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Article

Synthesis, Crystal Structure, Aqueous Speciation, and Kinetics of Substitution Reactions in a Water-Soluble Mo_3S_4 Cluster Bearing Hydroxymethyl Diphosphine Ligands

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The $[Mo_3S_4Cl_3(dhmpe)_3]Cl$ ([**1**]Cl) cluster has been prepared from $[Mo_3S_7Cl_6]^{2-}$ and the water-soluble 1,2-bis(bis-(hydroxymethyl)-phosphino)ethane (dhmpe, L) ligand. The crystal structure has been determined by X-ray diffraction methods and shows the incomplete cuboidal structure typical of the M_3Q_4 clusters (M = Mo, W; Q = S, Se), with a capping sulfide ligand to the three metal centers and the other three sulfides acting as bridges between two Mo atoms. The octahedral coordination around each metal center is completed with a chlorine and two phosphorus atoms of one L ligand. The chemistry of aqueous solutions of [**1**]Cl is dominated by the formation of the $[Mo_3S_4L(L\text{-}H)_2(H_2O)]^{2+}$ complex ([**2**]$^{2+}$), where the three chlorides have been replaced by one water molecule and two alkoxo groups of two different dhmpe ligands, thus leading to a solution structure where the three metal centers are not equivalent. A detailed study based on stopped-flow, $^{31}P\{^1H\}$ NMR, and electrospray ionization mass spectrometry techniques has been carried out to understand the behavior of [**2**]$^{2+}$ in aqueous solution. In this way, it has been established that the addition of an excess of X^- (Cl^-, SCN^-) leads to $[Mo_3S_4X_3(dhmpe)_3]^+$ complexes in three resolved kinetic steps that correspond to the sequential coordination of X^- at the three metal centers. However, whereas the first two steps involve the opening of the chelate rings formed with the alkoxo groups of the dhmpe ligands, the third one corresponds to the substitution of the coordinated water molecule. These results demonstrate that the asymmetry introduced by the closure of chelate rings at only two of the three Mo centers makes the kinetics of the reaction deviate significantly from the statistical behavior typically associated with M_3Q_4 clusters. The results obtained for the reaction of [**2**]$^{2+}$ with acid and base are also described, and they complete the picture of the aqueous speciation of this cluster.

Introduction

The chemistry of water-soluble transition-metal complexes containing phosphine ligands is of interest because of the potential usefulness of these complexes in biphasic (aqueous−organic) catalysis and biomedicine.[1−5] In particular, two-phase catalysis can solve basic problems in homogeneous catalysis such as the separation and further recycling of the catalyst, making these processes environmentally friendly. On the other hand, water-soluble transition-metal complexes of specific metals such as Cu, Tc, or Re can be useful as pharmaceutical or radiopharmaceutical agents. Among the various ligand families available to produce aqueous soluble coordination compounds, functionalized phosphines are among the most attractive because of their

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[†] Universidad de Cádiz.

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(1) Pinault, N.; Bruce, D. W. *Coord. Chem. Rev.* **2003**, *241*, 1−25.

(2) Herrmann, W. A.; Kohlpaintner, C. W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1524−1544.

(3) Kothari, K. K.; Raghuraman, K.; Pillarsetty, N. K.; Hoffman, T. J.; Owen, N. K.; Katti, K. V.; Volkert, W. A. *Appl. Radiat. Isot.* **2003**, *58*, 543−549.

(4) Dilworth, J. R.; Parrott, S. J. *Chem. Soc. Rev.* **1998**, *27*, 43−55.

(5) Blower, P. J. *Trans. Met. Chem.* **1998**, *23*, 109−112.

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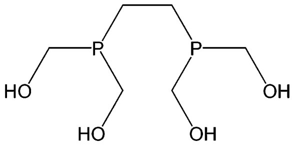
versatile coordination chemistry.[1,6] In particular, phosphines with hydroxyalkyl groups such as the tris(hydroxymethyl)-phosphine (THP) have enabled the development of a wide spectrum of water-soluble transition/organometallic complexes of Pd,[7] Pt,[7] Rh,[8] Re,[9] Ru,[10] or Ir.[11] The coordination chemistry of hydroxyalkyl diphosphines with early and late transition metals (Fe,[12] Ni, Ru, Rh,[13] Pt,[14,15] Pd,[15] Re,[16] or Au[17]) has also been investigated, and in some cases, the activity of the complexes in biphasic catalytic reactions has been explored.

Despite the fact that hydroxyalkyl-functionalized diphosphines have proved to be excellent chelating agents to afford water-soluble mononuclear complexes, their coordination chemistry on higher-nuclearity systems remains unknown. As with their mononuclear counterparts, the access to water-soluble cluster complexes also represents a major focus in biomedicine and biphasic catalysis. For example, the water-soluble trinuclear $W_3(\mu_3\text{-}S)(\mu\text{-}Q)_3$ ($Q = O$, S) complexes bearing polyaminopolycarboxylate ligands represent a new generation of contrast agents with several advantages in comparison with the traditionally used compounds.[18,19] On the other hand, several ruthenium carbonyl clusters bearing sulfonated phosphines or the cluster hydride $[H_4Ru_4(\eta_6\text{-arene})_4]^{2+}$ have been employed as catalysts in hydrogenation reactions in aqueous media and biphasic conditions, respectively.[20]

An interesting family of water-soluble cluster complexes is that based on the cuboidal M_3S_4 core ($M = Mo$, W), to which a variety of heterometals can be readily incorporated to give $M_3M'S_4$ cluster complexes ($M' =$ transition or post-transition metal). For several decades, the aqueous chemistry of this family of complexes has been dominated by species of general formula $[M_3S_4(H_2O)_9]^{4+}$ or $[M_3M'S_4(H_2O)_{10}]^{4+}$ but their stability is limited to very acidic media, i.e., pH <1.[21] In the last years, our group has been working in the development of M_3Q_4 and $M_3M'Q_4$ complexes where an increased stability is achieved upon water substitution by diphosphine ligands, the resulting compounds usually being soluble in common organic media.[22] The catalytic activity of $Mo_3M'S_4$ ($M = Cu$,[23] Pd,[24,25] Ru[26]) complexes has been demonstrated for a wide spectrum of reactions, including the addition of alcohols or carboxylic acids to deficient alkynes, N−N bond cleavages, or the inter- and intramolecular cyclopropanation of diazocompounds. It is expected that all the previous knowledge of the chemistry of these compounds acquired from work in nonaqueous solvents can be a useful starting point to get a better understanding of the processes that might actually occur in aqueous solutions. The adaptation of efficient catalysts in organic solvents to aqueous media is one of the current major trends in homogeneous catalysis research. In addition, for this particular case, the potential biomedical applications of M_3Q_4 complexes also requires stable water-soluble compounds,[18,19] in parallel with the development of environmentally friendly $Mo_3M'S_4$ cluster-based catalysts.

Chart 1



dhmpe, L

Previously, we have taken the approach of the direct coordination of hydroxo groups to the metal site in W_3Q_4 complexes to produce the $[W_3(\mu_3\text{-}Q)(\mu\text{-}Q)_3(OH)_3(dmpe)_3]^+$ ($Q = S$, Se) complexes with a limited water solubility, ca. 0.08 mM at pH 7.[27,28] Besides metal functionalization, another attractive approach to obtain water-soluble cluster complexes involves the decoration of the outer coordination sphere with substituents that either ionize in water (sulfonates, carboxylates, phosphonates, ammonium, etc.) or establish strong hydrogen-bonding interactions in an aqueous medium (e.g., OH, NH_2, etc.). In this context, we have extended our research toward the coordination chemistry of diphosphine-containing Mo_3S_4 clusters containing the water-soluble 1,2-bis(bis(hydroxymethyl)-phosphino)ethane (dhmpe, L) diphosphine ligand (see Chart 1), and here we report the high-yield synthesis, crystal structure, and aqueous speciation of the $[Mo_3S_4Cl_3L_3]Cl$ ([**1**]Cl) cluster complex.

