Inorganica Chimica Acta 395 (2013) 11–18

Contents lists available at SciVerse ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

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

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ARTICLE INFO

Article history:
Received 6 May 2012
Received in revised form 23 August 2012
Accepted 24 August 2012
Available online 25 September 2012

Keywords:
Sulfide clusters
Chiral complexes
Lactic acid
Mandelic acid
Alanine
Crystal structures

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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0020-1693/$ - see front matter © 2012 Published by Elsevier B.V.
http://dx.doi.org/10.1016/j.ica.2012.08.023

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

Table 1
Crystal data and structure refinement details for **1**–**4**.

Crystal data	**2**	**3**	**4**
Chemical formula	$C_{70}H_{64}Br_3N_4O_{3.50}P_3S_4W_3$	$C_{69.80}H_{71.20}Br_4N_{7.40}O_2P_3S_4W_3$	$C_{63.50}H_{64.50}Mo_3O_{11.25}P_3S_4$
M_r	2029.68	2138.08	1516.62
Crystal system, space group	monoclinic, $P2_1/c$	triclinic, $P\bar{1}$	orthorhombic, $P2_12_12_1$
T (K)	100	100	293
a (Å)	14.5594 (4)	13.3719 (3)	15.6999 (13)
b (Å)	18.7654 (6)	14.3382 (4)	18.5547 (15)
c (Å)	26.2254 (8)	23.0576 (6)	24.3054 (19)
α (°)	90	71.921 (1)	90
β (°)	90.447 (1)	74.761 (1)	90
γ (°)	90	73.491 (1)	90
V (Å^3)	7164.9 (4)	3954.63 (18)	7080.3 (10)
Z	4	2	4
Radiation type	Mo Kα	Mo Kα	Mo Kα
m (mm^{-1})	6.71	6.59	0.76
Crystal size (mm)	0.26 × 0.14 × 0.04	0.17 × 0.16 × 0.13	0.16 × 0.16 × 0.08
Diffractometer	Bruker Nonius X8Apex CCD	Bruker Nonius X8Apex CCD	Bruker Nonius X8Apex CCD
Absorption correction	empirical based on intensities (*SADABS*)	empirical based on intensities (*SADABS*)	empirical based on intensities (*SADABS*)
T_{min}, T_{max}	0.721, 1	0.816, 1	0.888, 0.942
No. of measured, independent and observed [$I > 2s(I)$] reflections	56458, 21210, 13696	46699, 21344, 15139	45942, 15572, 12160
R_{int}	0.057	0.048	0.041
$R[F^2 > 2s(F^2)]$, $wR(F^2)$, S	0.051, 0.098, 1.04	0.046, 0.088, 1.08	0.042, 0.124, 1.00
No. of reflections	21210	21344	15572
No. of parameters	780	883	782
No. of restraints	0	0	2
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
$D\rho_{max}$, $D\rho_{min}$ (e Å^{-3})	4.05, −1.52	1.97, −1.17	1.58, −1.00
Flack parameter	–	–	−0.02(3)
	$w = 1/[s^2(F_o^2) + (0.0425P)^2 + 26.8562P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[s^2(F_o^2) + (0.022P)^2 + 33.4553P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[s^2(F_o^2) + (0.0073P)^2 + 16.1946P]$ where $P = (F_o^2 + 2F_c^2)/3$

Computer programs used for structure solution and refinement: *APEX2* (Bruker-AXS, 2004), *SAINT* (Bruker-AXS, 2004), *SHELXS97* (Sheldrick, 1998), *SHELXL97* (Sheldrick, 1998), *SHELXTL* (Bruker-AXS, 2004), CIFTAB-97 (Sheldrick, 1998).

Table 2
Main bond distances and angles in **2**–**4**.

