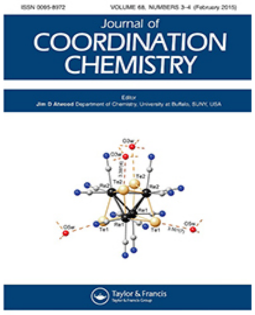

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Cyanato- and thiocyanato-substituted triangular clusters of molybdenum, $[Mo_3S_4(dppe)_3X_3]^+$ ($X = NCO^-, NCS^-$; dppe = 1,2-bis(diphenylphosphino)ethane)

MIKHAIL YU. AFONIN†, ANTON I. SMOLENTSEV†‡, SERGEY N. KONCHENKO†‡
and PAVEL A. PETROV*†‡

†Nikolaev Institute of Inorganic Chemistry, Siberian Branch of Russian Academy of Sciences, Novosibirsk, Russian Federation
‡Department of Natural Sciences, Novosibirsk State University, Novosibirsk, Russian Federation

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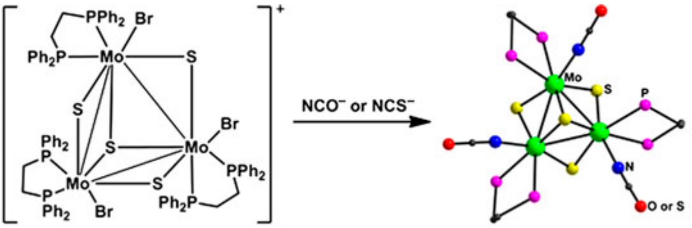

Two pseudohalido-substituted cluster complexes, $[Mo_3S_4(dppe)_3(NCS)_3]NCS$ (**1**) and $[Mo_3S_4(dppe)_3(NCO)_3]Br$ (**2**) (dppe = 1,2-bis(diphenylphosphino)ethane), have been synthesized by substitution between $[Mo_3S_4(dppe)_3Br_3]Br$ and potassium thiocyanate or sodium cyanate, respectively, in boiling acetonitrile. The compounds were characterized by IR-spectroscopy, elemental analysis, electrospray mass-spectrometry, and single-crystal X-ray diffraction analysis. Both compounds crystallize as toluene solvates (**1**$\cdot 3C_6H_5CH_3$ and **2**$\cdot 2.5C_6H_5CH_3$) in $P\bar{1}$ space group with similar unit cell dimensions and adopt very similar molecular geometries. Both structures consist of discrete cluster cations $[Mo_3S_4(dppe)_3X_3]^+$, NCS^- or Br^- anions, and solvate toluene molecules.

Keywords: Molybdenum; Triangular clusters; Chalcogenides; Pseudohalides; Mass-spectrometry; Crystal structure

1. Introduction

Polynuclear species with metal–metal bonding dominate the chemistry of Mo and W chalcogenides [1], and the triangular cluster core $\{M_3Q_4\}^{4+}$ (where M = Mo or W and Q = S or Se) is one of the most common units within this family. Judicious choice of ligands coordinated to the $\{M_3S_4\}^{4+}$ core tunes the functional properties of the resulting

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*Corresponding author. Email: panah@niic.nsc.ru

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complexes, which can be used as catalysts for nitroarene reduction [2] or C–F bond activation [3], cocatalysts in hydrogen evolution reactions [4, 5], and nonlinear optical materials [6, 7]. Heterometallic derivatives of the $\{M_3S_4\}^{4+}$ core is also known. An additional heterometal vertex can be connected to the bridging chalcogenides to produce heterometallic cubane-like units $\{M_3S_4\ M'\}$. Another approach to the design of heterometallic derivatives of the $\{M_3S_4\}^{4+}$ core is the use of ambidentate ligands which link the cluster to the heterometal. Ligand substitution in the diphosphine-coordinated clusters $[M_3S_4(\text{diphosphine})_3X_3]^+$ (X = Hal, H, OH, SH) has been studied very intensively within the last decades [8–13]. The ancillary diphosphines decrease the number of ligands (for example, halides) capable of substitution, and thus, simplify the substitution processes. In some cases, diphosphine also gives additional functionalities to the cluster core (such as chirality [14] or redox activity [15]) or provides additional donors allowing surface immobilization of the cluster [16–18].