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(6) Katti, K. V.; Gali, H.; Smith, C. J.; Berning, D. E. *Acc. Chem. Res.* **1999**, *32*, 9−17.

(7) Ellis, J. W.; Harrison, K. N.; Hoye, P. A. T.; Orpen, A. G.; Pringle, P. G.; Smith, M. B. *Inorg. Chem.* **1992**, *31*, 3026−3033.

(8) Chatt, J.; Leigh, J. G.; Slade, R. M. *J. Chem. Soc., Dalton Trans.* **1973**, 2021−2028.

(9) Berning, D. E.; Katti, K. V.; Barbour, L. J.; Volkert, W. A. *Inorg. Chem.* **1998**, *37*, 334−339.

(10) Driessen-Hölscher, B.; Heinen, J. *J. Organomet. Chem.* **1998**, *570*, 141−146.

(11) Fukoka, A.; Kosugi, W.; Morishita, F.; Hirano, M.; McCaffrey, L.; Henderson, W.; Komiya, S. *Chem. Commun.* **1999**, 489−490.

(12) Miller, W. K.; Gilbertson, J. D.; Leiva-Paredes, C.; Bernatis, P. R.; Weakley, T. J. R.; Lyon, D. K.; Tyler, D. R. *Inorg. Chem.* **2002**, *41*, 5453−5465.

(13) Baxley, G. T.; Miller, W. K.; Lyon, D. K.; Miller, B. E.; Nieckarz, G. F.; Weakley, T. J. R.; Tyler, D. R. *Inorg. Chem.* **1996**, *35*, 6688−6693.

(14) Reddy, V. S.; Katti, K. V.; Barnes, C. L. *Inorg. Chim. Acta* **1995**, *240*, 367−370.

(15) Reddy, V. S.; Katti, K. V.; Barnes, C. L. *J. Chem. Soc., Dalton Trans.* **1996**, 1301−1304.

(16) Reddy, V. S.; Katti, K. V.; Berning, D. E.; Volkert, W. A.; Barnes, C. L. *Inorg. Chem.* **1996**, *35*, 1753−1757.

(17) Berning, D. E.; Katti, K. V.; Barnes, C. L.; Volkert, W. A.; Ketring, A. R. *Inorg. Chem.* **1997**, *36*, 2765−2769.

(18) Yu, S. B.; Droege, M.; Segal, B.; Kim, S. H.; Sanderson, T.; Watson, A. D. *Inorg. Chem.* **2000**, *39*, 1325−1328.

(19) Yu, S. B.; Droege, M.; Downney, S.; Segal, B.; Newcomb, W.; Sanderson, T.; Crofts, S.; Suravajjala, S.; Bacon, E.; Earley, W.; Delecki, D.; Watson, A. D. *Inorg. Chem.* **2001**, *50*, 1576−1581.

(20) Dyson, P. J. *Coord. Chem. Rev.* **2004**, *248*, 2443−2458.

(21) Hernandez-Molina, R.; Sokolov, M. N.; Sykes, A. G. *Acc. Chem. Res.* **2001**, *34*, 223−230.

(22) Llusar, R.; Uriel, S. *Eur. J. Inorg. Chem.* **2003**, 1271−1290.

(23) Feliz, M.; Guillamon, E.; Llusar, R.; Vicent, C.; Stiriba, S. E.; Perez-Prieto, J.; Barberis, M. *Chem.−Eur. J.* **2006**, *12*, 1486−1492.

(24) Wakabayashi, T.; Ishii, Y.; Ishikawa, K.; Hidai, M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2123−2124.

(25) Wakabayashi, T.; Ishii, Y.; Murata, T.; Mizobe, Y.; Hidai, M. *Tetrahedron Lett.* **1995**, *36*, 5585−5588.

(26) Takei, L.; Dohki, K.; Kobayashi, K.; Suzuki, T.; Hidai, M. *Inorg. Chem.* **2005**, *44*, 3768−3770.

(27) Basallote, M. G.; Feliz, M.; Fernandez-Trujillo, M. J.; Llusar, R.; Safont, V. S.; Uriel, S. *Chem.−Eur. J.* **2004**, *10*, 1463−1471.

(28) Basallote, M. G.; Estevan, F.; Feliz, M.; Fernandez-Trujillo, M. J.; Hoyos, D. A.; Llusar, R.; Uriel, S.; Vicent, C. *Dalton Trans.* **2004**, 530−536.

Kinetic and reactivity studies indicate that the identity of the species present in [**1**]Cl aqueous solutions is strongly dependent on the actual conditions (for example, pH and added salts). A combined electrospray ionization mass spectrometry (ESI-MS), $^{31}P\{^1H\}$ NMR, and stopped-flow study is carried out to analyze the aqueous speciation chemistry of the [**1**]$^+$ cluster cation. At neutral pH, the predominant species in solution can be formulated as $[Mo_3S_4L(L-H)_2(H_2O)]^{2+}$, where two of the dhmpe ligands are deprotonated and act as tridentate ligands with the coordination of one hydroxo group. These results put forward an active role of the diphosphine, which can ultimately act as a polydentate ligand as previously anticipated by Tyler et al.[12] However, in the present case, diphosphine coordination to the idealized C_3 symmetry Mo_3S_4 core results in a lowering of the symmetry, which has major consequences on the kinetic features. The results of the kinetic studies show that the asymmetry introduced in the Mo_3S_4 cluster by the closure of only two chelate rings causes significant deviations from the statistical behavior for the substitution reactions, traditionally associated with the M_3Q_4 cluster reactions.

Experimental Section

General Remarks. All reactions were carried out under a nitrogen atmosphere using standard Schlenck techniques. The dhmpe diphosphine and $[n\text{-}Bu_4N]_2[Mo_3S_7Cl_6]$ were prepared according to literature methods.[29,30] The remaining reactants were obtained from commercial sources and used as received. Solvents for syntheses were dried and degassed by standard methods before use.

Physical Measurements. Elemental analyses were performed on an EA 1108 CHNS microanalyzer. $^{31}P\{H\}$ NMR spectra were recorded on Varian Mercury 300 MHz or Varian Inova 400 instruments. Chemical shifts were referenced to external 85% H_3PO_4. Electronic absorption spectra were obtained on a Perkin-Elmer Lambda-19 spectrophotometer in water. ESI-MS spectra were recorded with a quadrupole-hexapole-time-of-flight (Q-TOF I) mass spectrometer with an orthogonal Z-spray electrospray interface (Micromass, Manchester, U.K.) operating at a resolution of approximately 5000 (FWHM). The instrument was calibrated using a solution of NaI in 2-propanol/water from m/z 100 to 1900. Sample solutions (5×10^{-4} 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. Reactivity studies were monitored by ESI-MS using increasing amounts of HCl, KCl, KSCN, NaOH, and NH_3 typically up to a 10-fold excess with respect to the cluster concentration. The cone voltage was set at 10 V unless otherwise stated to control the extent of fragmentation. Nitrogen was employed as the drying and nebulizing gas. Isotope experimental patterns were compared with theoretical patterns obtained using the *MassLynx* 4.0 program.[31]

Synthesis. $[Mo_3S_4Cl_3(dhmpe)_3]Cl$ ([1]Cl). An excess of dhmpe (0.096 g, 0.448 mmol) dissolved in 15 mL of CH_3OH was added to a 5 mL volume acetonitrile solution of $[n\text{-}Bu_4N]_2[Mo_3S_7Cl_6]$ (0.100 g, 0.083 mmol), and the resulting mixture was acidified with 0.5 mL of 0.1 M aqueous HCl. The reaction occurs with an immediate color change from orange to green. The reaction mixture was stirred for 1 day at 40 °C and then cooled at room temperature. The product precipitated as a green solid, and it was separated by filtration. Recrystallization from 0.1 M aqueous HCl and 2-propanol affords a green microcrystalline product characterized as $[Mo_3S_4Cl_3(dhmpe)_3]Cl$ ([**1**]Cl) (0.080 g, 81%).