2	**3**	**4**
W1 W2 2.7161(4)	W1 W2 2.7224(4)	Mo1 Mo2 2.7578(6)
W1 W3 2.7616(4)	W1 W3 2.7571(4)	Mo1 Mo3 2.7749(6)
W2 W3 2.7459(4)	W2 W3 2.7429(4)	Mo2 Mo3 2.7501(6)
W1 S1 2.3572(17)	W1 S1 2.3600(16)	Mo1 S1 2.3636(14)
W1 S2 2.3074(17)	W1 S2 2.3145(15)	Mo1 S3 2.3111(13)
W1 S3 2.3158(16)	W1 S3 2.3023(16)	Mo1 S4 2.2976(14)
W2 S1 2.3496(16)	W2 S1 2.3559(15)	Mo2 S1 2.3601(15)
W2 S2 2.3172(17)	W2 S2 2.3175(15)	Mo2 S2 2.2968(12)
W2 S4 2.3072(16)	W2 S4 2.3020(16)	Mo2 S4 2.2950(13)
W3 S1 2.3507(15)	W3 S1 2.3641(17)	Mo3 S1 2.3639(13)
W3 S3 2.3219(17)	W3 S3 2.3109(15)	Mo3 S2 2.2808(14)
W3 S4 2.3075(16)	W3 S4 2.3054(15)	Mo3 S3 2.2944(14)
W-P(av) 2.592(1)	W-P(av) 2.586(1)	Mo-P(av) 2.644(1)
W-Br(av) 2.585(1)	W-Br(av) 2.588(1)	Mo1 O11 2.092(3)
W1 O1 2.205(4)	W1 O1 2.198(4)	Mo1 O12 2.155(4)
W2 O2 2.198(4)	W2 O2 2.210(4)	Mo2 O22 2.080(4)
W3 N1L 2.214(6)	W3 N1L 2.185(5)	Mo2 O21 2.179(4)
		Mo3 O32 2.083(4)
		Mo3 O31 2.228(4)

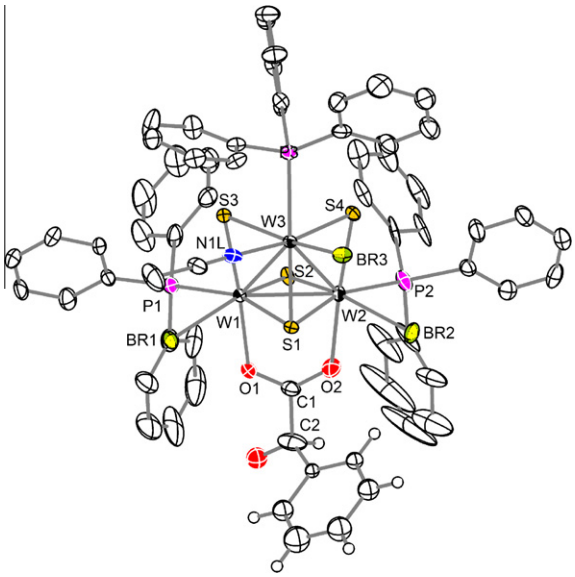
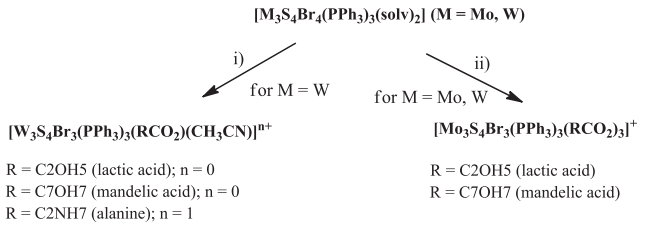


Fig. 1. Cluster complex **2** (a.d.p. at 50% probability level). Second position of mandelate ligand and hydrogen atoms of PPh_3 and CH_3CN ligands are omitted for clarity.



Scheme 1. (i) 1 eq. RCO_2H/CH_3CN; (ii) 3 eq. $RCO_2H/CH_3CN/HR_2N$.

characterization in solution. Attempts to improve solubility by heating produce cloudy solutions due to decomposition.