Substitution of halides with ambidentate ligands in the diphosphine-bearing triangular clusters is less explored. To the best of our knowledge, only cyanido- [19] and dicyanamido-substituted [20] clusters have been fully characterized. The former was also utilized to build assemblies via the cyanide bridges, and the resultant complex $[Mo_3S_4(\text{dmpe})_3\{CN–Mo(CO)_5\}_3]^+$ (dmpe = 1,2-bis(dimethylphosphino)ethane) is stable both in solution and gas phase. Thus, bridging via the ambidentate ligands can be a rational route to cluster-based heterometallic complexes or coordination polymers.

The study of exchange-coupled polynuclear complexes bridged by pseudohalides is an active area of research due to their diverse magnetic properties [21]. However, thiocyanate and, particularly, cyanate bridges have been less explored and the magnetic exchange interactions through these bridges were not studied extensively [22–25]. The paramagnetism of the cluster core can also play a role in exchange interactions. The diphosphine-supported diamagnetic $[M_3S_4(\text{dppe})_3Br_3]^+$ clusters (M = Mo or W) can undergo one-electron reduction to form paramagnetic $[M_3S_4(\text{dppe})_3Br_3]$ [26, 27]. Moreover, the paramagnetic $[Re_3S_4(\text{dppe})_3Br_3]Br$ cluster features high-spin ground state with $S = 3/2$ [28], which remains intact upon changing the terminal bromides for thiocyanates [29]. In this work, we focus on the studies on substitution of bromides in the cluster $[Mo_3S_4(\text{dppe})_3Br_3]Br$ for pseudohalide ligands (thiocyanate and cyanate). Here, we report the synthesis and characterization of two compounds possessing an ionic structure, $[Mo_3S_4(\text{dppe})_3(NCS)_3]NCS\cdot3C_6H_5CH_3$ (**1**$\cdot3C_6H_5CH_3$) and $[Mo_3S_4(\text{dppe})_3(NCO)_3]Br\cdot2.5C_6H_5CH_3$ (**2**$\cdot2.5C_6H_5CH_3$).

2. Experimental

2.1. *Materials and instrumentation*

All reagents were used without purification. The reaction course was monitored with thin layer chromatography using the foils with silica gel 60 (Merck). For column chromatography silica gel 60 (0.063–0.100 mm, Merck) was used. The starting cluster $[Mo_3S_4(\text{dppe})_3Br_3]Br$ (**3**) was prepared as described previously [30]. Infrared spectra in KBr pellets were recorded using a Scimitar FTS 2000 spectrometer from 4000 to 400 cm^{-1}. $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker Avance 500 instrument. Electrospray ionization mass spectra were recorded with a Q-TOF I (quadrupole–hexapole-time-of-flight) mass spectrometer with an orthogonal *Z*-spray electrospray interface (Micromass, Manchester, UK) operating at resolution of approximately 5000 (FWHM). The instrument was calibrated using a solution of NaI in isopropanol/water from *m/z* 100 to 1900. Sample solutions (2×10^{-5} M) in water were introduced through a fused-silica capillary to the ESI source via syringe pump at a flow rate of 10 μL min^{-1}. The cone voltage was set at 10 V to control the extent of fragmentation. Nitrogen was employed as the drying and nebulizing gas. Isotope experimental patterns were compared with the theoretical patterns obtained using the MassLynx 4.0 program. Elemental analysis was carried out with a Euro Vector EA 3000 CHNS-analyzer.