Anal. Calcd for $Mo_3Cl_4S_4P_6C_{18}H_{48}O_{12}$: C, 17.99; H, 4.04; S, 10.66. Found: C, 17.90; H, 3.87: S, 10.33. $^{31}P\{^1H\}$ NMR (ca. 0.05 M HCl in 1:1 H_2O/D_2O, 121 MHz): δ (ppm): 41.5 (d, $^2J_{P-P} = 9$ Hz), 49.7 (d, $^2J_{P-P} = 9$ Hz). ESI-MS (aqueous 1×10^{-2} M HCl, 10 V): m/z (%) = 1164.7 (M)$^+$ (100). λ max (nm): 613 (w), 409 (s).

X-ray Studies. Suitable crystals for X-ray studies were grown by the slow evaporation of a 0.1 M HCl aqueous solution of [**1**]Cl. The crystals are air-stable and were mounted on the tip of a glass fiber with the use of epoxy cement. X-ray diffraction experiments were carried out on a Bruker SMART CCD diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å) at room temperature. The data were collected with a frame width of 0.3° in ω and a counting time of 25 s per frame. The diffraction frames were integrated using the *SAINT* package and corrected for absorption with *SADABS*.[32,33] The structures were solved by direct methods and refined by the full-matrix method based on F^2 using the *SHELXTL* software package.[34] The structure of [**1**]Cl was successfully solved in the hexagonal $R\bar{3}$ space group. All the non-hydrogen atoms both in the cluster and the anion were refined anisotropically. An isolated chlorine atom was found on a "*c*" special position and refined anisotropically. Two terminal hydroxo groups appear disordered over two positions, O(2)/O(22) and O(3)/O(33), with partial occupancies of 70/30 and 75/25, respectively. Crystal data for [**1**]-Cl: $C_{18}H_{48}Cl_4O_{18}P_6S_4Mo_3$, M =1200.24, hexagonal, space group $R\bar{3}$, $a = 12.6863(12)$ Å, $c = 43.813(8)$ Å, $\alpha = 90°$, $\gamma = 120°$, $V = 6106.6(14)$ Å^3, $T = 293$ K, $Z = 6$, μ(Mo Kα) = 1.663 mm^{-1}. Reflections collected/unique = 16730/3983 ($R_{int} = 0.0615$). Final refinement converged with $R_1 = 0.0770$ and $R_2 = 0.1300$ for all reflections, GOF = 1.072, max/min residual electron density 1.080/−1.076 e·Å^{-3}.

Kinetic Experiments. The kinetic experiments were carried out with an Applied Photophysics SX17MV stopped-flow spectrometer provided with a PDA1 photodiode array (PDA) detector. All experiments were carried out at 25.0 °C by mixing an aqueous solution of $[Mo_3S_4Cl_3(dhmpe)_3]Cl$ with another solution containing an excess of the other reagent (salt, acid, or base) and the amount of KNO_3 required to achieve a constant ionic strength of 0.5 M in the solution arriving into the stopped-flow cell. The solutions of the complex were prepared at concentrations of ca. 1.0×10^{-3} M, and preliminary experiments were carried out for each reaction at two or three different complex concentrations to confirm the first-order dependence of the observed rate constants with respect to the complex. The reaction kinetics were monitored by recording the spectral changes with time using the PDA detector, and the data were analyzed with the *SPECFIT* program[35] using the appropriate kinetic model (single or multiple exponential).

Results and Discussion

Synthesis, Solid-State, and Solution Structures of the [1]Cl Complex. The use of rational synthetic procedures for

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(29) Nieckarz, G. F.; Weakley, T. J. R.; Miller, W. K.; Miller, B. E.; Lyon, D. K.; Tyler, D. R. *Inorg. Chem.* **1996**, *35*, 1721−1724.

(30) Fedin, V. P.; Sokolov, M. N.; Mironov, Y. V.; Kolesov, B. A.; Tkachev, S. V.; Fedorov, V. Y. *Inorg. Chim. Acta* **1990**, *167*, 39−45.

(31) *MassLynx 4.0*, 2004.

(32) *SAINT*, version 5.0; Bruker Analytical X-Ray Systems: Madison, WI, 1996.

(33) Sheldrick, G. M. *SADABS Empirical Absorption Program*; University of Göttingen: Göttingen, Germany, 1996.

(34) Sheldrick, G. M. *SHELXTL*, version 5.1; Bruker Analytical X-Ray Systems: Madison, WI, 1997.

(35) Binstead, R. A.; Jung, B.; Zuberbühler, A. D. *SPECFIT;* Spectrum Software Associates: Chapel Hill, NC, 2000.

the preparation of trinuclear metal chalcogenides has contributed enormously to the development of the chemistry of transition-metal clusters. Solid cluster phases of crystal formula $M_3Q_7X_{4/2}X_2$ (M = Mo, W; X = Cl, Br) have been shown to be excellent precursors for the syntheses of molecular complexes containing $M_3(\mu_3\text{-Q})(\mu\text{-Q}_2)_3$ and $M_3(\mu_3\text{-Q})(\mu\text{-Q})_3$ cluster units.[36−38] For example, complexes of formula $[M_3Q_4X_3(\text{diphosphine})_3]^+$ can be obtained in high yield by the excision of these polymeric $M_3Q_7X_{4/2}X_2$ phases in acetonitrile in the presence of a diphosphine, i.e., dmpe and dppe.[39,40] Our synthetic approach to extend this chemistry to aqueous media relies essentially on the incorporation in the diphosphine ligands of substituents able to form strong hydrogen bonds in an aqueous medium, and the 1,2-bis(bis(hydroxymethyl)phosphino)ethane (dhmpe) diphosphine, bearing four terminal hydroxo groups, was selected for this purpose. Although all attempts to coordinate this diphosphine to the trinuclear Mo_3S_4 unit starting from the polymeric $Mo_3S_7Cl_{4/2}Cl_2$ phase in acetonitrile solution were unsuccessful, this water-soluble phosphine reacts with the molecular $[Mo_3S_7Cl_6]^{2-}$ complex in methanol/acetonitrile mixtures to afford the $[Mo_3S_4Cl_3(\text{dhmpe})_3]^+$ ($[\mathbf{1}]^+$) trinuclear cluster, isolated as the chloride salt in 81% yields.

Compound [**1**]Cl moderately dissolves in aqueous HCl or methanol (ca. 1×10^{-3} M) to afford green solutions. $^{31}P\{^1H\}$ NMR in aqueous HCl solutions shows two signals at 41.5 and 49.7 ppm corresponding to two kinds of phosphorus nuclei, located above and below the plane defined by the three metal atoms, in agreement with the solid-state structure (see below). The slow evaporation of an aqueous HCl solution afforded green single crystals whose structure is represented in Figure 1 together with a list of selected bond distances. These distances compare well with those observed for other $[Mo_3S_4Cl_3(\text{diphos})_3]^+$ (diphos = dmpe, dppe) trinuclear clusters.[22] The structure was solved in the centrosymmetric space group $R\bar{3}$ where the three metal atoms are symmetry related, with one capping S(1) sulfur lying on a three-fold axis. The specific arrangement of two phosphorus and one chorine atom around molybdenum is reflected in differences in the Mo-(μ-S) bond lengths which results in chiral trinuclear complexes with deviations from the ideal C_{3v} symmetry.