Our attempts to refine the crystal structure of **1** failed because of systematic poor quality of crystals, though obtained model was not inconsistent with the proposed formulation. Single crystals of **2** suitable for X-ray analysis can be prepared directly from reaction solution after slow cooling. Synthesis of **3** as single crystals is very sensitive to the temperature regime, tending to form

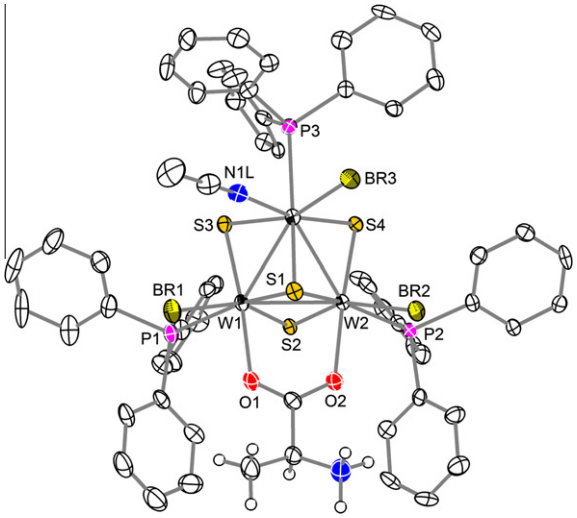


Fig. 2. Cluster complex **3** (a.d.p. at 50% probability level). Only one orientation of $MeNH_3CHCOO^-$ ligand is shown. The hydrogen atoms of PPh_3 and MeCN ligands are omitted for clarity.

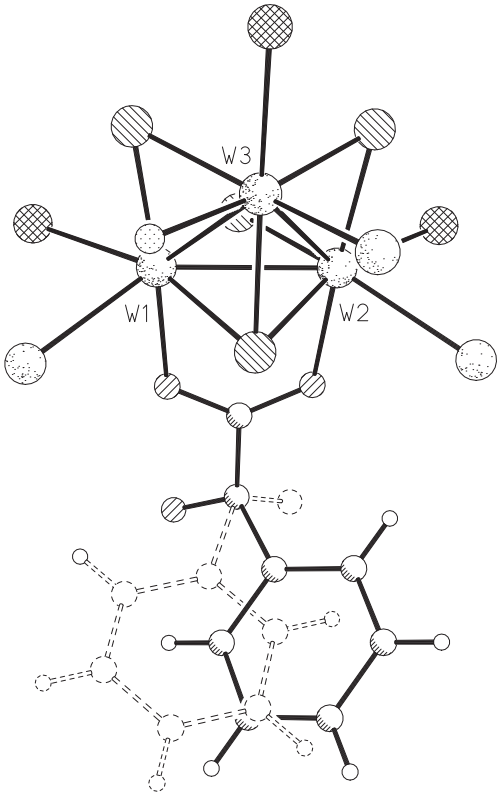


Fig. 3. The 0.5/0.5 positional disorder of $PhC(O)(H)COO^-$ ligand in **2**. Carbon and hydrogen atoms of PPh_3 ligands are omitted for clarity.

powders if temperature changes too rapidly. Complex **2** contains only one anionic rest of monodeprotonated α-oxyacid (mandelate), coordinated to the cluster as μ_2-bridge between two tungsten atoms. The PPh_3 ligands occupy *trans*-positions to μ_3-S (Fig. 1). The absence of counter-ions in **2** indicates that mandelate α-hydroxy groups remain protonated. Coordination around one of the tungsten atoms is completed by terminal CH_3CN ligand.

The coordination mode of alanine in **3** is similar (Fig. 2). The crystal contains also Br^- anion disordered over three close positions with relative weights of 0.47/0.42/0.11. The charge balance of the structure can be achieved if alanine is in neutral zwitter-ionic form $(CH_3)(NH_3^+)CHCOO^-$.

