic
Space group	$P\bar{1}$
Temperature, K	100
a, Å	12.2537(8)
b, Å	13.1205(7)
c, Å	16.3599(10)
α, deg	71.032(2)
β, deg	83.010(2)
γ, deg	72.423(2)
V, Å^3	2370.5(2)
Z	2
$F(000)$	1694
μ, mm^{-1}	5.31
Crystal sizes, mm	0.58 × 0.23 × 0.05
Absorption correction	SADABS
T_{min}, T_{max}	0.566, 1
Measured/independent/observed ($I > 2\sigma(I)$) reflections	19377/10339/8428
R_{int}	0.020
θ range, deg	2.1–27.5
($F^2 > 2\sigma(F^2)$), $wR(F^2)$, S	0.046, 0.109, 1.24
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	2.24/–2.00

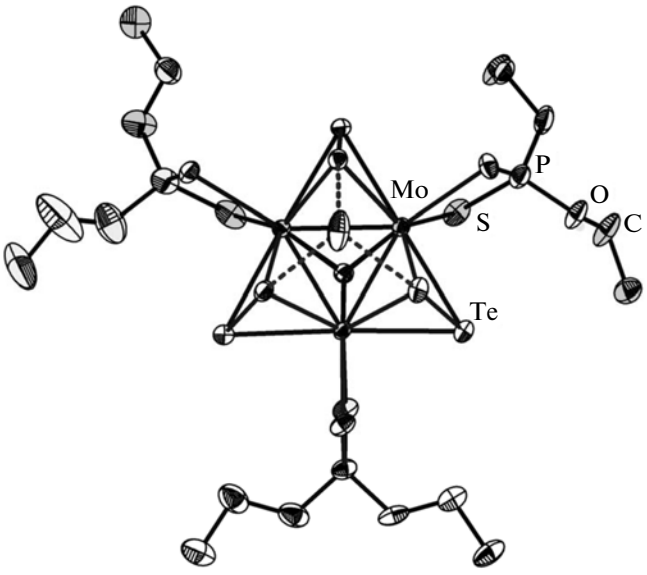
According to the ESI-MS data, the second product of these reactions is the oxo derivative $[Mo_3(\mu_3\text{-}O)(\mu_2\text{-}Te_2)_3(Dtp)_3]^+$. For example, the ESI-MS spectrum of a solution of compound **II** exhibits two isotopic distributions with maxima of approximately equal intensities at $m/z = 1627$ and 1644 corresponding to the cluster cations $[Mo_3OTe_6(Dtp)_3]^+$ and $[Mo_3STe_6(Dtp)_3]^+$, respectively. However, this mixture could not be separated by chromatography on silica gel.

Table 2. Selected bond lengths and nonvalent contacts in the structure of compound **I**

Bond, contact	*d*, Å
M–M	2.7790(11)–2.7809(10)
Mo–μ_3-O	1.980(14)–2.047(13)
Mo–μ_3-Se	2.527(2)–2.577(2)
Mo–Te_{ax}	2.7310(9)–2.7514(9)
Mo–Te_{eq}	2.7965(10)–2.8308(10)
Mo–S_{Dtp}	2.553(3)–2.586(2)
Te_{ax}–Te_{eq}	2.6484(9)–2.6890(9)
S_{Dtp}...Te_{ax}	3.130(6)–3.160(6)

The geometry of the cluster core $Mo_3QTe_6^{4+}$ in compound **I** is similar to that for the earlier described telluride complexes [26]. The Dtp^- ligands are bound to the molybdenum atoms in the bidentate mode similarly to other dithiophosphate complexes [26, 30].

The crystal structures of clusters $M_3Q_7^{4+}$ (M = Mo, W; Q = S, Se, Te) almost always contain so-called axial contacts [26] involving the axial chalcogen atoms (Q_{ax}) of ligands Q_2. Structure **I** (figure) is not an exception. This structure includes three axial tellurium atoms (Te_{ax}) forming strongly shortened contacts (3.130(6)–3.160(6) Å) with one of the sulfur atoms of the out-of-sphere dithiophosphate ligand. This results in the formation of neutral cation–anion associates $\{[Mo_3QTe_6(Dtp)_3](Dtp)\}$ similar to those observed, for example, in $[Mo_3S_7(S_2PEt_2)_3](S_2PEt_2)$ [31] and $[Mo_3S_7(S_2CNEt_2)_3](S_2CNEt_2)$ [32].



