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Complexes of $M_3S_4^{4+}$ (M = Mo, W) with chiral alpha-hydroxy and aminoacids: Synthesis, structure and solution studies

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ABSTRACT

New complexes of triangular clusters $M_3S_4^{4+}$ (M = Mo, W) with incomplete cuboidal metal–chalcogenide framework bearing chiral α-hydroxy and amino acids have been prepared. L-lactic acid (H_2lac), L-mandelic acid (H_2man), and L-alanine (Hala) react with $[W_3S_4Br_4(PPh_3)_3]$ in 1:1 ratio to yield, respectively, monosubstituted complexes $[W_3S_4(PPh_3)_3Br_3(Hlac)(CH_3CN)]$ (**1**), $[W_3S_4(PPh_3)_3Br_3(Hman)(CH_3CN)]$ (**2**), and $[W_3S_4(PPh_3)_3Br_3(Hala)(CH_3CN)]Br$ (**3**). In the presence of base $[Mo_3S_4Cl_4(PPh_3)_3]$ gives trisubstituted complexes $[Mo_3S_4(PPh_3)_3(Hlac)_2(lac)]$ (**4**) and $[Mo_3S_4(PPh_3)_3(Hman)_3]Cl$ (**5**). Circular dichroism studies of **4** indicate chirality transfer from the ligand to the $Mo_3S_4^{4+}$ cluster core. These complexes incorporate Cu^+ with the formation of corresponding $\{M_3CuS_4\}^{5+}$ cuboidal derivatives. NMR and ESI-MS studies of solution behavior are presented.

1. Introduction

Transition metal chalcogen-bridged clusters with cuboidal M_4Q_4 framework are known for most of the transition metals, and are of interest as models for metalloenzymes and industrial catalysts [1–5]. Of particular interest are heterometal clusters $M_3M'Q_4$ (M = Mo, W; M′ is a late transition metal, Q = S, Se). When M′ is Cu, Ni, Pd or Ru, they display catalytic activity in various reactions such as nucleophilic addition to the alkynes [6–9], cyclopropanation [10,11], N–N bond cleavage in hydrazines [12]. These clusters are available in various coordination environments which can be selected in order to modify the electronic structure or steric requirements of the cluster. The use of enantiomerically pure ligands offers a route for preparation of chiral $M_3Q_4^{4+}$ clusters. For example, by coordinating bidentate chiral phosphines, (R,R)-Me-BPE or (S,S)-Me-BPE, stereoselective formation of $[Mo_3S_4\{(R,R)\text{-Me-BPE}\}_3Cl_3]^+$ (*P*-enantiomer) and $[Mo_3S_4\{(S,S)\text{-Me-BPE}\}_3Cl_3]^+$ (*M*-enantiomer) was achieved (Me-BPE is 2,5-(dimethylphospholan-1-yl)ethane). By incorporating Cu^+ into these clusters, enatiomerically pure cuboidal $Mo_3CuS_4^{5+}$ clusters with moderate stereoselectivity in the intermolecular cyclopropanation of the alkenes have been obtained [10]. It is obvious that the choice of potential chiral ligands should by no means be restricted to the phosphines.

In this respect, naturally occurring chiral α-hydroxyacids or amino acids (such as mandelic acid, lactic acid or α-alanine) constitute easily accessible and versatile ligand class [13–15]. Complexes of M^{2+} (M = Cu, Ni, Zn [16] and Co [17]), Ti(IV) [18] and V(V) [19] with α-hydroxyacids are well documented. As far as coordination chemistry of group 6 complexes is concerned, interaction of glycolate and lactate with molybdate and tungstate have been reported [20–24], and polynuclear $[Mo_2(Hglyc)_4]$ [25], $[NH_4]_3[GdMo_6(lact)_6O_{15}]$ [26], $\{Na_2[MoO_2(S\text{-lact})_2]\}_3$, $K_6[(MoO_2)_8(glyc)_6(Hglyc)_2]$ [27] are known. Tetrakis(D-mandelato)dimolybdenum(II), a complex with four carboxylates bridging a quadruply bonded Mo_2^{4+} unit [28] and two cis-formamidinate Mo_2^{4+} entities linked via the L-tartrate [29], have been described by Cotton's group.