The μ_2-bridge type of coordination of carboxylate ligands was first detected in complexes containing dithiophosphate and carboxylate ligands of the general formula $[M_3S_4(dtp)_3(\mu\text{-}CH_3COO)(L)]$ (M = Mo, W) [33,34]. This type of coordination causes a distortion of the M_3 triangle: the M–M bond between the pair of atoms linked by the carboxylate becomes shorter than two other M–M bonds. In compounds **2** and **3** this shortening lies between 0.021 and 0.046 Å. In the crystal structures of $[W_3S_4\{S_2P(OEt)_2\}_3(py)(\mu\text{-}CH_3COO)]$ [44] and $[W_3S_4\{S_2P(OEt)_2\}_3(py)(\mu\text{-}CH_3COO)]\cdot 0.5dmf$ [45] even larger shortening, 0.060–0.077 Å, was reported. Analysis of 22 crystal structures of this type with $\{Mo_3S_4\}$ core with Cambridge Structural Database (CSD) software reveals similar tendency, the shortening being from 0.044 to 0.086 Å.

An unusual feature of compounds **2** and **3** is that they crystallize in centrosymmetric space groups ($P2_1/c$ and $P\bar{1}$), while being intrinsically chiral. In our opinion the reason is that the chiral fragments are relatively small in comparison with whole structure, while the rest of the structure is not in contradiction with the presence of inversion symmetry. Indeed, in **2**, the whole cluster core $\{W_3S_4\}$ together coordinated PPh_3 and Br^- is almost 'racemic' because of a pseudo-mirror plane that bisects the W_3 triangle in the mid-point of W(1)–W(2) edge and passes through W(3) atom (Fig. 1). The same 'mirror plane' passes through C(1) and C(2) atoms of the chiral mandelate ligand. However H, OH and Ph substituents at C(2) break this pseudo-reflection. Therefore, the centrosymmetric space group corresponds to a *substructure* that is disordered due to the presence of chiral fragment. This is the situation that we clearly observe in **2**: the C(OH)(H)Ph fragment is disordered over two positions with equal weight (Fig. 3).

One of the solvent MeCN molecules follows this disorder. In the second orientation the configuration of optical center at C(2) is opposite relative to the first one. The real space group of **2** that describes the whole (super)structure without any disorder must be chiral. But super-structural reflections corresponding to it are expected to be weak because diffraction is almost completely determined by heavy pseudo-centrosymmetric fragments. Our attempts to detect them by careful analysis of diffraction pattern (CCD frames from diffractometer) were unsuccessful and we decided to leave our centrosymmetric sub-structural description of **2** as is.

In the crystal structure of **3** the explanation of centrosymmetric space group is the same but here the chirality is additionally 'hidden' by diffraction similarity of NH_3 and CH_3 groups (Fig. 2). During the refinement of structure we had to assume C/N 0.5/0.5 disorder in these positions.

Analysis of data from CSD helped us to find another example when similar phenomenon was observed. Slawin et al. found centrosymmetric space group $P2_1/c$ in the crystal structure of ***cis***-$[PdCl_2(bdppalO\text{-}P,O)]\cdot CHCl_3$ (bdppalO = (*S*)-*N*-(diphenylphosphino)-*N*-(diphenylphosphinoyl)alanine) that contains chiral alanine-substituted ligand [46]. The authors mention that '*there was some disorder in complex **14**. C(4) was refined anisotropically in two 50% occupancy sites*' [46] but give no explanation for this fact and does not correlate it with the contradiction between chirality of the molecule and presence of inversion centers in the crystal.

3.2. Trisubstituted $M_3S_4^{4+}$ clusters of general formula $[M_3S_4(PPh_3)_3(RCO_2)_2(RCO_2\text{–}H)]$

Motivated by the successful incorporation of α-hydroxyacids and alanine into the coordination sphere of the M_3S_4 clusters, we decided to increase the number of chiral ligands coordinated at

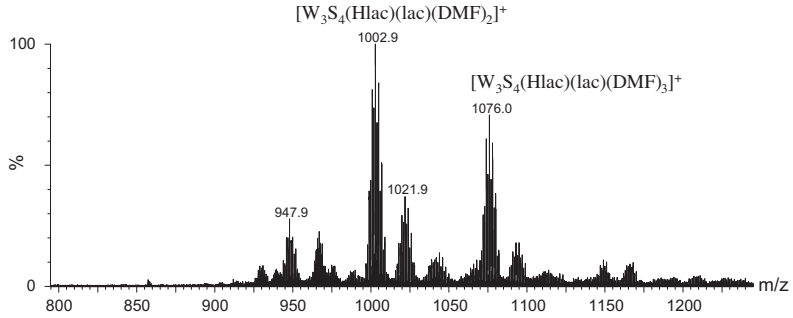


Fig. 4. Positive ESI(+) mass spectrum of $CHCl_3$/dimethylfomamide solutions of the solid obtained from the reaction mixture of $[W_3S_4(PPh_3)_3Br_4]$, lactic acid and *i*-Pr_2NH recorded at a cone voltage U_c = 15 V.

