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Coordination modes of aminodiphosphane ligands to the cuboidal Mo_3S_4 cluster unit

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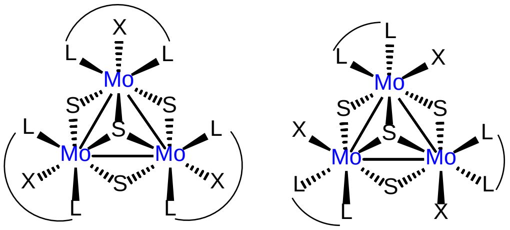
Abstract: The aminodiphosphane molybdenum (IV) cluster complex of formula $[Mo_3S_4Cl_3(\kappa^2(P,N)\text{-}PNP)_3]Cl$ (PNP = bis[(2-di-i-propylphosphino)ethyl]amine) [**Mo-1**]Cl has been isolated in high yields by reacting $[Mo_3S_4Cl_4(PPh_3)_3(H_2O)_2]$ with stoichiometric amounts of the PNP ligand. Characterization of $[\textbf{Mo-1}]^+$ by ESI-MS, $^{31}P\{^1H\}$ NMR and single-crystal X-ray diffraction confirms that aminodiphosphanes bind as bidentate ligands to the Mo_3S_4 unit leaving three uncoordinated phosphino groups. The dangling phosphino groups can substitute the chloride ligands and coordinate to the cluster core in the presence of $AgBF_4$ to give the complex of formula $[Mo_3S_4(\kappa^3\text{-}PNP)_3](BF_4)_4$ ($[\textbf{Mo-2}](BF_4)_4$). The tridentate coordination of the aminodiphosphane ligands to the Mo_3S_4 cluster unit in ($[\textbf{Mo-2}]^+$ is confirmed by $^{31}P\{^1H\}$ NMR and elemental analysis.

Keywords: Molybdenum sulphides, trinuclear clusters, aminodiphosphane complexes, denticity.

1. INTRODUCTION

Trimetallic $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3$ cluster units with incomplete cubane-type structures are ubiquitous species in the chemistry of group six transition metal chalcogenides.[1] The coordination sphere around each metal is completed by ligands in a pseudooctahedral environment defined by one capping and two bridging sulphur atoms plus three outer ligands. Proper ligand choice leads to Mo_3S_4 based clusters with specific activities in catalysis. In particular, diphosphino derivatives catalyse the hydrodefluorination of pentafluoropyridine as well as the reduction of nitroarenes with high selectivity.[2-7] Functionalization of this cluster unit with diamine ligands has been used for the selective catalytic hydrosilylation of nitro and azo compounds under mild conditions.[7] Interestingly, trinuclear Mo_3S_4 clusters decorated with cyclopentadienyl ligands catalyse the evolution of hydrogen when coupled to a p-type silicon semiconductor, which harvest most of the solar spectrum.[8] The photocatalytic performance of $NaTaO_3$ for water splitting improves significantly in the presence of the $[Mo_3S_4(H_2O)_9]^{4+}$ aquo cluster as co-catalyst.[9]

Numerous species based on coordination of mono-, bi- and tridentate ligands to the Mo_3S_4 cluster core have been reported.[6, 10-13] In general, coordination of three bidentate LL ligands to the Mo_3S_4 unit results in $[Mo_3S_4X_3(LL)_3]^n$ complexes with two different ligand distribution around the cluster core as shown in Figures 1a and 1b. In the case of oxalate and acetylacetonate ligands, each donor atom is located *trans* to the bridging sulfur so the C_{3v}-symmetry of the cluster core is preserved (Figure 1a). [14, 15] In contrast, functionalization with diphosphane, aminophosphane, diamine and diimine ligands takes place with one donor atom *trans* to the capping sulfur and the other *trans* to the bridging one resulting in chiral clusters with C_3 symmetry, as depicted in Figure 1b. [7, 12, 13, 16-25]



(a) (b)

Figure 1. Ligands distribution in Mo_3S_4 cluster complexes.

During the past years, research in our group has been devoted to the chemistry of chiral $[Mo_3S_4X_3(LL)_3]^+$ clusters derivatized with bidentate ligands containing phosphorous and/or nitrogen donor atoms. Up to date, a large number of complexes differing in the nature of the X ligands such as halide, pseudohalide, hydride, hydroxo, hydrosulphido, or alkoxo have been isolated.[7, 12, 13, 16-24] Incidentally, the number of Mo_3S_4 derivatives bound to outer ligands coordinated in a tridentate fashion is limited to few examples

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such as 1,4,7-triazacyclononane, iminodiacetic acid, nitrilotriacetic and some hydroxyalkylphosphanes.[10, 26-28]

Herein, we report the coordination of an amino-diphosphane (PNP) ligand to the cuboidal Mo_3S_4 core. While most reported PNP mononuclear complexes contain the ligand bound in a tridentate fashion, coordination to the Mo_3S_4 unit can occur in both bidentate or tridentate modes.