Our interest was motivated primarily by the capability of α-hydroxyacids to form optically chiral complexes having metal–metal bonded units. However, the coordination of these ligands to the $M_3Q_4^{4+}$ and $M_4Q_4^{4+}$clusters has been scarcely explored, the only example being the preparation of the $[Mo_3(Nipy)S_4(EtO\text{-dtp})_3(L\text{-lactic})(py)]$ cluster (EtO-dtp = diethyldithiophosphate) [30]. Herein we report our exploration of coordination chemistry of $Mo_3S_4^{4+}$

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and $W_3S_4^{4+}$ with L-lactic, L-mandelic acids, and L-alanine, structural characterization of the solid products, as well as electrospray ionization (ESI) mass spectrometric studies and spectroscopic NMR, and circular dichroism spectra in solutions.

2. Experimental

2.1. General

Starting complex $[Mo_3S_4Cl_4(PPh_3)_3]$ was prepared from $(Et_4N)_2[Mo_3S_7Cl_6]$ and PPh_3 [31]. For the preparation of $[W_3S_4Br_4(PPh_3)_3]$ a modified version of the synthesis of $[W_3S_4Cl_4(PPh_3)_3(H_2O)_2]\cdot 2THF$ was adopted [32], based on refluxing the polymeric $W_3S_7Br_4$ with 6 eq. of PPh_3 in CH_3CN for 48 h, followed by evaporation of the blue solution and washing the solid copiously with a 1:1 toluene–hexane mixture to remove unreacted PPh_3 and PPh_3S, yield 70%. L-lactic (Hlac), L-mandelic (Hman) acids and L-alanine (HAla) were purchased from Sigma–Aldrich. PPh_3 was recrystallized from hot ethanol. Solvents were purified by the standard procedures. All manipulations were carried out in air unless otherwise stated. $^{31}P\{^1H\}$ NMR spectra were recorded on Varian Mercury 300 MHz spectrometer and ^1H, $^{13}C\{^1H\}$ gCOSY and gHSQC spectra were acquired with a Varian System 500 MHz using $CDCl_3$/dimethylformamide mixtures as solvents. Circular dichroism measurements were recorded on a JASCO J-810 spectropolarimeter in dimethylformamide solutions. The IR spectra (4000–400 cm^{-1}) were obtained on a Vertex 80 Fourier spectrometer in KBr.

2.2. Electrospray ionization (ESI) mass-spectrometry

A hybrid QTOF I (quadrupole-hexapole-TOF) mass spectrometer with an orthogonal Z-spray-electrospray interface (Waters, Manchester, UK) was used. The drying gas as well as nebulizing gas was dinitrogen at flow rates of 800 and 20 L/h, respectively. The temperature of the source block was set to 100 °C and the desolvation temperature was 120 °C. Capillary voltage of 3.5 kV was used in the positive scan mode, and the cone voltage was varied from 5 to 55 V to explore the characteristic fragmentation reactions of the identified ions. Sample solutions were infused via syringe pump directly connected to the ESI source at a flow rate of 10 μL/min. Mass calibration was performed using a solution of sodium iodide in 2-propanol/water (50:50) mixture for m/z range from 50 to 1700.

2.3. Synthesis of $[W_3S_4(PPh_3)_3Br_3(Hlac)(CH_3CN)]$ (**1**)

Fifty milligrams (0.028 mmol) of $[W_3S_4(PPh_3)_3Br_4]$ were dissolved in 1 ml of acetonitrile and 4 ml (0.04 mmol) of 85% aqueous solution of L-lactic acid (H_2lac) in water was added. The reaction mixture was put into a thick-glass screw-capped vial, heated to 70 °C within 20 min and maintained for 10 h at this conditions, then slowly cooled down to room temperature. The product separated from the solution as large dark blue crystals. Yield: 91%. *Anal.* Calc. for $C_{59}H_{53}NO_3P_3W_3S_4Br_3$: C, 38.59; H, 2.91; N, 0.76. Found: C, 38.40; H, 2.85; N, 2.2%. IR: 3465 w, 3053 m, 2316 w, 1653 w, 1518 s, 1480 s, 1432 s, 1350 m, 1190 m, 1122 m, 1088 s, 1029 w, 997 w, 854 w, 743 s, 693 s, 619 w, 518 s, 448 w, 419 w.

2.4. Synthesis of $[W_3S_4(PPh_3)_3Br_3(Hman)(CH_3CN)]$ (**2**)

Similarly the preparation of **1**, blue single crystals of **2** were obtained from 50 mg (0.028 mmol) of $[W_3S_4(PPh_3)_3Br_4]$ and 5 mg (0.032 mmol) of mandelic acid. Yield: 89%. *Anal.* Calc. for $C_{64}H_{55}NO_3P_3W_3S_4Br_3$: C, 40.5; H, 2.9; N, 0.7. Found: C, 40.7; H, 2.8; N, 1.6%. IR: 3526 w, 3053 w, 1810 w, 1673 w, 1537 s, 1480 s, 1432 s, 1356 s, 1280 w, 1188 m, 1088 s, 1027 m, 997 w, 943 w, 846 w, 742 s, 692 s, 618 w, 520 s, 447 m, 419 w.