the cluster core. When we reacted $[M_3S_4(PPh_3)_3Br_4]$ with an excess of α-hydroxyacid under prolonged heating (typically 70–80 °C, acetonitrile, 10–12 h), only the mono-substituted forms **1**–**3** and unidentifiable products were obtained for tungsten and molybdenum, respectively. It is not surprising that once sparingly soluble compounds **1**–**3** are formed, they crystallize out from the reaction mixture providing a rather simple and efficient synthetic protocol for their preparation. We also attempted to achieve a higher degree of coordination in the presence of alkylamines that would act as a base and deprotonate the α-hydroxyacid (Scheme 1). For M = W we observed that solutions of $[W_3S_4(PPh_3)_3Br_4]$ in acetonitrile changed the color from blue to different shades of violet if lactic acid or mandelic acid, together with *i*-Pr_2NH, were added. The corresponding violet (lactic) or red-violet (mandelic) solid products were separated and thoroughly washed with CH_3OH and diethylether, redissolved in $CDCl_3$/dimethylformamide mixtures and the identity of the formed species was investigated by $^{31}P\{^1H\}$ NMR and ESI mass spectrometry. The $^{31}P\{^1H\}$ NMR spectroscopy revealed the presence of free PPh_3, thus highlighting that replacement of PPh_3 ligands by dimethylformamide occurs in solution. ESI(+) MS of the solid obtained from the reaction mixture of $[W_3S_4(PPh_3)_3Br_4]$, lactic acid and *i*-Pr_2NH is shown in Fig. 4 and supports this hypothesis.

The presence of species featuring both coordinated solvent and lactate ligands and lacking the PPh_3 ligands in the $W_3S_4^{4+}$ coordination sphere is evident from the ESI(+) mass spectrum. On the basis of the *m*/*z* values as well as characteristic isotopic pattern, the dominant observed peaks were attributed to $[W_3S_4(Hlac)(lac)(DMF)_3]^+$ (*m*/*z* = 1076.0) and $[W_3S_4(Hlac)(lac)(DMF)_2]^+$ (*m*/*z* = 1002.9). Negative ESI mass spectra revealed the presence of $[W_3S_4(DMF)_x(Hlac)lac_2]^-$ species (*x* = 0–2) in which DMF for PPh_3 exchange was also evident. Identical species were identified for M = Mo, where $[Mo_3S_4(PPh_3)_3(Hlac)_2lac]$ (**4**) was isolated in analytically pure form. We may assume that the bulk of the solids obtained from $[W_3S_4(PPh_3)_3Br_4]$, lactic acid (or mandelic acid) and *i*-Pr_2NH correspond primarily to $[W_3S_4(PPh_3)_3(Hlac)_2lac]$ and $[W_3S_4(PPh_3)_3(Hman)_2man]$, respectively. However our efforts to isolate salts of anionic $[W_3S_4(PPh_3)_3(Hlac)lac_2]^-$ and $[W_3S_4(PPh_3)_3lac_3]^{2-}$ complexes by further deprotonation of hydroxyacids with an excess of different amines failed to give identifiable products.