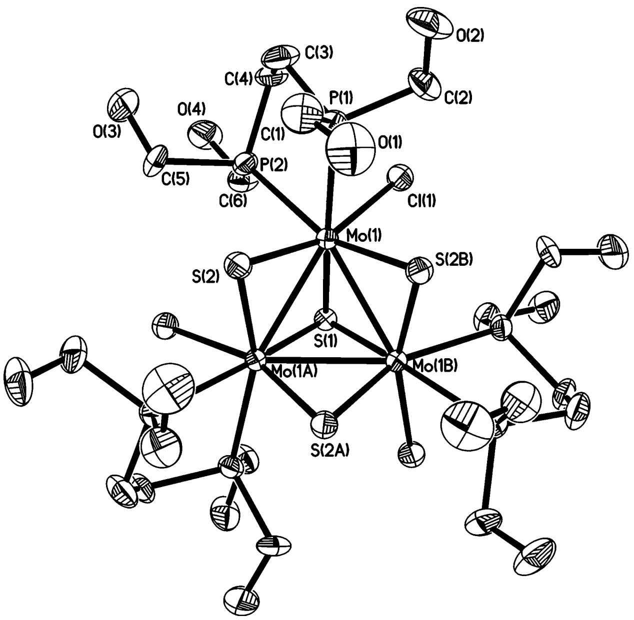

Figure 1. ORTEP representation (50% probability ellipsoids) of the cationic cluster $[\mathbf{1}]^+$ with the atom-numbering scheme. Disordered oxygen atoms are omitted for clarity. Selected bond lengths (Å): Mo−Mo 2.7702(7), Mo-(μ_3-S(1)) 2.3599(14), Mo-(μ-S(2)) 2.2757(12), Mo-(μ-S(2B)) 2.3232(12), Mo−P(1) 2.5288 (13), Mo−P(2) 2.5852(13), Mo−Cl 2.5178(12).

Converse to the green color of aqueous HCl solutions of [**1**]Cl and its two-signal $^{31}P\{^1H\}$ NMR pattern, water solutions of complex $[\mathbf{1}]^+$ are brown-colored and show a complex $^{31}P\{^1H\}$ NMR spectrum (six signals at 58.3, 57.0, 50.5, 50.0, 40.4, and 36.8 ppm). This experimental evidence put forward an active role of the solvent or the diphosphine on the solution structure of the trinuclear [**1**]Cl dhmpe derivative. The appearance of six signals in the NMR spectra has been previously reported for intermediates formed in reactions of related clusters containing coordinated diphosphines, and they have been interpreted as the result of the nonequivalence of the three metal centers due to partial substitution at only one or two of the metals.[27,28,41,42] This lowering of symmetry has also been observed in other idealized C_3 symmetry Mo_3S_4 complexes upon dissolving in some coordinating solvents. For example, excision of the $Mo_3S_7Cl_{4/2}Cl_2$ polymeric phase with PPh_3 in pyridine affords the $Mo_3S_4Cl_4(py)_5$ complex where two metal centers contain a chlorine and two pyridine molecules while the third one is coordinated to two chlorine and one pyridine ligands.[43]

Previous studies by Tyler et al. on the coordination chemistry of dhmpe and related hydroxyalkyl disphoshines to iron have shown that the nature and stereochemistry of the final mononuclear Fe(II) complex depends on the solvent, the counterion, and the diphosphine alkyl chain length. In particular, the octahedral *cis*-$[Fe(dhp_rpe)_2]^{2+}$ mononuclear complex,[12] where dhp_rpe is 1,2-bis(bis(hydroxypropyl)-phophino)ethane, has four coordination positions occupied by the diphosphine phosphorus atoms and the remaining two sites by oxygens atoms of the diphosphine hydroxyl group. However, other hydroxyalkyl diphosphines such as dhmpe

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(36) Fedin, V. P.; Sokolov, M. N.; Gerasko, O. A.; Kolesov, B. A.; Fedorov, V. Y.; Mironov, A. V.; Yufit, D. S.; Slovohotov, Y. L.; Struchkov, Y. T. *Inorg. Chim. Acta* **1990**, *175*, 217−229.

(37) Fedin, V. P.; Sokolov, M. N.; Gerasko, O. A.; Virovets, A. V.; Podberezskaya, N. V.; Fedorov, V. Y. *Inorg. Chim. Acta* **1991**, *187*, 81−90.

(38) Llusar, R.; Vicent, C. In *Trinuclear Molybdenum and Tungsten Cluster Chalcogenides: From Solid State to Molecular Materials;* Inorganic Chemistry in Focus III; Meyer, G., Naumann, D., Wesemann, L., Eds.; Wiley-VCH Verlag: Weinheim, Germany, 2006.

(39) Feliz, M.; Llusar, R.; Uriel, S.; Vicent, C.; Humphrey, M. G.; Lucas, N. T.; Samoc, M.; Luther-Davies, B. *Inorg. Chim. Acta* **2003**, *349*, 69−77.

(40) Estevan, F.; Feliz, M.; Llusar, R.; Mata, J. A.; Uriel, S. *Polyhedron* **2001**, *20*, 527−535.

(41) Algarra, A. G.; Basallote, M. G.; Castillo, C. E.; Corao, C.; Llusar, R.; Fernandez-Trujillo, M. J.; Vicent, C. *Dalton Trans.* **2006**, 5725−5733.

(42) Algarra, A. S. G.; Basallote, M. G.; Fernandez-Trujillo, M. J.; Llusar, R.; Safont, V. S.; Vicent, C. *Inorg. Chem.* **2006**, *45*, 5774−5784.

(43) Mizutani, J.; Yajima, S.; Imoto, H.; Saito, T. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 631−636.

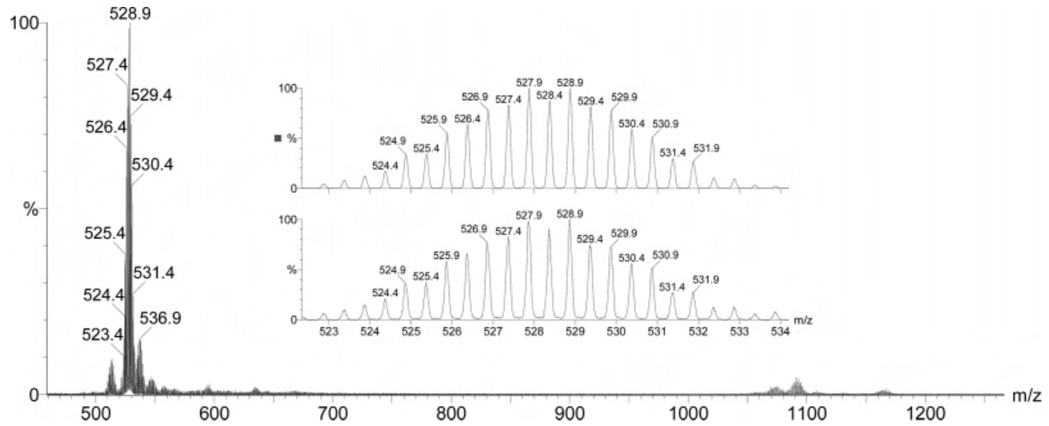
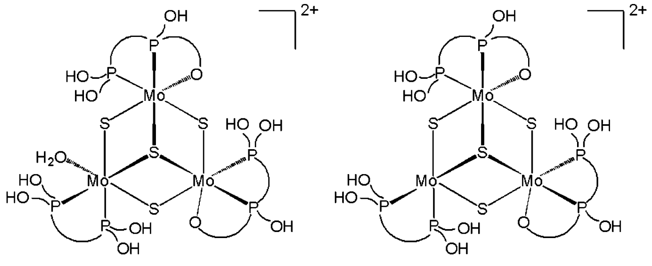


Figure 2. ESI-MS spectra of water solutions of compound [**1**]Cl at $U_c = 10$ V together with the simulated isotopic distribution for $[Mo_3S_4L(L\text{-}H)_2]^{2+}$. Note the appearance of an additional signal centered at 536.9 that corresponds to the parent $[\mathbf{2}]^{2+}$ cation (see discussion in text).

do not show coordination of the hydroxyl group oxygen atoms to Fe(II), and this has been attributed to the lower stabitility of the resulting ring. Therefore, the potential noninnocent character of the hydroxo groups regarding metal coordination in this class of water-soluble diphosphines has to be taken into consideration. In the case of the trinuclear diphosphino Mo_3S_4 complexes, the presence of three diphosphine ligands and three metal sites can lead to a large variety of species whose identification by NMR techniques may be quite complicated. In our case, all attempts to monitor the solution and reactivity behavior of $[\mathbf{1}]^+$ using proton NMR were not conclusive because the spectra are dominated by broad overlapping signals, a behavior that has been previously observed in metal complexes with these kinds of phosphines.[12] In this context, ESI-MS was used for the characterization and reactivity studies, as it has proved to be very fruitful in related M_3Q_4 complexes.[41,44] The ESI-MS spectra of aqueous solutions of [**1**] Cl are presented in Figure 2 together with the chemical formula employed to reproduce the isotopic distribution of the most intense peaks.