2. MATERIALS AND METHOD

Standard Schlenk techniques were used for reactions carried out under nitrogen atmosphere. Electrospray ionization (ESI) mass spectra were recorded with a Quattro LC (quadrupole-hexapole-quadrupole) mass spectrometer with an orthogonal Z-spray electrospray interface (Micromass, Manchester, UK). The cone voltage was set at 20 V using CH_3CN as the mobile phase solvent. Nitrogen was employed as drying and nebulising gas. ^{31}P NMR spectra were recorded on a Varian Innova 300 MHz using CD_2Cl_2 as solvent. Compounds $(Bu_4N)_2[Mo_3S_7Cl_6]$ and $[Mo_3S_4Cl_4(PPh_3)_3(H_2O)_2]$ were prepared by following literature procedures.[11, 29, 30] The remaining reactants were obtained from commercial sources and used as received. Solvents were dried and degassed by standard methods before use.

3. EXPERIMENTAL

Preparation of $[Mo_3S_4Cl_3(\kappa^2(P,N)\text{-PNP})_3]Cl$, [Mo-1]Cl. To a green solution of $[Mo_3S_4Cl_4(PPh_3)_3(H_2O)_2]$ (86.7 mg, 0.062 mmol) in ethanol (15 mL) was added an excess of PNP ligand (63.0 mg, 0.206 mmol; PNP = bis[(2-di-i-propylphosphino)ethyl]amine) under nitrogen atmosphere and the reaction mixture was stirred for 3 hours at room temperature. The solution was concentrated to *ca.* 4 mL under reduced pressure and the product was precipitated with hexane. Finally, the solid was separated by centrifugation and washed with hexane, to afford 76.9 mg of a green powder identified as [**Mo-1**]Cl (83% yield).

^{31}P {^1H} NMR (CD_2Cl_2, 121 MHz) δ= 47.63 (s, 3P), -2.04 (s, 3P). ESI-MS (CH_3CN, 20 V) m/z: 1438 [M+]. Anal. Calc. $Mo_3S_4Cl_4P_6N_3C_{48}H_{111}$ (%): C: 39.10; H: 7.58; N: 2.85; S: 8.70; Exp (%): C: 37.92; H: 7.65; N: 2.60; S: 8.64.

Preparation of $[Mo_3S_4(\kappa^3\text{-PNP})_3](BF_4)_4$, [Mo-2]$(BF_4)_4$. $AgBF_4$ (15.4 mg , 0.079 mmol) was added to a green solution of **[Mo-1]**Cl (19.5 mg, 0.013 mmol) in dichloromethane (10 mL). The mixture was stirred for a few minutes and 1 mL of diethylether was added to solubilize the silver salt. The reaction occurs with a colour change from green to brown and the formation of a precipitate. After four hours of stirring at room temperature, the solid was separated by filtration and *ca.* 5 mL of methanol were added to afford a brown solution and a white solid. The white solid was separated by filtration and the solvent evaporated under reduced pressured to afford 18.3 mg of a brown powder identified as **[Mo-2]**$(BF_4)_4$ (83 % yield).

^{31}P {^1H} NMR (DMSO, 121 MHz) δ= 27.09 (s, 3P, $^2J(^{31}P,^{31}P)$=36.1 Hz), 22.91 (d, 3P, $^2J(^{31}P,^{31}P)$=36.7 Hz). Anal. Calc. $Mo_3S_4P_6N_3C_{48}H_{111}B_4F_{16}$ (%): C: 39.10; H: 7.58; N: 2.85; S: 8.70; Exp (%): C: 40.52; H: 8.65; N: 2.91; S: 9.21.