Structure of the cluster cation $[Mo_3(\mu_3\text{-}O)_{0.5}(\mu_3\text{-}Se)_{0.5}(\mu_2\text{-}Te_2)_3(Dtp)_3]^+$ in compound **I** (atomic shift ellipsoids of 50% probability). The nonvalent $S_{Dtp}\cdots Te_{ax}$ contacts are shown by dash.

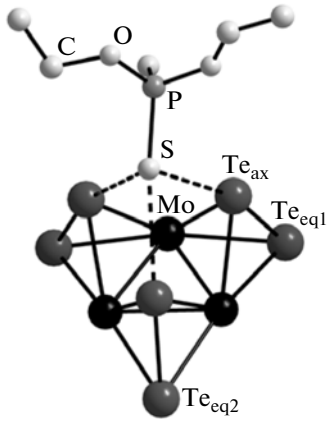
The ^{125}Te NMR spectra of solutions of compounds **I** and **II** in chloroform are also consistent with the mass spectral data and show four main signals and two less intense signals caused by the presence of two forms in each solution: $[Mo_3SeTe_6(Dtp)_3]^+$ and $[Mo_3OTe_6(Dtp)_3]^+$ for compound **I** and $[Mo_3STe_6(Dtp)_3]^+$ and $[Mo_3OTe_6(Dtp)_3]^+$ for compound **II**. The quantum-chemical calculations were performed to interpret the spectra and to assign the signals to particular forms. The calculated average distances for different complexes consistent with the literature data for the structurally characterized telluride clusters are given in Table 3. The calculated chemical shifts for a series of compounds $[Mo_3QTe_6(Dtp)_3](Dtp)$ (Q = O, S, and Se) are listed in Table 4. They indicate the presence of three types of tellurium atoms instead of the expected two types: equivalent axial (Te_{ax}), two equatorial (Te_{eq1}), and one equatorial atom of another type (Te_{eq2}). Nonequivalence of one of the equatorial tellurium atoms is related to the nonsymmetrical coordination of the additional dithiophosphate anion in a solution forming short axial contacts $S_{Dtp}\cdots Te_{ax}$ (see below). It can be assumed that due to this the Te_{eq2} atom is more remote from the anion than other tellurium atoms. The absolute values of chemical shifts change in the following sequence: $Te_{ax} > Te_{eq1} > Te_{eq2}$. The sensitivity of the chemical shifts of Te_{eq} to the axial contacts agrees with the accepted interpretation of the latter as donor–acceptor bonds formed due to the donation of a lone pair on the out-of-sphere anion to the σ^* orbitals of the Te_2^{2-} ligand [33]. Thus, based on the quantum-chemical calculations, two most intense signals can be interpreted as the signals from Te_{ax} and Te_{eq1} of complex $[Mo_3QTe_6(Dtp)_3]^+$ (Q = S, Se). Two less intense signals, which have the same values of chemical shifts in the spectra of both solutions, can be assigned to Te_{ax} and Te_{eq1} of complex $[Mo_3OTe_6((EtO)_2PS_2)_3]^+$. The spectrum of a solution of compound **I** also exhibits two low-intensity signals neighboring with more intense signals from Te_{eq1}, which are attributed to the Te_{eq2} of complexes $[Mo_3SeTe_6((EtO)_2PS_2)_3]^+$ and $[Mo_3OTe_6((EtO)_2PS_2)_3]^+$.