The ESI mass spectrum of [**1**]Cl in water shows a doubly charged species formulated as $[Mo_3S_4L(L\text{-}H)_2]^{2+}$ with 527.9 as the base peak. This signal is accompanied by a minor peak centered at 536.9 that corresponds to the water-containing $[Mo_3S_4L(L\text{-}H)_2(H_2O)]^{2+}$ related species. One plausible explanation for the observation of peaks at 527.9 and 536.9 is that the species existing in aqueous solutions of [**1**]Cl would be $[Mo_3S_4L(L\text{-}H)_2(H_2O)]^{2+}$ ($[\mathbf{2}]^{2+}$), coming from the substitution of the three chloride ligands by one water molecule and two alkoxo groups, which result from the deprotonation of one hydroxyl groups on two different dhmpe ligands. This species is expected to yield a phosphorus spectrum with six signals and a mass spectrum with peaks centered at 536.9 for the $[\mathbf{2}]^{2+}$ complex and at 527.9 for the species resulting from water dissociation under the conditions of the ESI-MS experiments. Unfortunately, all attempts to obtain single-crystals of salts containing the $[\mathbf{2}]^{2+}$ species were unsuccessful. However, the NMR and ESI-MS spectra strongly favor this interpretation, and the proposed molecular structures expected for both species are shown in Scheme 1, where two of the Mo centers are coordinated to tridentate dhmpe ligands and the third one is coordinated to one dhmpe acting as a bidentate ligand, as observed in the crystal structure of [**1**]Cl.

Scheme 1



$[Mo_3S_4L(L\text{-}H)_2(H_2O)]^{2+}$ ($[\mathbf{2}]^{2+}$) $[Mo_3S_4L(L\text{-}H)_2]^{2+}$

The results of the reactivity and kinetic studies described below add further support to the proposed solution structure. It is interesting to note that the tridentate coordination mode of the negatively charged $(L\text{-}H)^-$ ligands in $[Mo_3S_4L(L\text{-}H)_2(H_2O)]^{2+}$ differs from that described for the related mononuclear *cis*-$[Fe(dhp_rpe)_2]^{2+}$ complex, where each diphosphine acts as a *neutral* polydentate ligand with coordinated hydroxyl groups.[12]

Kinetic Studies and Aqueous Speciation of [1]Cl. Once the unexpected formation of $[\mathbf{2}]^{2+}$ in aqueous solutions of [**1**]Cl was established, it was considered of interest to carry out an exploratory study of its kinetic properties and the aqueous speciation at different pH levels. Thus, while the comprehensive studies carried out over the years by the group of Sykes provide a satisfactory understanding of the kinetics and mechanism for the reactions of the M_3Q_4 and related M_4Q_4 and $M_3M'Q_4$ clusters in aqueous solution, the results available refer almost exclusively to the reactivity of the corresponding aquo clusters with equivalent reaction sites at all metal centers.[21] One of the most firmly established conclusions is that the reaction kinetics in this kind of complexes is dominated by statistical factors, although kinetic and mechanistic information on lower-symmetry clusters, usually imposed by the ancillary ligands, is missing.

As pointed out above, the acidification of aqueous solutions of ($[\mathbf{2}]^{2+}$) with an excess of HCl results in $^{31}P\{^1H\}$ NMR and ESI-MS spectra consistent with the presence in

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(44) Guillamon, E.; Llusar, R.; Pozo, O.; Vicent, C. *Int. J. Mass Spectrom.* **2006**, *254*, 28−36.

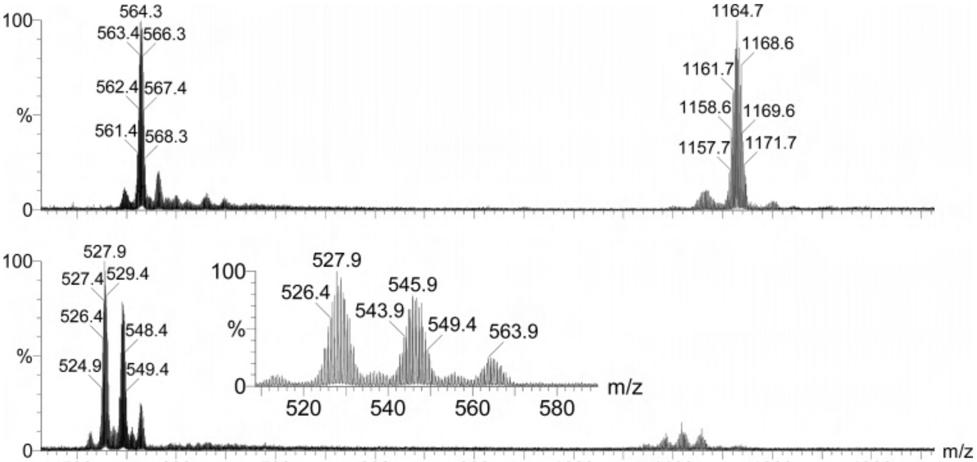
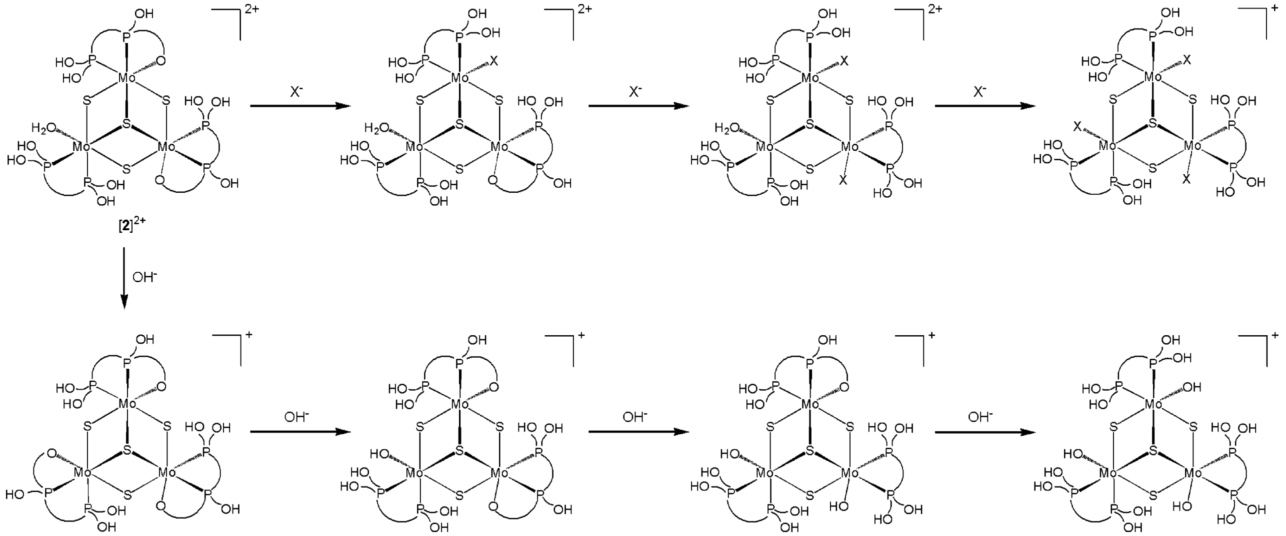


Figure 3. ESI-MS spectra of water solutions of [**1**]Cl after the addition of a 5-fold excess of HCl where the inset shows the doubly charged region (bottom) and a 10-fold excess of KCl (top).