X-ray data collection and structure refinement. Suitable crystals for X-Ray studies of $[Mo_3S_4Cl_3(\kappa^2(P,N)\text{-PNP})_3]Cl$ (**[Mo-1]**Cl) were grown by slow diffusion of hexane into a sample solution in CH_2Cl_2. Diffraction data for **[Mo-1]**Cl were collected on a Agilent Supernova diffractometer equipped with an Atlas CCD detector using Mo Kα radiation (λ = 0.71073 Å). Absorption corrections based on the multiscan method were applied.[31, 32] Structures were solved using direct methods in SHELX-2013 and refined by the full matrix method based on F^2 using the OLEX software package.[33, 34] Crystal data for **[Mo-1]**Cl: $C_{48}H_{111}Cl_4Mo_3N_3P_6S_4$, M = 1474.07, cubic, space group Pa-3, a = b = c = 24.21458 (13) Å, $\alpha = \beta = \gamma$ = 90.00 º, V = 14198.1 (2) Å^3, T = 199.95 (10) K, Z = 8, μ = 0.957 mm^{-1}. Reflections (collected/unique) = 51257/6122 (R_{int} = 0.0332). Final refinement converged with R_1 = 0.0553 and wR_2 = 0.1157 for all reflections, GOF = 1.158, max/min residual electron density 1.21/-0.42 e· Å^{-3}. The last Fourier map showed two peaks in general position (24d) which displayed similar intensities (*ca.* 2.7 e$^-$/ Å^3). They were assigned to two chlorine atoms and refined anisotropically with a fixed ocuppancy of 1/6, in order to balance the cluster charge. Anisotropic displacement parameters were refined for all non-H atoms.

4. RESULTS AND DISCUSSIONS

Our group has recently reported efficient synthetic strategies for the preparation of diphosphane, amino-phosphane and diamino derivatives of the cuboidal Mo_3S_4 cluster unit starting from the $[Mo_3S_4Cl_4(PPh_3)_3(H_2O)_2]$ molecular precursor by simple ligand exchange reactions.[21, 24] Motivated by these results, we decided to extend this procedure to the aminodiphosphane bis[(2-di-i-propylphosphino)ethyl]amine ligand (PNP). The reaction between $[Mo_3S_4Cl_4(PPh_3)_3(H_2O)_2]$ and stoichiometric amounts of PNP leads to the isolation of the $[Mo_3S_4Cl_3(\kappa^2(P,N)\text{-PNP})_3]Cl$ (**[Mo-1]**Cl) cluster salt in 83% yields, according to equation 1.

$$[Mo_3S_4Cl_4(PPh_3)_3(H_2O)_2] + 3\ PNP \rightarrow [Mo_3S_4Cl_3(\kappa^2(P,N)\text{-}PNP)_3]Cl + 3\ PPh_3 + 2\ H_2O \quad (1)$$

The ESI mass spectrum of the reaction product shows one peak centred at 1438 *m/z* associated to the molecular $[Mo_3S_4Cl_3(PNP)_3]^+$ cation on the basis of the *m/z* value and its characteristic isotopic pattern (see Figure 2). This formulation reveals a bidentate coordination of the PNP ligand to the metal centre. The structure of the new cluster salt has been determined by single crystal X-ray diffraction and confirmed by phosphorus NMR spectroscopy.

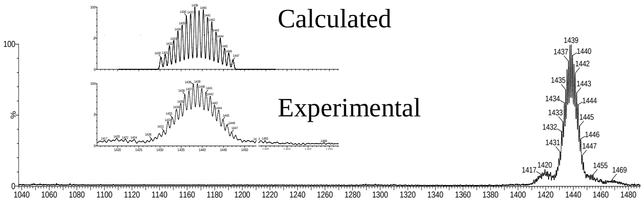

Figure 2. Calculated and experimental ESI mass spectra of **[Mo-1]**$^+$.

ORTEP **representations** of the **[Mo-1]**$^+$ cation are given in Figure 3. The structure was solved in the cubic Pa-3 space group with the capping sulphur atom of the $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3$ core lying on a three-fold axis. Accordingly, the three metal atoms define an equilateral triangle with Mo-Mo distances of 2.7772(4) Å consistent with the presence of three single metal-metal bonds and a +4 oxidation state for the metal. All molybdenum atoms present a pseudo-octahedral environment, defined by one capping and two bridging sulphur atoms, a chloride ligand, one phosphorous and one nitrogen atoms. Table 1 lists the most relevant bond lengths for **[Mo-1]**$^+$ together with those of two aminophosphino related cluster complexes. The Mo-Mo and Mo-S bond distances follow the trends observed for other Mo_3S_4 cluster compounds bearing aminophosphane ligands. As it is the case of the previously reported $[Mo_3S_4Cl_3((1S,2S)\text{-PPro})_3]^+$ and $[Mo_3S_4Cl_3(edpp)_3]^+$ complexes, only the isomer with the phosphorous atom bound *trans* to the capping sulphur is being formed. [13, 24, 25]