Table 3. Calculated average distances in the telluride clusters

Compound	Mo–Mo	Mo–μ_3-Q	Mo–Te_{ax}, Mo–Te_{eq}	Mo–S_{Dtp}	Te_{ax}–Te_{eq}	X···Te_{ax}, X = S_{Dtp}, Br, I
	d, Å					
$[Mo_3(\mu_3\text{-}O)(Te_{ax}–Te_{eq})_3(Dtp)_3](Dtp)$	2.78	2.07	2.84, 2.89	2.67	2.80	3.20
$[Mo_3(\mu_3\text{-}S)(Te_{ax}–Te_{eq})_3(Dtp)_3](Dtp)$	2.90	2.42	2.84, 2.92	2.66	2.79	3.23
$[Mo_3(\mu_3\text{-}Se)(Te_{ax}–Te_{eq})_3(Dtp)_3](Dtp)$	2.94	2.55	2.84, 2.91	2.66	2.78	3.23
$[Mo_3(\mu_3\text{-}Te)(Te_{ax}–Te_{eq})_3(Dtp)_3](Dtp)$	2.96	2.77	2.84, 2.91	2.67	2.78	3.26
$[Mo_3(\mu_3\text{-}Te)(Te_{ax}–Te_{eq})_3(Dtp)_3]Br$	2.96	2.77	2.84, 2.91	2.67	2.78	3.24
$[Mo_3(\mu_3\text{-}Te)(Te_{ax}–Te_{eq})_3(Dtp)_3]I$	2.96	2.77	2.84, 2.91	2.67	2.79	3.47

Table 4. Calculated chemical shifts in the ^{125}Te NMR spectra

Te atom	$[Mo_3Te_6O(Dtp)_4]$	$[Mo_3Te_6S(Dtp)_4]$	$[Mo_3Te_6Se(Dtp)_4]$	$[Mo_3Te_7(Dtp)_4]$	$[Mo_3Te_7(Dtp)_3Br]$	$[Mo_3Te_7(Dtp)_3I]$
μ_3-Te				–231	–201	–162
Te_{ax}	–660, –719, –602	–563, –614, –460	–561, –659, –474	–408, –427, –315	–498, –499, –482	–443, –439, –423
Te_{eq1}	–1241, –1226	–1284, –1305	–1344, –1434	–1263, –1276	–1354, –1302	–1358, –1308
Te_{eq2}	–1923	–1979	–2055	–1884	–1315	–1315



The ^{31}P NMR data are consistent with the ^{125}Te NMR data. The spectra of solutions of compounds **I** and **II** exhibit two main signals from the coordinated dithiophosphate groups of complexes $[Mo_3QTe_6(Dtp)_3]^+$ (Q = S, Se) and $[Mo_3OTe_6(Dtp)_3]^+$ and two lower-intensity signals from the out-of-sphere Dtp^- anions bound to the axial tellurium atoms. One signal from the selenium atom in the μ_3 position (617.18 ppm) of complex $[Mo_3SeTe_6(Dtp)_3]^+$ is observed in the ^{77}Se NMR spectrum of a solution of compound **I**.

The ^{125}Te spectrum of a solution of $[Mo_3Te_7(Dtp)_3]I$ was also detected. The spectrum shows a set of three signals at 256, –23, and –790 ppm, which is typical of NMR spectra of the family of clusters $\{M_3Q_7\}^{4+}$ (Q = Se, Te). The chemical shifts were calculated for compounds $[Mo_3Te_7(Dtp)_3]X$ (X = Dtp, Br, and I) with the Te_{ax}···X contact, and the sequence of signals in the spectra was established (by the absolute value of chemical shifts): μ_3-Te > Te_{ax} > Te_{eq} (Table 4). For $[Mo_3Te_7(Dtp)_3](Dtp)$, one of the equatorial tellurium atoms also differs substantially from two other atoms, and its signal is shifted to more negative values of chemical shifts. On going from $[Mo_3Te_7(Dtp)_3]I$ to $[Mo_3Te_7(Dtp)_3]Br$, the chemical shifts from μ_3-Te and Te_{ax} are shifted to a more negative region and the values from Te_{eq} remain almost unchanged. Interestingly, the chemical shifts of μ_3-Te are very sensitive to the nature of partner X in the axial contact Te_{ax}···X in spite of the fact that the "capped" tellurium atoms are not directly involved in contacts with X.

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