2.2. *Synthesis and characterization*

2.2.1. Synthesis of [Mo_3S_4(dppe)$_3$(NCS)$_3$]NCS (1). A solution of [Mo_3S_4(dppe)$_3$Br$_3$]Br (200 mg, 0.1 mM) and KSCN (120 mg, 1.2 mM) in 15 mL acetonitrile was heated under reflux for 30 min. After cooling the mixture, the off-white precipitate was filtered off and the filtrate was evaporated to dryness in vacuum. The residue was separated by column chromatography on silica gel. After elution with toluene–acetone mixture (1 : 1 v/v), elution with acetone gave two brown fractions. The second fraction corresponding to **1** was collected and evaporated to dryness. The residue was dissolved in 10 mL of acetone–toluene mixture (1 : 2 v/v) and the solution was left for unsupported evaporation. After a few days, brown prismatic crystals were collected and dried *in vacuo*. Yield 140 mg (73%). $^{31}P\{^1H\}$ ($CDCl_3$, δ): 36.54 (s), 26.85 (s). IR-spectrum (KBr, cm^{-1}): 3409 m, 3052 m, 2923 m, 2029 very strong (vs), 1627 w, 1482 m, 1432 s, 1411 w, 1379 sh, 1332 w, 1309 w, 1273 w, 1189 w, 1158 w, 1096 m, 1028 w, 997 w, 871 m, 818 m, 739 s, 692 vs, 674 s, 652 m, 517 s, 482 s, 414 m. ES-MS (MeCN, *m/z*): 1786.0 ([Mo_3S_4(dppe)$_3$(NCS)$_3$]$^+$, 100%). Anal. Calcd for $C_{82}H_{72}Mo_3N_4P_6S_8$ (%): C, 53.4; H, 3.9; N, 3.0; S, 13.9. Found: C, 53.0; H, 4.3; N, 3.5; S, 13.8.

2.2.2. Synthesis of [Mo_3S_4(dppe)$_3$(NCO)$_3$]Br (2). Complex **2** in the form of green prismatic crystals was prepared in a similar manner as **1**, but instead of potassium thiocyanate, sodium cyanate (80 mg, 1.2 mM) was used. Yield 137 mg (69%). $^{31}P\{^1H\}$ ($CDCl_3$, δ): 36.00 (s), 23.23 (s). IR-spectrum (KBr, cm^{-1}): 3398 m, 3053 m, 2919 m, 2209 vs, 1622 m, 1483 m, 1483 s, 1433 w, 1411 w, 1384 w, 1333 w, 1310 w, 1274 w, 1190 w, 1159 w, 1098 m, 1027 w, 999 w, 867 m, 818 w, 740 s, 695 vs, 671 m, 648 m, 609 m, 592 m, 521 s, 513 s, 490 m, 479 m, 415 w. ES-MS (MeCN, *m/z*): 1737.7 ([Mo_3S_4(dppe)$_3$(NCO)$_3$]$^+$, 100%). Anal. Calcd for $C_{81}H_{72}BrN_3Mo_3O_3P_6S_4$ (%): C, 53.5; H, 4.0; N, 2.3; S, 7.1. Found: C, 53.8; H, 4.5; N, 2.3; S, 7.3.

2.3. *Crystal structure determination*

Suitable crystals of **1**·3$C_6H_5CH_3$ and **2**·2.5$C_6H_5CH_3$ were selected under a microscope and mounted to the tip of a thin glass fiber with epoxy resin. X-ray intensity data were collected on a Bruker-Nonius X8Apex CCD diffractometer at 296(2) and 150(2) K for **1**·3$C_6H_5CH_3$ and **2**·2.5$C_6H_5CH_3$, respectively, using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The standard technique was used (combined φ- and ω-scans of narrow frames). Data reduction and multi-scan absorption were carried out using SADABS [31]. The structures were solved by direct methods and refined by full-matrix least-squares on F^2

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using the SHELXTL software package [31]. All non-hydrogen atoms were refined anisotropically. Hydrogens of dppe and toluene were placed in geometrically idealized positions and refined as riding on their parent carbons. The structures contain a number of solvate toluene molecules, which, regardless of the temperature of the experiment, could not be located completely. Therefore, the structures were treated with the PLATON/SQUEEZE [32, 33] procedure to remove the contribution of the solvent electron density to the intensity data. The total solvent accessible void volume and the number of recovered electrons per unit cell were estimated to be 718 Å^3 and 182 for **1** and 410 Å^3 and 94 for **2**, allowing us to include 2 and 1 additional toluene molecules in the final formulas of **1** and **2** solvates, respectively. Crystallographic data and refinement details are summarized in table 1. Selected bond lengths are given in table 2.