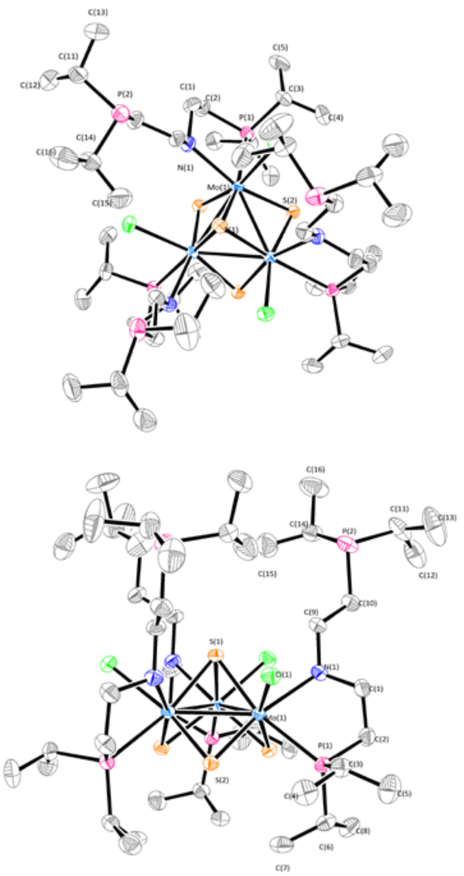

Figure 3. ORTEP representations of two different views of the cluster **[Mo-1]**$^+$ (ellipsoids 50 % probability). Hydrogen atoms have been omitted for clarity.

As shown in Figure 3, the PNP aminodiphosphane ligand coordinates to the Mo_3S_4 unit in a bidentate mode with the phosphorus atom *trans* to the capping sulphur and the nitrogen atom *trans* to a bridging sulphur leaving three dangling phosphino groups. To our knowledge, coordination of the PNP ligand to molybdenum always occurs in a tridentate mode while dangling phosphino groups are found in mononuclear complexes functionalized with NP_3-type tripodal aminophosphane ligands.[35-38] The most remarkable differences in the bond distances between the metal and the atoms (P, N and Cl) of the outer ligands refer to the Mo-N bond lengths that are *ca.* 0.07 Å longer in **[Mo-1]**$^+$ than those observed for previously reported $[Mo_3S_4Cl_3(\text{aminophosphane})_3]^+$ complexes. [13, 24, 25] This fact can be attributed to steric effects caused by the bulky PNP ligand.

Table 1. Selected Averaged Bond Distances for compounds [Mo-1]$^+$, (*P*)- $[Mo_3S_4Cl_3((1S,2S)\text{-PPro})_3]^+$ and $[Mo_3S_4Cl_3(edpp)_3]^+$.

Distance (Å)[a]	[Mo-1]$^+$	$[Mo_3S_4Cl_3((1S,2S)\text{-PPro})_3]^{+b}$	$[Mo_3S_4Cl_3(edpp)_3]^{+c}$
Mo-Mo	2.7772(4)	2.757(1)	2.7464[7]
Mo-(μ_3-S)	2.3539(10)	2.353(3)	2.3610[13]
Mo-(μ-S)[d]	2.2936(8)	2.293(2)	2.2862[12]
Mo-(μ-S)[e]	2.2923(8)	2.294(2)	2.2961[12]
Mo-P	2.5746(8)	2.550(2)	2.5413[14]
Mo-N	2.346(3)	2.289(7)	2.273[4]
Mo-Cl	2.4910(8)	2.484(2)	2.4626[15]

[a]Standard deviations for measured values are given in brackets. Standard deviations for averaged values are given in square brackets [b]Data taken from ref [24]. [c]Data taken from ref [25]. [d]Distance *trans* to the Mo-N bond. [e]Distance *trans* to the Mo-P bond

The ^{31}P $\{^1H\}$-NMR spectrum of $[Mo_3S_4Cl_3(\kappa^2(P,N)\text{-}PNP)_3]^+$ (**[Mo-1]**$^+$) shows two independent signals of equal intensity at 47.63 ppm and -2.04 ppm (see Figure 4, top). The signal at higher fields corresponds to the three equivalent dangling group phosphorus atoms.