In the case of M = Mo, $[Mo_3S_4(PPh_3)_3Br_4]$ with α-hydroxyacid in the presence of alkylamines give the *tris* complexes (see Scheme 1). In both acetonitrile and chloroform the same product is obtained, while running the reaction in alcohols leads to separation of unidentified oils. The yield of $[Mo_3S_4(PPh_3)_3(Hlac)_3]Cl$ does not depend whether Et_2NH or Bu_3N were used as base. Coordination of amine itself does not occur even in 10-fold molar excess of amine. $[Mo_3S_4(PPh_3)_3(Hlac)_3]Cl$ is analytically pure, green crystalline solid, well soluble in polar organic solvents. Evaporation of a solution in a CH_2Cl_2/CH_3OH (or ethanol) mixture leads to $[Mo_3S_4(PPh_3)_3(Hlac)_2(lac)]$ (**4**) as result of further deprotonation of one of the lactates. Single crystals are obtained by diethyl ether vapor diffusion into solutions of $[Mo_3S_4(PPh_3)_3(Hlac)_3]Cl$ in CH_3OH or CH_3CN.

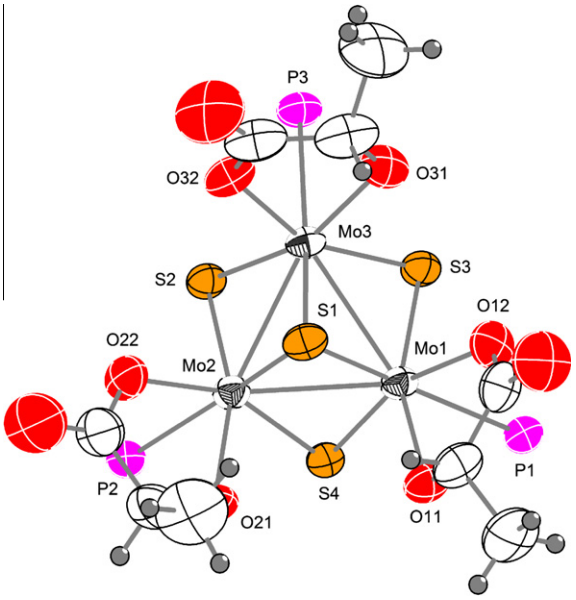
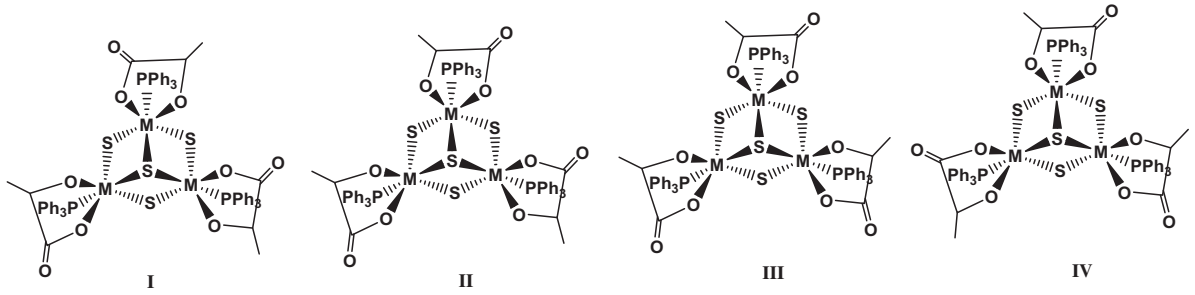


Fig. 5. Cluster complex **4** (a.d.p. at 50% probability level). The phenyl groups of PPh_3 ligands are omitted for clarity.

Compound **4** crystallizes in orthorhombic chiral space group $P2_12_12$. The lactate ligands are coordinated by both carboxylic and hydroxy functional groups to form stable five-membered chelate ring (Fig. 5).

As is the case when acetylacetonate [35–37] and oxalate is coordinated to $M_3S_4^{4+}$ [38] (in $[M_3S_4(acac)_3(Py)_3]PF_6$ and $[M_3Q_4(C_2O_4)_3(H_2O)_3]^{2-}$), and contrary to what is routinely observed in the diphosphine [39,40] and dithiophosphate complexes [30,34], the coordination type of the lactate is *cis*–*cis* regarding the capping μ_3-S atom. The *trans*-positions to the capping μ_3-S atom are occupied by PPh_3 ligands.