3. Results and discussion

3.1. *Synthesis and spectra*

Treatment of a solution of [Mo_3S_4(dppe)$_3$$Br_3$]Br (**3**) with excess potassium thiocyanate or sodium cyanate in refluxing acetonitrile leads to substitution of the terminal halides. [Mo_3S_4(dppe)$_3$(NCS)$_3$](NCS) (**1**) and [Mo_3S_4(dppe)$_3$(NCO)$_3$]Br (**2**) have been isolated as

Table 1. Crystal data, data collection, and refinement parameters for **1**·3$C_6H_5CH_3$ and **2**·2.5$C_6H_5CH_3$.

Empirical formula	$C_{103}H_{96}Mo_3N_4P_6S_8$	$C_{98.5}H_{92}BrMo_3N_3O_3P_6S_4$
Formula weight	2119.96	2047.54
Crystal size (mm)	0.32 × 0.14 × 0.12	0.24 × 0.20 × 0.12
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	14.0040(4)	13.8352(6)
b (Å)	14.0192(4)	13.8877(6)
c (Å)	25.6158(8)	24.8882(12)
α (°)	89.7470(10)	74.538(2)
β (°)	74.5620(10)	88.449(2)
γ (°)	83.1350(10)	82.722(2)
Volume (Å^3)	4810.8(2)	4571.7(4)
Z	2	2
D_{Calcd} (g cm^{-3})	1.463	1.487
Absorption coefficient (mm^{-1})	0.708	1.091
F(0 0 0)	2172	2086
θ range (°)	1.46–27.57	1.48–27.55
h, k, l ranges	$-17 \le h \le 18$, $-18 \le k \le 18$, $-33 \le l \le 33$	$-17 \le h \le 17$, $-17 \le k \le 18$, $-19 \le l \le 32$
Reflections collected	33,935	35,639
Unique reflections	22,104 (R_{int} = 0.0440)	20,906 (R_{int} = 0.0366)
Observed reflections [$I > 2\sigma(I)$]	12,805	14,196
Parameters refined	941	1006
$R[F^2 > 2\sigma(F^2)]$	R_1 = 0.0594, wR_2 = 0.1377	R_1 = 0.0633, wR_2 = 0.1616
$R(F^2)$ (all data)	R_1 = 0.1085, wR_2 = 0.1554	R_1 = 0.0998, wR_2 = 0.1757
Goodness-of-fit on F^2	0.912	1.057
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.263, −1.170	2.083, −1.148

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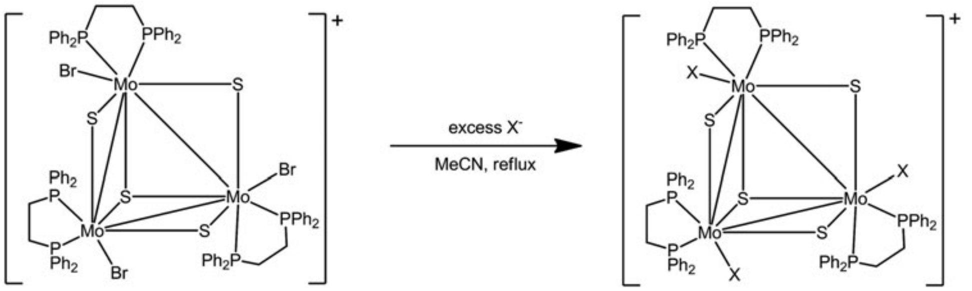
Table 2. Selected bond lengths (Å) for **1**·$3C_6H_5CH_3$ and **2**·$2.5C_6H_5CH_3$.