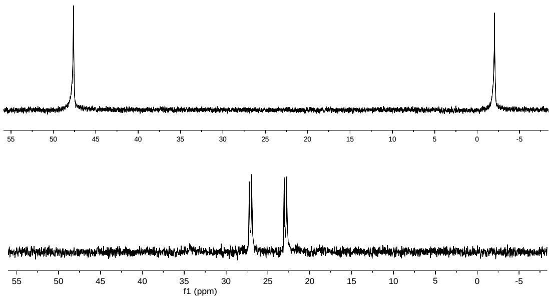

Figure 4. ^{31}P $\{^1H\}$-NMR spectra of **[Mo-1]**$^+$ (top) and **[Mo-2]**$^{4+}$(bottom)

With the aim to achieve a tridententate mode coordination of the PNP ligand to the Mo_3S_4 cluster unit, the **[Mo-1]**$^+$ cation was reacted with a silver salt causing precipitation of AgCl, according to equation 2.

$$[Mo_3S_4Cl_3(\kappa^2(P,N)\text{-}PNP)_3]Cl + 4\ AgBF_4 \rightarrow [Mo_3S_4(\kappa^3\text{-}PNP)_3](BF_4)_4 + 4\ AgCl \quad (2)$$

The reaction product precipitates from the mixture as a brown solid which was redisolved in methanol and separated from the AgCl white precipitate. The resulting brown solid isolated upon solvent evaporation has been identified as $[Mo_3S_4(\kappa^3\text{-}PNP)_3](BF_4)_4$ (**[Mo-2]**$(BF_4)_4$) by ^{31}P $\{^1H\}$-NMR spectroscopy and elemental analysis. Complex **[Mo-2]**$^+$ shows two doublets centered at 27.09 and 22.91 ppm (see Figure 4 bottom) in agreement with the coordination of two non-equivalent phosphorus atoms of the PNP to the same metal center. This pattern is found in the series of $[M_3S_4X_3(\text{diphosphane})_3]^+$ (M = Mo, W; X = Cl, Br, H) complexes with C_3 symmetry.[6, 12] Formulation of [**Mo-2**]$(BF_4)_4$ as $[Mo_3S_4(\kappa^3\text{-PNP})_3](BF_4)_4$ has also been confirmed by elemental analysis. Unfortunately, the [**Mo-2**]$^{4+}$ has not been detected by ESI-MS and all attempts to grown single crystals failed.

Changes in the coordination mode of the ligand from bidentate to tridentate in Mo_3S_4 complexes is not unprecedented. In this context, our group has reported that $[Mo_3S_4Cl_3(\kappa^2(PP)\text{-hydroxialkylphosphane})_3]^+$ (hydroxialkylphosphane = dhmpe, dhprpe) complexes transform into $[Mo_3S_4Cl_3(\kappa^3\text{-hydroxialkylphosphane-H})_3]^+$ cations in aqueous solutions under basic conditions.[18, 20, 21] This transformation can be reverted upon acidification.

Reactivity studies of complex $[Mo_3S_4Cl_3(\kappa^2(P,N)\text{-PNP})_3]^+$ ([**Mo-1**]$^+$**)** with other metals directed towards the formation of heterobimetallic clusters are in progress. The presence of two different coordination modes in [**Mo-1**]$^+$, that is the bridging Mo_3S_4 sulfur atoms and the dangling phosphorous atoms, increase the versatility of this complex as precursor of a large variety of multimetallic systems. These reactivity studies are of relevance within the framework of our research on new catalytic applications of cluster based compounds.

CONCLUSION

Two trinuclear Mo_3S_4 clusters bearing the PNP aminodiphosphane ligand, namely $[Mo_3S_4Cl_3(\kappa^2(P,N)\text{-PNP})_3]Cl$ ([**Mo-1**]Cl) and $[Mo_3S_4Cl_3(\kappa^3\text{-PNP})_3](BF_4)_4$ ([**Mo-2**]$(BF_4)_4$), have been isolated in high (83%) yields. The crystal structure of [**Mo-1**]$^+$ shows the presence of three dangling phosphino groups pointing towards the same side of the triangle defined by the three metal atoms. Transformation of **[Mo-1]**$^+$ into **[Mo-2]**$^{4+}$ by treatment with $AgBF_4$ promotes the intramolecular substitution of chlorides by the dangling phosphino groups to yield **[Mo-2]**$(BF_4)_4$ and AgCl. The presence of dangling phosphino groups in **[Mo-1]**$^+$ that could react with other metal opens new opportunities in cluster catalysis.

LIST OF ABBREVIATIONS

edpp: 2-(aminoethyl)diphenylphosphane

dhmpe: 1,2-bis(bis(hydroxymethyl)phosphinoethane

dhprpe: 1,2-bis(bis(hydroxypropyl)phosphinoethane

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SUPPLEMENTARY MATERIAL

CCDC 1523502 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or e-mail:deposit@ccdc.cam.ac.uk).

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GRAPHICAL ABSTRACT