Coordination modes of aminodiphosphane ligands to the cuboidal Mo$_3$S$_4$ cluster unit

Carmina Alfonso$^a$, Rosa Llusar$^{*a}$ and Marta Feliz$^b$

$^a$Departament de Química Física i Analítica, Universitat Jaume I, Av. Sos Baynat s/n, 12071 Castelló, Spain $^b$Instituto de Tecnología Química, Universitat Politècnica de València - Consejo Superior de Investigaciones Científicas, Avda. de los Naranjos s/n, 46022, Valencia, Spain

Abstract: The aminodiphosphanes molybdenum (IV) cluster complex of formula [Mo$_3$S$_4$Cl$_3$(κ$^2$(P,N)-PNP)$_3$]Cl (PNP = bis[(2-di-i-propylphosphino)ethyl]amine) [Mo-1]Cl has been isolated in high yields by reacting [Mo$_3$S$_4$Cl$_4$(PPh$_3$)$_3$(H$_2$O)$_2$] with stoichiometric amounts of the PNP ligand. Characterization of [Mo-1]$^+$ by ESI-MS, $^{31}$P{$_1$H} NMR and single-crystal X-ray diffraction confirms that aminodiphosphanes bind as bidentate ligands to the Mo$_3$S$_4$ 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$_3$S$_4$(κ$^3$-PNP)$_3$](BF$_4$)$_4$ ([Mo-2](BF$_4$)$_4$). The tridentate coordination of the aminodiphosphane ligands to the Mo$_3$S$_4$ cluster unit in ([Mo-2]$^+$ is confirmed by $^{31}$P{$_1$H} NMR and elemental analysis.

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

1. INTRODUCTION

Trimetallic Mo$_3$($\mu$_3-$S$)($\mu$_3-$S$)$_3$ 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 pseudo-octahedral environment defined by one capping and two bridging sulphur atoms plus three outer ligands. Proper ligand choice leads to Mo$_3$S$_4$ based clusters with specific activities in catalysis. In particular, diphosphine 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$_3$S$_4$ 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$_3$S$_4$(H$_2$O)$_9$]$^{4+}$ aquo cluster as co-catalyst.[9]

Numerous species based on coordination of mono-, bi- and tridentate ligands to the Mo$_3$S$_4$ cluster core have been reported.[6, 10-13] In general, coordination of three bidentate LL ligands to the Mo$_3$S$_4$ unit results in [Mo$_3$S$_4$L$_3$(LL)$_3$]$^+$ 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 diphosphate, 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]

Figure 1. Ligands distribution in Mo$_3$S$_4$ cluster complexes.

During the past years, research in our group has been devoted to the chemistry of chiral [Mo$_3$S$_4$L$_3$(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$_3$S$_4$ derivatives bound to outer ligands coordinated in a tridentate fashion is limited to few examples.

[Address correspondence to this author at the Department of Química Física i Analítica, Universitat Jaume I, Avda. Sos Baynat s/n, 12071, Castelló (Spain); Tel/Fax: +34964728086, +34964728066; E-mail: rosa.llusar@uji.es.]

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

Herein, we report the coordination of an amino-diphosphane (PNP) ligand to the cuboidal Mo$_3$S$_4$ core. While most reported PNP mononuclear complexes contain the ligand bound in a tridentate fashion, coordination to the Mo$_3$S$_4$ 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$_3$CN 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$_2$Cl$_2$ as solvent. Compounds [Bu$_4$N]$_2$[Mo$_3$S$_7$Cl$_6$] and [Mo$_3$S$_4$Cl$_3$(PPh$_3$)$_3$(H$_2$O)$_2$] were prepared by following literature procedures.[11, 29, 30] The remaining reactants were obtained from commercial sources and used as received.

Solvants were dried and degassed by standard methods before use.

3. EXPERIMENTAL

Preparation of [Mo$_3$S$_4$Cl$_3$(κ$_2$(P,N)-PNP)]Cl$_2$ (Mo-1)Cl. To a green solution of [Mo$_3$S$_4$Cl$_3$(PPh$_3$)$_3$(H$_2$O)$_2$] (86.7 mg, 0.062 mmol) in ethanol (15 mL) was added an excess of PNP ligand (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 $^1$H NMR (CD$_2$Cl$_2$, 121 MHz) δ = 47.63 (s, 3P), -2.04 (s, 3P). ESI-MS (CH$_3$CN, 20 V) m/z: 1438 [M$^+$. Anal. Calc. Mo$_3$S$_4$Cl$_3$P$_6$N$_3$C$_{48}$H$_{111}$ (%): C: 39.10; H: 7.58; N: 2.85; S: 8.70; Exp (%): C: 39.72; H: 7.65; N: 2.60; S: 8.64.