Bond	**1**·$3C_6H_5CH_3$	**2**·$2.5C_6H_5CH_3$
Mo1–Mo2	2.7743(6)	2.7747(6)
Mo1–Mo3	2.7740(6)	2.7651(6)
Mo2–Mo3	2.7848(6)	2.7830(6)
Mo1–S1	2.3058(13)	2.3027(14)
Mo1–S3	2.2816(12)	2.2840(13)
Mo1–S4	2.3646(12)	2.3617(12)
Mo2–S1	2.2824(13)	2.2893(13)
Mo2–S2	2.3156(13)	2.3174(14)
Mo2–S4	2.3532(13)	2.3481(13)
Mo3–S2	2.2826(14)	2.2939(14)
Mo3–S3	2.3100(13)	2.3134(12)
Mo3–S4	2.3635(12)	2.3625(13)
Mo1–N1	2.166(4)	2.121(4)
Mo2–N2	2.199(4)	2.130(4)
Mo3–N3	2.155(4)	2.131(5)
Mo1–P11	2.6445(15)	2.6268(14)
Mo1–P12	2.5594(13)	2.5519(13)
Mo2–P21	2.6572(14)	2.6437(14)
Mo2–P22	2.5782(15)	2.5707(15)
Mo3–P31	2.6391(13)	2.6263(14)
Mo3–P32	2.5681(13)	2.5548(14)
C1–N1	1.073(7)	1.143(7)
C2–N2	1.021(6)	1.142(7)
C3–N3	1.143(6)	1.162(7)
C4–N4	1.164(9)	–
C1–S5	1.652(7)	–
C2–S6	1.671(7)	–
C3–S7	1.614(6)	–
C4–S8	1.668(7)	–
C1–O1	–	1.205(7)
C2–O2	–	1.202(7)
C3–O3	–	1.198(7)



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1, X = NCS
2, X = NCO

Scheme 1. Synthesis of **1** and **2**.

air-stable solids after purification with column chromatography (scheme 1). In both cases, some unidentified by-products were separated. According to $^{31}P\{^1H\}$ NMR spectra, the reaction with KSCN produces some 1,2-bis(diphenylphosphino)ethane disulfide

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$dppeS_2$, probably indicating partial destruction of the Mo_3S_4 cluster core in the course of the reaction.

As we reported earlier, triangular clusters of Mo, and particularly those of Re, feature very labile terminal bromides. Thus, the mixed-halide complex $[Mo_3S_4(dppe)_3Br_{2.5}Cl_{0.5}](Br_{0.8}Cl_{0.2})$ was obtained when **3** was recrystallized from a dichloromethane–toluene mixture at room temperature [26]. When $[Mo_3S_4(dppe)_3Br_{2.5}Cl_{0.5}](Br_{0.8}Cl_{0.2})$ was reacted with KSCN, the mixed chloro/thiocyanato cluster cations $[Mo_3S_4(dppe)_3(NCS)_{3-n}Cl_n]^+$ were observed in the mass spectrum of the reaction product (*m/z* 1785.8, 1761.9 and 1740.7 for $n = 0$, 1 and 2, respectively). This fact may indicate that the chlorides in clusters of this type are substituted less readily than the bromides. Therefore, $[Mo_3S_4(dppe)_3Br_3]Br$ (**3**) is a more convenient precursor for the pseudohalide-substituted clusters and their syntheses and purification should be carried out in halogen-free solvents. The completeness of halide substitution in **1** and **2** was also confirmed by mass spectrometry. In the reaction of **3** with KNCS, the bromide in the outer sphere is also substituted by NCS^-, while the cyanate-substituted complex crystallizes as the bromide salt. In both cases, the X-ray diffraction data are in agreement with the elemental analysis.

$^{31}P\{^1H\}$ NMR spectra of both complexes exhibit two signals of coordinated dppe ligands at 26.85 and 36.54 ppm for **1** and at 23.23 and 36.00 ppm for **2**. Each signal corresponds to the phosphorus atoms located above and below the Mo_3 plane.