2.5. Synthesis of $[W_3S_4(PPh_3)_3Br_3(Hala)(CH_3CN)]Br$ (**3**)

Similarly the preparation of **1**, blue single crystals of **3** were obtained from 50 mg (0.028 mmol) of $[W_3S_4(PPh_3)_3Br_4]$ and 2.5 mg (0.035 mmol) of alanine. Yield: 85%. *Anal.* Calc. for $C_{59}H_{55}N_2O_2P_3W_3S_4Br_4$: C, 37.0; H, 2.9; N, 1.5. Found: C, 37.2; H, 3.0, N, 2.5%.

2.6. Synthesis of $[Mo_3S_4(PPh_3)_3(Hlac)_2lac]$ (**4**)

Sixty mcl (0.67 mmol) of 85% aqueous solution of L-lactic acid (H_2lac), 70 mcl (0.67 mmol) of Et_2NH and 10 ml of acetonitrile were mixed together. Then 300 mg (0.223 mmol) of $[Mo_3S_4(PPh_3)_3Cl_4]$ was added, the mixture was stirred and refluxed for 1 h. After cooling down and filtration, the resulting green solution was evaporated. Resulting dark green solid was redissolved in dichloromethane and kept at −30 °C overnight. Element analysis data of recrystallized product correspond to $[Mo_3S_4(PPh_3)_3(Hlac)_3]Cl$ formula (*Anal.* Calc. for $C_{63}H_{60}ClMo_3O_9P_3S_4$: C, 50.3; H, 4.0; Cl, 2.35. Found: C, 50.5; H, 4.2; Cl, 2.38%). When dissolving this product in CH_2Cl_2 and adding equal volume of ethanol, the slow evaporation yields in single crystals of **4.** Yield: 75–80%. *Anal.* Calc. for $C_{63}H_{59}Mo_3O_9P_3S_4$: C, 51.50; H, 4.06. Found: C, 50.9; H, 4.2%. IR: 3509 m, 3466 m, 3056 m, 2981 m, 2935 w, 2879 w, 1737 s, 1686 s, 1571 w, 1536 m, 1481 s, 1456 s, 1434 s, 1374 m, 1304 w, 1267 w, 1188 s, 1161 m, 1127 s, 1090 s, 1036 s, 998 s, 923 m, 855 s, 744 s, 693 s, 618 w, 552 w, 519 s, 484 s, 445 s, 418 w.

2.7. Synthesis of $[Mo_3S_4(PPh_3)_3(Hman)_3]Cl$ (**5**)

All manipulations were carried out analogically to **4**, taking 10 mg (0.670 mmol)of R-mandelic acid instead. Yield: 80%. *Anal.* Calc. for $C_{84}H_{66}ClMo_3O_9P_3S_4$: C, 55.37; H, 3.93; Cl, 2.09. Found: C, 54.95; H, 4.23; Cl, 1.97%.

2.8. X-ray diffractometry

Crystallographic data and structure refinement details for **2**–**4** are summarized in Table 1. Selected bond distances are given in Table 2. Further details may be obtained from the Cambridge Crystallographic Data Centre on quoting the depository numbers CCDC 864192–864194. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

3. Results and discussion

3.1. Mono-substituted $M_3S_4^{4+}$ clusters of general formula $[W_3S_4(PPh_3)_3Br_3(RCO_2)(MeCN)]$

Reaction of compound $[W_3S_4(PPh_3)_3Br_4]$ with one equivalent of L-lactic or L-mandelic acids gives mono-substituted products **1** and **2** in high yields (up to 90%) according to the Scheme 1. Reaction of $[W_3S_4(PPh_3)_3Br_4]$ with α-alanine leads to analogous product, but contrary to the α-hydroxyacids, the aminoacid is not deprotonated and coordinates in the zwitterionic form to give $[W_3S_4(PPh_3)_3Br_3(Hala)(MeCN)]Br$ (**3**).

Attempts to use the molybdenum homologue, namely $[Mo_3S_4(PPh_3)_3Br_4]$ under identical reaction conditions did not lead to identifiable products.

Compounds **1–3** are sparingly soluble in common solvents (H_2O, CH_3OH, CH_3CN, CH_2Cl_2, DMF), thus precluding further