Scheme 2



solution of the $[\mathbf{1}]^+$ cation as the only species under these conditions. Similar conclusions are obtained when KCl is used instead of HCl. Because of the limited solubility of [**1**]Cl, the appearance of reaction intermediates in the formation of $[Mo_3S_4Cl_3L_3]^+$ could not be monitored using NMR, but very useful information was obtained from ESI-MS recorded for reaction mixtures containing controlled amounts of added HCl or KCl. Figure 3 shows the ESI-MS spectra of aqueous solutions of [**1**]Cl in the presence of increasing amounts of aqueous HCl.

The addition of a 5-fold excess of aqueous HCl leads to the disappearance of the peak centered at 527.9 for species $[\mathbf{2}]^{2+}$, with the successive appearance of new signals at 546.9 and 564.9 that can be assigned to species formulated as $[Mo_3S_4L_2(L\text{-}H)Cl]^{2+}$ and $[Mo_3S_4L_3Cl_2]^{2+}$, respectively. Minor signals due to the water-coordinated related species are also observed at 555.9 and 573.9, respectively. These results strongly suggest that the conversion of $[\mathbf{2}]^{2+}$ to $[Mo_3S_4Cl_3L_3]^+$ goes through the successive formation of intermediates of formulas $[Mo_3S_4L_2(L\text{-}H)Cl(H_2O)]^{2+}$ and $[Mo_3S_4L_3Cl_2(H_2O)]^{2+}$ (see Scheme 2), which lose the coordination water under ESI conditions. Further addition of HCl leads to the disappearance of these intermediates with formation of the final trichloro product (see Figure 3, top).

When an excess of SCN^- is added to aqueous solutions of [**1**]Cl, the phosphorus NMR spectra show two signals at 54.1 and 43.8 ppm consistent with the formation of the C_3 symmetry $[Mo_3S_4(NCS)_3L_3]^+$ cluster cation. The use of a large KSCN excess (typically KSCN/Mo_3S_4 ratios >10) for the ESI-MS monitoring resulted in dramatic losses of sensitivity regarding the detection of cluster species, so the complete picture of the ligand substitution could not be obtained. Nevertheless, the ESI mass spectrum recorded upon the addition of a 10-fold excess of KSCN allows the detection of signals at 557.4 and 566.7 that could be assigned to $[Mo_3S_4L_2(L\text{-}H)(NCS)]^{2+}$ and $[Mo_3S_4L_2(L\text{-}H)(NCS)(H_2O)]^{2+}$, thus showing that the reaction with SCN^- goes through a pathway similar to that operating for the reaction with Cl^-. Although the data available do not provide information about the thiocyanate ligand donor atoms, comparison with other related structures leads us to postulate that the SCN^- ligands are N-coordinated, and no evidence of linkage isomerization has been obtained from either the NMR or the kinetic studies

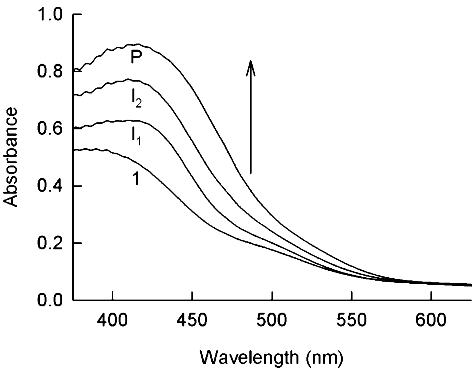


Figure 4. Electronic spectra calculated for the different species involved in the reaction of [**2**]$^{2+}$ with SCN$^-$ in aqueous solution. The spectra were calculated from the fit of the spectral changes with time to a kinetic model with three consecutive exponentials.

described below.[45−48] The whole set of NMR and ESI-MS experimental evidence indicates that the chemical transformation of [**1**]$^+$ to [**2**]$^{2+}$ that occurs in aqueous solutions is a reversible process that involves chloride dissociation coupled to intramolecular motions associated with the arms of the diphosphine ligands. In the presence of a suitable entering monodentate ligand as Cl$^-$ itself or SCN$^-$, there is the reopening of the chelate rings and coordination of the monodentate ligand, as indicated in Scheme 2.

Stopped-flow experiments indicate that the conversion of [**2**]$^{2+}$ to [**1**]$^+$ or [$Mo_3S_4L_3(NCS)_3$]$^+$ does not occur in a single measurable kinetic step, and a satisfactory fit of the spectral changes requires a model with three consecutive exponentials. The spectra calculated for the corresponding reaction intermediates in the reaction with thiocyanate are shown in Figure 4, whereas Figure 5 illustrates the dependence of the observed rate constants on the concentration of added reagent.

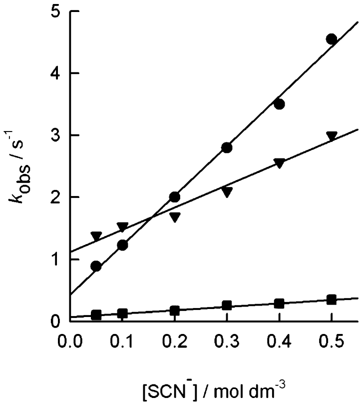


Figure 5. Plots of the dependence of [SCN$^-$] on the rate constants for the three resolved steps in the reaction of [**2**]$^{2+}$ with thiocyanate in aqueous solution. Some of the rate constants have been multiplied by 10, so while the circles correspond to $k_{1\mathrm{obs}}$ values, the triangles and squares correspond to 10 × $k_{2\mathrm{obs}}$ and 10 × $k_{3\mathrm{obs}}$ values, respectively.

Table 1. Summary of Resolved Rate Constants for the Reaction of [$Mo_3S_4L(L\text{-}H)_2(H_2O)$]$^{2+}$ with Different Anions[a]

	$X^- = Cl^-$	$X^- = SCN^-$	$X^- = OH^-$
k_{f1}/M^{-1} s^{-1}	4.0(2)	8.0(2)	0.47(2)
k_{f2}/M^{-1} s^{-1}	0.36(5)	0.36(3)	0.056(4)
k_{f3}/M^{-1} s^{-1}	0.018(2)	0.056(5)	
k_{r1}/s^{-1}	0.73(5)	0.43(8)	0.057(6)
k_{r2}/s^{-1}	0.055(3)	0.112(8)	0.005(1)
k_{r3}/s^{-1}	0.0065(5)	0.007(1)	
K_1/M^{-1}	5.5(3)	18.6(5)	8.2(3)
K_2/M^{-1}	6.5(9)	3.2(3)	11.2(8)
K_3/M^{-1}	2.8(3)	8.0(7)	

[a] The figures in parentheses represent the standard deviation in the last significant figure.