Preparation of [Mo$_3$S$_4$(κ$_3$-PNP)]$^3^+$ (BF$_4$)$_3$, [Mo-2](BF$_4$)$_3$. 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 pressure to afford 18.3 mg of a brown powder identified as [Mo-2](BF$_4$)$_3$ (83% yield).

$^{31}$P $^1$H NMR (DMSO, 121 MHz) δ = 27.09 (s, 3P), 2(J$^{31}$P,$^{31}$P=36.1 Hz), 22.91 (d, 3P, J$^{31}$P,$^{31}$P=36.7 Hz). Anal. Calc. Mo$_3$S$_4$P$_6$N$_3$C$_{48}$H$_{111}$[BF$_4$]$_3$ (%): 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$_3$S$_4$Cl$_3$(κ$_2$(P,N)-PNP)]Cl$_2$ (Mo-1)Cl were grown by slow diffusion of hexane into a sample solution in CH$_2$Cl$_2$. Diffraction data for [Mo-1]Cl were collected on an 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: Ca$_{11}$Cl$_3$Mo$_3$N$_3$P$_6$S$_7$, M = 1474.07, cubic, space group Pa-3, a = 4.09 Å, α = γ = 90.00°, 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 occupancy 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$_3$S$_4$ cluster unit starting from the [Mo$_3$S$_4$Cl$_3$(PPh$_3$)$_3$(H$_2$O)$_2$] 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$_3$S$_4$Cl$_3$(PPh$_3$)$_3$(H$_2$O)$_2$] and stoichiometric amounts of PNP leads to the isolation of the [Mo$_3$S$_4$Cl$_3$(κ$_3$(P,N)-PNP)]Cl (Mo-1)Cl cluster salt in 83% yields, according to equation 1.

[Mo$_3$S$_4$Cl$_3$(PPh$_3$)$_3$(H$_2$O)$_2$] + 3 PNP $\rightarrow$ [Mo$_3$S$_4$Cl$_3$(κ$_3$(P,N)-PNP)]Cl + 3 PPh$_3$ + 2 H$_2$O (1)

The ESI mass spectrum of the reaction product shows one peak centred at 1438 m/z associated to the molecular [Mo$_3$S$_4$Cl$_3$(PNP)$_3$]$^{3^+}$ 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 cluster. 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$_3$S$_4$(μ$_3$-S)(μ$_S$-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 atom. Table 1 lists the most relevant bond lengths for \([\text{Mo-1}]^+\) together with those of two aminophosphino related cluster complexes. The Mo-Mo and Mo-S bond distances follow the trends observed for other Mo\(_3\)S\(_4\) cluster compounds bearing aminophosphane ligands. As it is the case of the previously reported \([\text{Mo}_3\text{S}_4\text{Cl}_3((1S,2S)-\text{PPro})_3]^+\) and \([\text{Mo}_3\text{S}_4\text{Cl}_3(\text{edpp})_3]^+\) complexes, only the isomer with the phosphorous atom bound \textit{trans} to the capping sulphur is being formed. [13, 24, 25]

\[\text{Mo-Mo} = 2.7772(4) \text{ Å} \quad \text{Mo-σ-S} = 2.3539(10) \quad \text{Mo-μ-S} = 2.2936(8) \quad \text{Mo-P} = 2.5746(8) \quad \text{Mo-N} = 2.346(3) \quad \text{Mo-Cl} = 2.4910(8)\]

\[\text{Mo-Mo} = 2.757(1) \quad \text{Mo-σ-S} = 2.353(3) \quad \text{Mo-μ-S}^a = 2.293(2) \quad \text{Mo-P} = 2.550(2) \quad \text{Mo-N} = 2.289(7) \quad \text{Mo-Cl} = 2.484(2)\]

\[\text{Mo-Mo} = 2.7464(7) \quad \text{Mo-σ-S} = 2.3610(13) \quad \text{Mo-μ-S}^a = 2.2862(12) \quad \text{Mo-P} = 2.5413(14) \quad \text{Mo-N} = 2.273(4) \quad \text{Mo-Cl} = 2.4626(15)\]

\(^a\)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 \textit{trans} to the Mo-N bond. \(^e\)Distance \textit{trans} to the Mo-P bond.