A number of isomers differing in mutual arrangement of the lactate ligands are potentially feasible (Scheme 2) with carboxylic groups pointing in the same direction (considering the capping μ_3-S atom above the Mo_3 plane, anticlockwise and clockwise isomers III and IV, respectively) or when two of them point at each other (isomers II and III). The observed stereochemistry of **4** (isomer II) breaks the higher symmetry which could arise if all the lactic ligands were oriented clockwise or anticlockwise by their carboxylic groups (isomers I and IV). The absence of counter-ions presupposes protonation of only two α-hydroxy groups of the lactate ligands.



Scheme 2. Possible isomers due to mutual arrangement of the lactate ligands in **4.**

From close inspections of the three Mo–$O_{hydroxyl}$ distances of 2233(3), 2183(4), and 2092(4) Å, these two hydrogen atoms can be assigned to the first two oxygen atoms with longer Mo–O distances (coordination of $Hlac^{-}$), while the shorter Mo–O distance should correspond to the coordination of the deprotonated hydroxogroup (lac^{2-}). It is worth stressing that all the crystallization techniques mentioned above (either by slow evaporation or by ether vapor diffusion) invariably produced the same isomer of **4**.

An important issue is whether the coordination modes of the lactate ligands and the overall symmetry might be preserved in solution. Like in the case of the solids obtained in the reaction of $[W_3S_4(PPh_3)_3Br_4]$, lactic acid and *i*-Pr_2NH, dimethylformamide was found to be the best solvent to dissolve **4**. We believe that DMF for PPh_3 substitution is at the origin of the enhanced solubility of **4** in DMF:

$$[Mo_3S_4(PPh_3)3(Hlac)_2lac] + DMF \rightarrow [Mo_3S_4(DMF)_3(Hlac)_2lac] + PPh_3 \quad (1)$$

^{31}P $\{^1H\}$ NMR of $CDCl_3$/dimethylformamide solutions of **4** showed the presence of free PPh_3, thus evidencing the replacement of PPh_3. The ^1H NMR spectrum contains signals characteristic of the CH_3 and CH groups of the lactate ligands as a doublet at 1.25 ppm and a quadruplet at 4.09 ppm, respectively, with $^3J_{HH}$ = 6.5 Hz. (Fig. 6).

Two minor doublets at 1.30 and 1.36 ppm with intensity ratio 1:6 with respect to the major doublet, together with a broad multiplet at 4.17 ppm are also observed. This experimental evidence suggest the presence of a dominant form together with two minor diastereoisomers in DMF solution for the $[Mo_3S_4(DMF)_3(Hlac)_2lac]$ species, as evidenced by the distinctive CH_3 and CH groups in the coordinated lactic acid molecules. Unfortunately, we could only detect ^{13}C signals associated to the major isomer (see ^{13}C $\{^1H\}$, gCOSY and gHSQC in the supplementary material).

UV–Vis and CD spectra were recorded at room temperature for chloroform/DMF solutions of **4** (Fig. 7). The electronic absorption studies show charge transfer (S to Mo) transition bands at 378 nm and characteristic d–d transition at around 650 nm. Significant dichroism is observed for all electronic absorptions. This particularly holds for the range between 500 and 650 nm which is associated with the molybdenum centers of the $Mo_3S_4^{4+}$ core. This clearly shows that the ligand imposed chirality is *transferred* to the $Mo_3S_4^{4+}$ core and that significant diastereoisomeric enrichment has occurred.

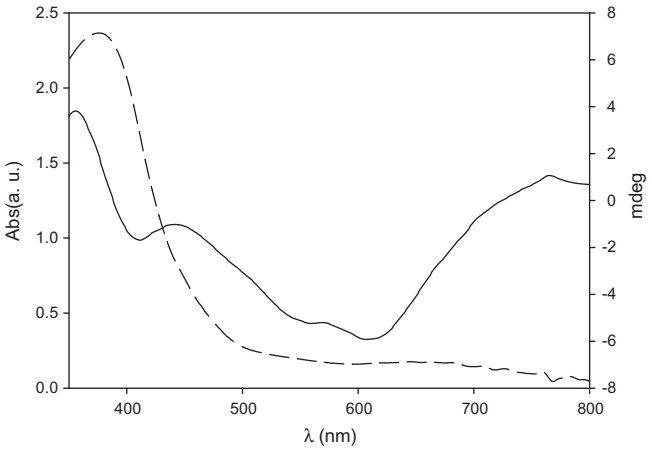


Fig. 7. Uv–Vis (---) and CD (—) spectrum of compound **4** in $CHCl_3$/dimethylformamide mixtures.