The first-order character of the three resolved steps with respect to the cluster was confirmed by the lack of change of the rate constants with the complex concentration. Experiments using different relative amounts of HCl and KCl showed that the kinetic results for the reaction with Cl$^-$ are independent of the acid concentration, which indicates that the acidity of the solution does not play any significant role in the kinetics of reaction. Figure 5 shows that the rate constants change linearly with the concentration of added SCN$^-$, although the plots show in all cases a significant nonzero intercept that suggests that all three steps occur under conditions of reversible equilibrium. The kinetic data for the three steps can be fitted by eq 1 with the values of the resolved rate constants included in Table 1. The values derived for the corresponding equilibrium constants are also included in Table 1. As the kinetic data indicate that all the steps require the participation of one entering X$^-$ ligand, it can be reasonably concluded that the measured rate constants correspond to the reaction sequence derived from the NMR and ESI-MS experiments (X$^-$ pathway in Scheme 2). In that case, it must be concluded that the Mo sites containing tridentate (L-H)$^-$ ligands are more labile than the ones containing the water molecule; i.e., upon attack by X$^-$, the opening of a chelate ring with a hydroxo group occurs faster than the substitution of coordinated water.

$$k_{i\mathrm{obs}} = k_{\mathrm{f}i}\,[\mathrm{X}^-] + k_{\mathrm{r}i} \qquad (1)$$

The $k_{\mathrm{f}i}$ values in Table 1 show that the rate constants for the consecutive steps are in a 222:20:1 ratio for Cl$^-$ and a 143:6:1 ratio for SCN$^-$; i.e., there is a significant decrease in the rate of coordination of the successive X$^-$ ligands. These ratios indicate that the asymmetry introduced by the closure of chelate rings at only two of the three metal centers results in significant deviations from the statistical kinetics. Although the third step corresponds to water substitution without the need of chelate ring opening and this could explain its deviation, the first two steps correspond to the same type of reaction and one would still reasonably expect their rate constants to be in the statistical 2:1 ratio. An inspection of the $k_{\mathrm{r}i}$ and K_i values in Table 1 indicates that similar deviations from statistical predictions also occur for the rates of the reverse step and the equilibrium constants.

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(45) Sokolov, M. N.; Dybtsev, D. N.; Virovets, A. V.; Fedin, V. P.; Esparza, P.; Hernandez-Molina, R.; Fenske, D.; Sykes, A. G. *Inorg. Chem.* **2002**, *41*, 1136−1139.

(46) McLean, I. J.; Hernandez-Molina, R.; Sokolov, M. N.; Seo, M. S.; Virovets, A. V.; Elsegood, M. R. J.; Clegg, W.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1998**, 2557−2562.

(47) Hernandez-Molina, R.; Dybtsev, D. N.; Fedin, V. P.; Elsegood, M. R. J.; Clegg, W.; Sykes, A. G. *Inorg. Chem.* **1998**, *37*, 2995−3001.

(48) Nasreldin, M.; Henkel, G.; Kampmann, G.; Krebs, B.; Lamprecht, G. J.; Routledge, C. A.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1993**, 737−746.

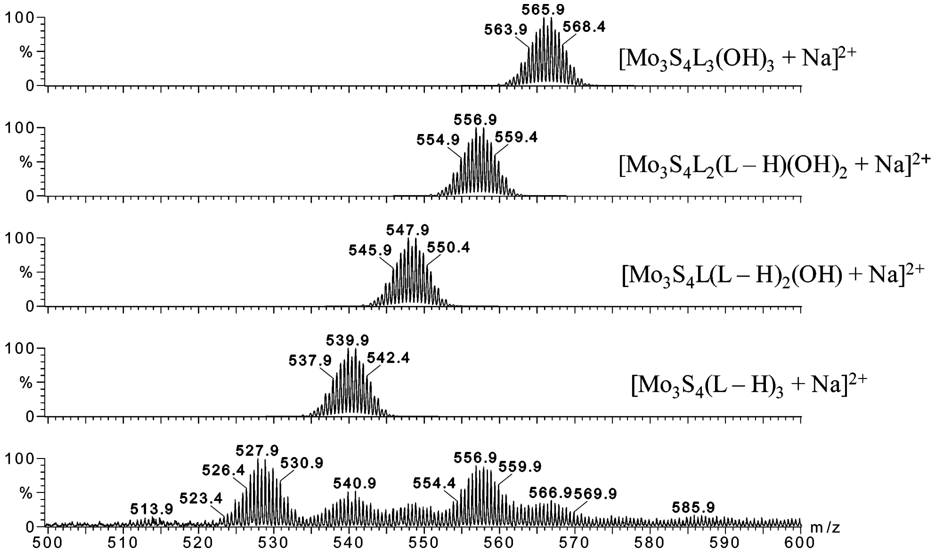

Figure 6. ESI-MS spectrum (bottom) of water solutions of [**1**]Cl after the addition of a 5-fold excess of NaOH. Upper traces correspond to calculated spectra for the different $[Mo_3S_4(L\text{-}H)_nL_{3-n}(OH)_{3-n} + Na]^{2+}$ sodium adducts.

We have recently observed these deviations from the statistical predictions in the kinetics of other reactions of this kind of cluster,[41,49] but this is to our knowledge the first time that they are detected for reactions of homometallic M_3Q_4 clusters in aqueous solution.

As pointed out above, substitution process kinetics in symmetrical $[M_3Q_4(H_2O)_9]^{4+}$ clusters are usually statistically controlled and the rates of reaction at the three metal centers are in a 3:2:1 ratio, although the operation of statistical kinetics leads to simplification of the kinetic traces to a single step with an apparent rate constant that corresponds to the rate of reaction at the third metal center.[50] At this point, it is important to note that the simplification of kinetic traces to a single exponential in the case of reactions occurring with statistical kinetics does not only require that the rate constants for the successive steps are in statistical ratio but also requires that the reacting centers behave as independent chromophores. Electronic communication between the reacting centers can make both the spectra and the rate constants deviate from the ideal isolated behavior, which should result in more complex kinetics. In the present case, the spectra in Figure 4 indicate a steady increase of the absorption band as the number of SCN^- ligands increase, thus showing that the three metal centers can still be reasonably considered to act as independent chromophores. Nevertheless, the kinetic results indicate that the communication between the metal centers is strong enough to make the rate constants deviate from the statistical expectation.

With regards to the intimate mechanism of the substitution processes, Sykes and co-workers have proposed the use of the k_{NCS}/k_{Cl} ratio as a measure of the associative–dissociative character of the ligand substitutions in M_3Q_4 aqua clusters.[21,51] For an associative interchange, there is a significant effect of the entering ligand and the ratio is substantially higher than 10, whereas for a dissociative interchange, the rate constants are little affected by the nature of the entering ligand and the ratio is close to 1. For the reactions of cluster $[\mathbf{2}]^{2+}$, the k_{NCS}/k_{Cl} ratios for the three steps are 2.0, 1.0, and 3.1, all of them significantly smaller than 10, so the substitution processes can be considered to occur through a predominantly dissociative interchange mechanism if the same criterion is applied.

Once it was established that complex $[\mathbf{1}]^+$ converts to $[\mathbf{2}]^{2+}$ in aqueous solution and that the process can be reversed by the addition of Cl^-, we considered it of interest to investigate the possibility of the formation of other species containing a different number of chelate rings and coordinated water molecules. Thus, the acidification of $[\mathbf{2}]^{2+}$ solutions with an acid lacking a coordinating anion is expected to result in the opening of the chelate rings with the successive formation of species formulated as $[Mo_3S_4L_2(L\text{-}H)(H_2O)_2]^{3+}$ and $[Mo_3S_4L_3(H_2O)_3]^{4+}$. Stopped-flow experiments using HNO_3 and Hpts (pts^-= *p*-toluenesulfonate) show very small spectral changes that occur with irreproducible kinetics. Attempts to monitor the reaction of $[\mathbf{2}]^{2+}$ with these acids using phosphorus NMR were also unsuccessful in detecting the two signals expected for the formation of symmetrical $[Mo_3S_4L_3(H_2O)_3]^{4+}$ species (even at acid concentrations as high as 0.5 M), so it must be concluded that this aquo species is not formed to a significant extent even under these strongly acidic solutions. ESI-MS spectra of $[\mathbf{2}]^{2+}$ recorded at increasing amounts of HNO_3 only reveal a moderate decrease of the signals centered at 527.9 and 536.9, associated to this dication, but no new signals are observed. Thus, the whole set of results from the stopped-flow, NMR, and ESI-MS experiments seems to indicate that $[\mathbf{2}]^{2+}$ is also the major species in acidic aqueous solutions of [**1**]Cl, although partial

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(49) Algarra, A. G.; Basallote, M. G.; Feliz, M.; Fernandez-Trujillo, M. J.; Llusar, R.; Safont, V. S. *Chem.—Eur. J.* **2006**, *12*, 1413–1426.