The coordinated NCX^- ligands (X = O, S) usually show three normal IR vibration modes, namely the antisymmetric stretching ν(CN), the pseudosymmetric stretching ν(CX), and the bending δ(NCX) [34]. IR spectra of the clusters under study show a strong absorption at 2029 cm^{-1} for **1** and 2209 cm^{-1} for **2**, related to the characteristic antisymmetric stretching ν(CN) frequencies of the coordinated cyanate and thiocyanate, respectively. The ν(CO) stretching frequency can be used to distinguish the coordination mode of cyanate. In the N-bonded cyanate complexes, ν(CO) is positively shifted to 1370–1300 cm^{-1} [35–37] as compared to the cyanate in KNCO (1296 and 1204 cm^{-1}) [38]. On the contrary, a negative shift by *ca.* 50 cm^{-1} should be expected for O-bonded cyanate compounds [38, 39]. Unfortunately, the region of the CO stretching vibrations is obscured in the IR spectrum of **2** by vibrations of dppe. Therefore, the coordination mode of the cyanate in **2** was assigned on the basis of the structural data.

3.2. *Crystal structures*

As shown by X-ray diffraction analysis, **1** and **2** crystallize in the triclinic space group $P\bar{1}$ with similar unit cell dimensions and $Z = 2$; the compounds can be considered as isotypic. The trinuclear cluster core $\{Mo_3S_4\}^{4+}$ of the $[Mo_3S_4(dppe)_3X_3]^+$ ($X = NCS^-$, NCO^-) cations has a geometry typical of incomplete cuboidal M_3Q_4 clusters (M = Mo, W; Q = S, Se), with one sulfide capping three metal centers and the other three sulfides bridging pairs of Mo ions. The octahedral coordination around each Mo is completed by nitrogen of the pseudohalide ligand and the bidentate dppe (figure 1). The Mo–Mo bond lengths are 2.7651(6)–2.7848(6) Å with the average of 2.778(6) for **1** and 2.774(9) Å for **2**. The Mo–μ_2-S, Mo–μ_3-S, and Mo–P bond lengths fall into the intervals 2.2816(12)–2.3174(14) (av. 2.30(14) Å), 2.3481(13)–2.3646(12) (av. 2.359(7) Å), and 2.5519(13)–2.6572(14) (av. 2.60(4) Å), respectively. The Mo–N_X distances depend largely on the type of ligand X, shorter in the case of $X = NCO^-$. In **1** the corresponding values are 2.155(4)–2.199(4) (av. 2.17(2) Å) and in **2** they are 2.121(4)–2.131(5) (av. 2.127(5) Å). As for numerous cationic

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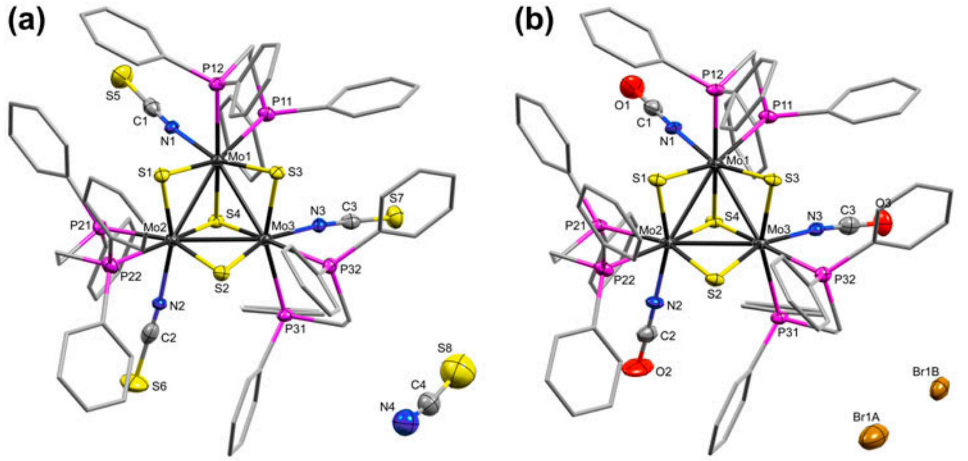

Figure 1. Thermal ellipsoid representation of (a) $[Mo_3S_4(dppe)_3(NCS)_3]^+$ cluster cation and NCS^- anion in **1**·$3C_6H_5CH_3$ (30% probability ellipsoids); (b) $[Mo_3S_4(dppe)_3(NCO)_3]^+$ cluster cation and Br^- anion disordered over two positions in **2**·$2.5C_6H_5CH_3$ (50% probability ellipsoids). Hydrogens of dppe ligands are omitted for clarity.