The \(^{31}\text{P} \{^1\text{H}\}-\text{NMR}\) spectrum of \([\text{Mo}_3\text{S}_4\text{Cl}_3(κ^2(P,N)-\text{PNP})_3]^+\) (\([\text{Mo-1}]^+\)) 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 3](image-url)

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

As shown in Figure 3, the PNP aminodiphosphane ligand coordinates to the Mo\(_3\)S\(_4\) unit in a bidentate mode with the phosphorus atom \textit{trans} to the capping sulphur and the nitrogen atom \textit{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 \([\text{Mo-1}]^+\) than those observed for previously reported \([\text{Mo}_3\text{S}_4\text{Cl}_3(\text{aminophosphane})_3]^+\) complexes. [13, 24, 25] This fact can be attributed to steric effects caused by the bulky PNP ligand.

\[\text{Mo-1} + 4 \text{AgBF}_4 \rightarrow \text{Mo}_3\text{S}_4(κ^2-PNP)_3(\text{BF}_4)_4 + 4 \text{AgCl} \] (2)

The reaction product precipitates from the mixture as a brown solid which was redissolved in methanol and separated from the AgCl white precipitate. The resulting brown solid isolated upon solvent evaporation has been identified as \([\text{Mo}_3\text{S}_4(κ^3-PNP)_3(\text{BF}_4)_4] (\text{Mo-2})^+\) by \(^{31}\text{P} \{^1\text{H}\}-\text{NMR}\) spectroscopy and elemental analysis. Complex \([\text{Mo-2}]^+\) shows two doublets centered at 27.09 and 22.91 ppm (see Figure 4 bottom) in agreement with the coordination of two

\[\begin{array}{cccc}
\text{Distance} & \text{[Mo-1]}^+ & \text{[Mo}_3\text{S}_4\text{Cl}_3((1S,2S)-\text{PPro})_3]^+ & \text{[Mo}_3\text{S}_4\text{Cl}_3(\text{edpp})_3]^+
\hline
\text{Mo-Mo} & 2.7772(4) & 2.757(1) & 2.7464(7)
\text{Mo-(μ-3-S)} & 2.3539(10) & 2.353(3) & 2.3610(13)
\text{Mo-(μ-S)}^a & 2.2936(8) & 2.293(2) & 2.2862(12)
\text{Mo-(μ-S)}^e & 2.2923(8) & 2.294(2) & 2.2961(12)
\text{Mo-P} & 2.5746(8) & 2.550(2) & 2.5413(14)
\text{Mo-N} & 2.346(3) & 2.289(7) & 2.273(4)
\text{Mo-Cl} & 2.4910(8) & 2.484(2) & 2.4626(15)
\end{array}\]
non-equivalent phosphorus atoms of the PNP to the same metal center. This pattern is found in the series of \([\text{Mo}_2\text{S}_3\text{X}_3(\text{diphasphane})]^{\text{+}}\) (M = Mo, W; X = Cl, Br, H) complexes with C\(_2\) symmetry.\cite{6, 12} Formulation of \([\text{Mo}_2\text{S}_3\text{Cl}_3(\text{κ}^3\text{-PNP})_3][\text{BF}_4]_4\) has also been confirmed by elemental analysis. Unfortunately, the \([\text{Mo}_2\text{S}_3\text{Cl}_3(\text{κ}^3\text{-PNP})_3][\text{BF}_4]_4\) 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 \([\text{Mo}_2\text{S}_3\text{Cl}_3(\text{κ}^3\text{-PNP})_3][\text{BF}_4]_4\) complexes is not unprecedented. In this context, our group has reported that \([\text{Mo}_2\text{S}_3\text{Cl}_3(\text{κ}^3\text{-PNC})_3][\text{BF}_4]_4\) has also been confirmed by elemental analysis. Unfortunately, the \([\text{Mo}_2\text{S}_3\text{Cl}_3(\text{κ}^3\text{-PNC})_3][\text{BF}_4]_4\) has not been detected by ESI-MS and all attempts to grown single crystals failed.