(50) Wilkins, R. G. *Kinetics and Mechanism of Reactions of Transition Metal Complexes,* 2nd ed.; VCH: Weinheim, Germany, 1991.

(51) Saysell, D. M.; Borman, C. D.; Kwak, C. H.; Sykes, A. G. *Inorg. Chem.* **1996**, *35*, 173–178.

conversion to the di-aqua $[Mo_3S_4L_2(L\text{-}H)(H_2O)_2]^{3+}$ complex cannot be completely ruled out in very strongly acidic solutions.

To achieve a better understanding of the behavior of [**1**]-Cl in aqueous solutions, the reactions with base, NaOH or ammonia, were also examined. ESI mass spectra of solutions resulting from a reaction with an excess of NaOH show a variety of signals that reveal the existence of a mixture of species in equilibrium. A typical mass spectrum is shown in Figure 6 together with the calculated signals for the expected reaction products.

These species are invariably observed as Na^+ adducts most likely generated in the mass spectrometer upon NaOH addition. Our experiments suggest that reaction with an excess of NaOH leads to a complex mixture of unreacted $[\mathbf{2}]^{2+}$, the tris-chelated $[Mo_3S_4(L\text{-}H)_3]^+$ complex (signal at 539.9 for its doubly charged Na^+ adduct), and the hydroxo complexes $[Mo_3S_4L(L\text{-}H)_2(OH)]^+$ (signal at 547.9 for its Na^+ adduct), $[Mo_3S_4L_2(L\text{-}H)(OH)_2]^+$ (signal at 556.9 for its Na^+ adduct), and $[Mo_3S_4L_3(OH)_3]^+$ (signal at 565.9 for its Na^+ adduct). Further information is obtained using NH_3 as the base due to the absence of cationizing agents. In this case, species formulated as $[Mo_3S_4L(L\text{-}H)_2(OH)]^+$ ($m/z = 1074.8$), $[Mo_3S_4L_2(L\text{-}H)(OH)]^+$ ($m/z = 1092.8$), and $[Mo_3S_4L_3(OH)_3]^+$ ($m/z = 1110.8$) are detected, which firmly complements the results obtained using NaOH. Attempts to follow the reaction by NMR spectroscopy were unsuccessfull due to the complexity of the reaction mixture and the low solubility of the species. The most informative experiments were obtained upon the addition of small amounts of NaOH and NH_3 that caused the appearance of only two signals in the $^{31}P\{^1H\}$ NMR spectrum, at 54.9 and 51.8 ppm, in agreement with the initial formation of $[Mo_3S_4(L\text{-}H)_3]^+$; i.e. these species are formed prior to the hydroxo complexes generation. Scheme 2 shows the sequence of the different species formed in the OH^- reaction of the $[\mathbf{2}]^{2+}$ cluster. As expected for the formation of a complex mixture of species from a complex with a low solubility, the further addition of base leads to low-quality NMR spectra even after very long acquisition times.

Stopped-flow experiments show that the reaction of aqueous solutions containing the $[\mathbf{2}]^{2+}$ cation with an excess of NaOH occurs with spectral changes that require a model with two consecutive steps. The changes of the rate constants for both steps with the varying of the base concentration (Figure 7) indicate that these processes also occur under conditions of reversible equilibrium, so the data can be fitted by eq 1 to yield the values of the forward and reverse rate constants included in Table 1.

In general, the values for the reaction with OH^- are about 1 order of magnitude smaller than the values found for the reactions with Cl^- and SCN^-. According to Scheme 2, up to four steps can be expected in the reaction with a base excess, and so a direct correlation cannot be established between the kinetic data and the spectroscopic results. One explanation for this discrepancy would be that the deprotonation of the coordinated water in $[\mathbf{2}]^{2+}$ can be a rapid process occurring within the mixing time of the stopped-flow instrument, so the two resolved steps could correspond to the OH^- attacks at the two chelate rings. However, the $[Mo_3S_4(L\text{-}H)_3]^+$ species would not be formed along this pathway, and there is no apparent reason to think that its observation in the NMR and MS experiments is the result of slower chelate ring-closure reactions. An alternative explanation to the observation of only two kinetics steps would be that the first one corresponds to the conversion of $[\mathbf{2}]^{2+}$ to the tris-chelated $[Mo_3S_4(L\text{-}H)_3]^+$ complex, which recovers the equivalence of the three metal sites and then reacts with statistical kinetics with more OH^- to form a mixture of hydroxo complexes. Because of the operation of statistical kinetics, the latter processes would occur in a single measurable kinetic step with rate constant k_{2obs}. This hypothesis agrees with the NMR and MS results and would also explain the fact that the k_{f1} value in Table 1 for the reaction with OH^- is significantly different (about 1 order of magnitude) from the values for the reactions with Cl^- and SCN^-. Although we favor this last explanation, an unequivocal interpretation of the kinetic data would require the isolation of the $[Mo_3S_4(L\text{-}H)_3]^+$ species to carry out a kinetic study of its reaction with base. Unfortunately, this species could not be isolated, and Figure 6 shows that it does not even exist as the major species in solution, so this study is not possible.

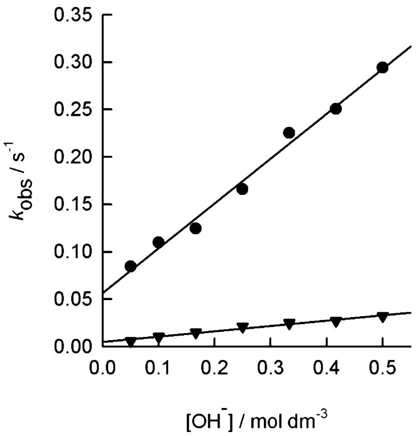

Figure 7. Plots of the dependence of $[OH^-]$ on the rate constants for the two resolved steps in the reaction of $[\mathbf{2}]^{2+}$ with NaOH in aqueous solution. The circles correspond to the k_{1obs} values, and the triangles correspond to the k_{2obs} values.

Conclusion

Coordination of the dhmpe diphosphine to the trinuclear Mo_3S_4 cluster core has been carried out to give a water-soluble [**1**]Cl complex whose structure displays all the typical features of other M_3Q_4 incomplete cuboidal clusters. However, the hydroxymethyl pendant groups in the dhmpe ligands are noninnocent in solution, and some of them are able to dissociate a proton to form an additional chelate ring with coordination of one hydroxomethyl group. The chloride ligands result dissociated and the major species in water solution is $[\mathbf{2}]^{2+}$, which contains a coordinated water and two tridentate dhmpe ligands. The process can be reversed upon the addition of an excess of Cl^-, so the main factor modulating the intramolecular reorganization is the concentration of that anion. As a consequence of the decreased symmetry imposed by the ancillary ligands of [**2**]$^{2+}$, the kinetics of substitution reactions of this compound deviate from the statistical behavior typical of reactions involving M_3Q_4 cluster complexes. These deviations indicate that there is some degree of electronic communication between the metal centers in this kind of cluster. The present results, when taken together with other recent observations showing deviations from statistical kinetics in some reactions of related symmetrical clusters in nonaqueous solution,[41] indicate that the behavior of the three metals as isolated or interacting reaction centers can to some extent be modulated by subtle factors such as the solvent or the ancillary ligands. Despite the fact that more work is required to achieve a precise understanding of the kinetic features associated with these interactions, it is now evident that the classical description of these clusters as undergoing statistically controlled reactions needs to be expanded. The potential of this M_3S_4 water-soluble complex as a metalloligand versus a second transition metal and the use of the resulting heterobimetallic clusters in biphasic catalysis is currently being investigated.

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Supporting Information Available: X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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