Mo and W clusters with coordinated diphosphines [6-20], the Mo–P bonds are somewhat shortened for phosphorus in the *trans* position to the μ_3-bridging sulfide. The same trend is observed for the Mo–μ_2-S distances: longer bonds are observed in the *trans* position to the pseudohalide ligands.

For **1**, the coordination mode of the NCS^- ligands is unambiguously determined from the X-ray diffraction data due to the difference in the scattering factors of N and S. For cyanate that is not the case, and elucidation of its coordination mode is not always straightforward [40–43]. We formulate **2** as tris–isocyanato complex (i.e. with all NCO^- ligands bonded via the nitrogen) on the basis of the following. First, although the values of *R*-factors differ insufficiently for the N- and O-bonded models of the cyanate ligands, the former fits the experimental data slightly better ($R_1 = 0.0633$ *versus* 0.0646). Second, the values of the thermal displacement parameters were unreasonable for the O-bonded model, with the two inner atoms (assigned as O2 and O3) having larger parameters than the corresponding outer ones (assigned as N2 and N3). On the other hand, within the Mo–N–C–O model, the thermal ellipsoids of all oxygens were larger than those of nitrogen, as one would expect. Third, the O-bonded cyanates are supposed to be bent [39, 41] with the M–O–C angles in the range 133–169° [44] as opposed to nearly linear coordination of the N-bonded cyanates. The Mo–N–C angles in **2** (171.5(4)–178.7(4)°) suggest the latter coordination mode. Finally, a search in the Cambridge Structural Database [44] revealed 324 entries with the terminal cyanate coordinated to the transition metal via N, 12 of them to Mo. The O-bound non-bridging cyanate was found only in 12 complexes (no examples for Mo). The Mo–N bond lengths in the N-bound model are close to those observed in **1** and to the Mo–N_{NCO} distances for reported complexes (av. 2.10(3) Å). To conclude, the N-bound coordination mode of the cyanates is better to describe the bonding in **2**.

The structures of **1** and **2** are ionic and the arrangement of the $[Mo_3S_4(dppe)_3X_3]^+$ cations can be regarded as a pseudo-body-centered cubic lattice (figure 2). The NCS^- and Br^- anions in **1** and **2**, respectively, occupy the same positions around the cationic complexes,