Reactivity studies of complex \([\text{Mo}_2\text{S}_3\text{Cl}_3(\text{κ}^3\text{-P,N})_3][\text{BF}_4]_4\) with other metals directed towards the formation of heterobimetallic clusters are in progress. The presence of two different coordination modes in \([\text{Mo}_2\text{S}_3\text{Cl}_3(\text{κ}^3\text{-P,N})_3][\text{BF}_4]_4\), that is the bridging \([\text{Mo}_2\text{S}_3\text{Cl}_3(\text{κ}^3\text{-P,N})_3][\text{BF}_4]_4\) complex transform into \([\text{Mo}_2\text{S}_3\text{Cl}_3(\text{κ}^3\text{-P,N})_3][\text{BF}_4]_4\) cations in aqueous solutions under basic conditions.\cite{18, 20, 21} This transformation can be reverted upon acidification.

Reactivity studies of complex \([\text{Mo}_2\text{S}_3\text{Cl}_3(\text{κ}^3\text{-P,N})_3][\text{BF}_4]_4\) with other metals directed towards the formation of heterobimetallic clusters are in progress. The presence of two different coordination modes in \([\text{Mo}_2\text{S}_3\text{Cl}_3(\text{κ}^3\text{-P,N})_3][\text{BF}_4]_4\), that is the bridging \([\text{Mo}_2\text{S}_3\text{Cl}_3(\text{κ}^3\text{-P,N})_3][\text{BF}_4]_4\) complex transform into \([\text{Mo}_2\text{S}_3\text{Cl}_3(\text{κ}^3\text{-P,N})_3][\text{BF}_4]_4\) cations in aqueous solutions under basic conditions.\cite{18, 20, 21} This transformation can be reverted upon acidification.

**CONCLUSION**

Two trinuclear \([\text{Mo}_2\text{S}_4]\) clusters bearing the PNP aminodiphosphane ligand, namely \([\text{Mo}_2\text{S}_3\text{Cl}_3(\text{κ}^3\text{-P,N})_3][\text{BF}_4]_4\) (\([\text{Mo}_2\text{S}_3\text{Cl}_3(\text{κ}^3\text{-P,N})_3][\text{BF}_4]_4\)) and \([\text{Mo}_2\text{S}_3\text{Cl}_3(\text{κ}^3\text{-P,N})_3][\text{BF}_4]_4\) (\([\text{Mo}_2\text{S}_3\text{Cl}_3(\text{κ}^3\text{-P,N})_3][\text{BF}_4]_4\)), have been isolated in high (83%) yields. The crystal structure of the \([\text{Mo}_2\text{S}_3\text{Cl}_3(\text{κ}^3\text{-P,N})_3][\text{BF}_4]_4\) and \([\text{Mo}_2\text{S}_3\text{Cl}_3(\text{κ}^3\text{-P,N})_3][\text{BF}_4]_4\) have also been confirmed by ESI-MS and all attempts to grown single crystals failed.

**LIST OF ABBREVIATIONS**

edpp: 2-(aminoethyl)diphenylphosphane
dhmpe: 1,2-bis(hydroxymethyl)phosphinoethane
dhprpe: 1,2-bis(hydroxypropyl)phosphinoethane

**ACKNOWLEDGEMENTS**

The financial support of the Spanish Ministerio de Economía y Competitividad (Grant CTQ2015-65207), Universitat Jaume I (Research Project P1-1B2013-19) and Generalitat Valenciana (Prometeo/2014/022) is gratefully acknowledged. The authors also thank the Servei Central d’Instrumentació Científica (SCIC) of the University Jaume I for providing us with the mass spectrometry, NMR, elemental analysis and X-ray facilities. C.A. thanks the Spanish Ministerio de Economía y Competitividad for a predoctoral fellowship (FPI).

Journal Name, 2014, Vol. 0, No. 0

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T. A. George, D. J. Rose, Y. Chang, Q. Chen and J. Zubieta, Reduction of Dinitrogen to Ammonia and Hydrazine in Iron(0) and Molybdenum(0) Complexes Containing the N(CH$_2$CH$_2$PPh$_2$)$_3$ Ligand. Crystal Structures of [FeH(L)(N(CH$_2$CH$_2$PPh$_2$)$_3$)][BPh$_4$] (L = N$_2$, CO), Inorg. Chem., 1995, 34, 1295-1298


Received: March 20, 2014 Revised: April 16, 2014 Accepted: April 20, 2014

GRAPHICAL ABSTRACT