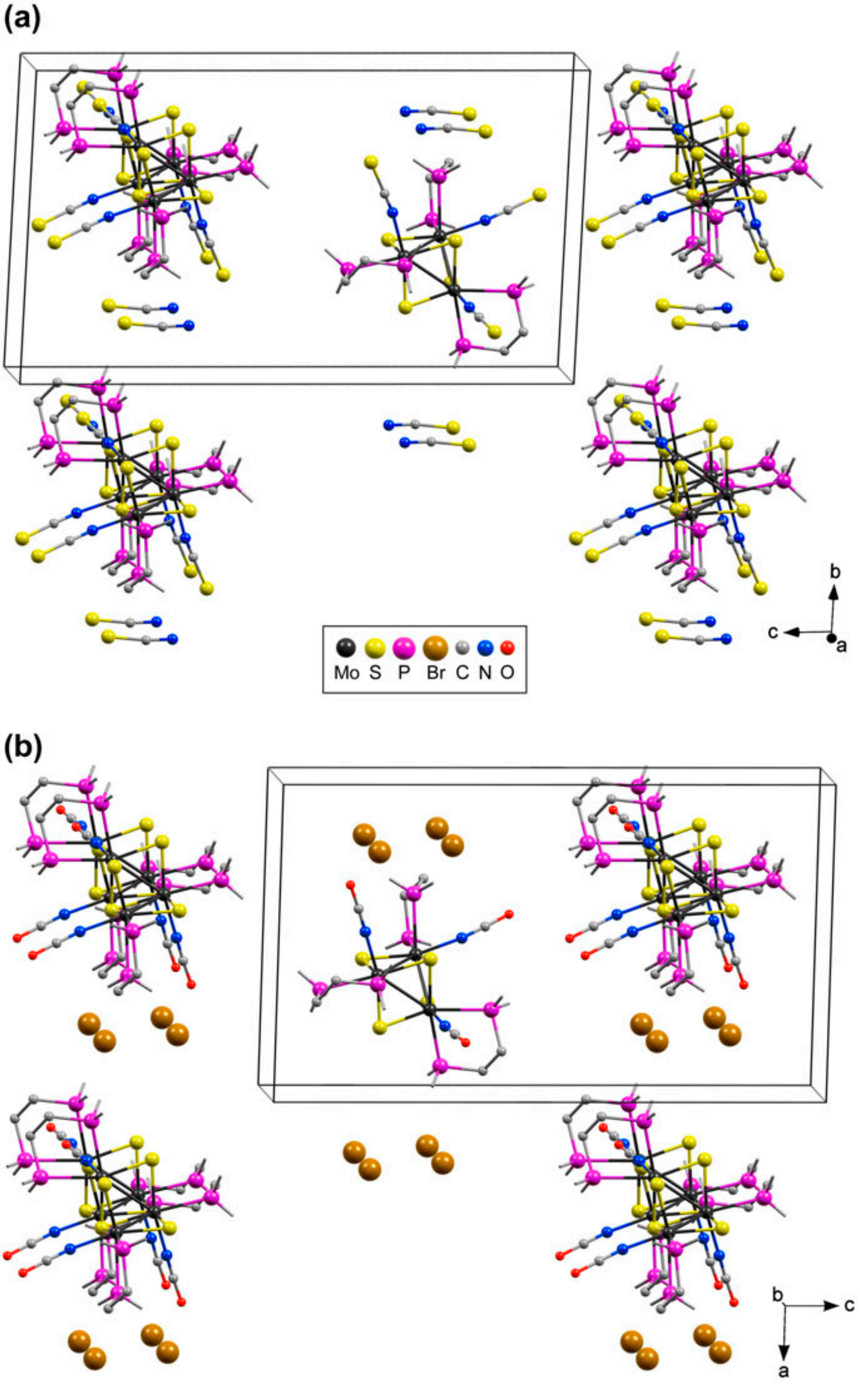

Figure 2. Packing diagrams of the structures of (a) $\mathbf{1}\cdot 3C_6H_5CH_3$ and (b) $\mathbf{2}\cdot 2.5C_6H_5CH_3$ viewed along the *a* and *b* axes, respectively. Dppe ligands are depicted schematically with phenyl groups and hydrogens omitted for clarity. Solvent toluene molecules are not shown.

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but in the latter case each Br^- is disordered over two sites (Br1A and Br1B) with refined site occupancy factors of 0.393(2) and 0.607(2). Despite the presence of a large number of aromatic rings, the structures show no substantial contribution of π–π and C–H···π interactions. These interactions only take place between the dppe ligands and solvate toluene molecules which fill the cavities around the bulky cationic complexes $[Mo_3S_4(dppe)_3X_3]^+$, and between toluene molecules themselves. In other words, the stabilizing effect of these interactions is weaker than could be expected for complexes of such composition. Likely, this fact is responsible for some rotational/positional freedom of the solvate toluene molecules. In our opinion, it is the main reason of the strong disorder of the solvate molecules, preventing them from being completely located from the X-ray diffraction data.

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4. Conclusion

The ligand substitution in $[Mo_3S_4(dppe)_3Br_3]Br$ has been studied. Two complexes $[Mo_3S_4(dppe)_3X_3]^+$ ($X = NCS^-$, NCO^-) with N-bound pseudohalide ligands have been isolated. Both compounds were characterized by IR and $^{31}P\{^1H\}$ NMR spectroscopy, elemental analysis, electrospray mass-spectrometry, and single-crystal X-ray diffraction. Attempts to synthetize heterometallic assemblies via NSC or NCO linkages are in progress.

Supplementary material

CCDC 1017732 and 1017734 contain the complete crystallographic data for **1**·$3C_6H_5CH_3$ and **2**·$2.5C_6H_5CH_3$, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336 033; or Email: deposit@ccdc.cam.ac.uk.

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