ESI(+) mass spectra of DMF solutions of **4** recorded at different cone voltages are shown in Fig. 8.

Complete replacement of PPh_3 is evident in the ESI mass spectrum recorded at U_c = 5 V where the main peak corresponds to $[Mo_3S_4(Hlac)(lac)(DMF)_3]^+$ (m/z = 814.9). Upon increase in the cone voltage consecutive liberation of DMF molecules occurs to yield $[Mo_3S_4(Hlac)(lac)(DMF)_2]^+$ (m/z = 741.9), together with minor peak of $[Mo_3S_4(Hlac)(lac)(DMF)]^+$ (m/z = 668.8) (see Fig. 8, middle). Complete loss of DMF takes place at higher sampling cone voltage (Fig. 8, top), giving rise to dominant peak centered at $[Mo_3S_4(Hlac)(lac)]^+$ (m/z = 595.7). Similar stepwise full loss of neutral ligand was reported for the acetylacetonate-pyridine [37,41] or

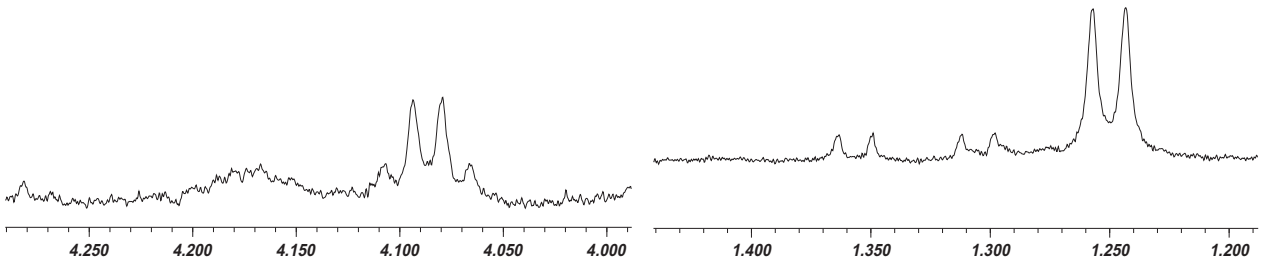


Fig. 6. ^1H regions of the CH and CH3 groups of the lactate ligands in the $[Mo_3S_4(DMF)_3(Hlac)_2lac]$ species recorded in $CDCl_3$/dimethylformamide (80:20).

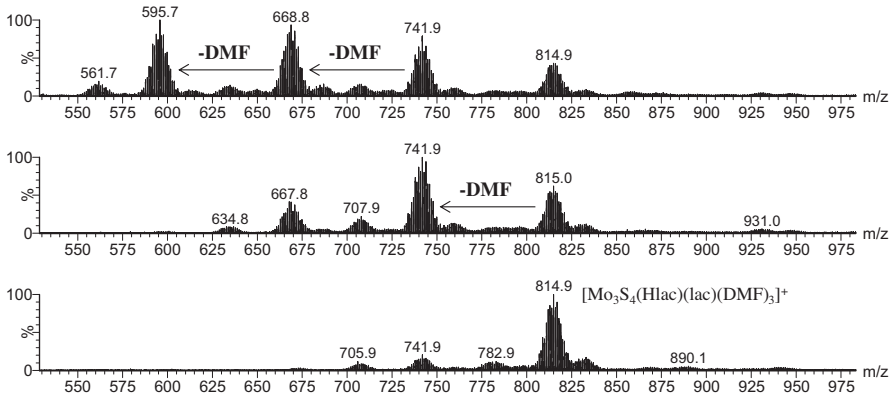


Fig. 8. ESI mass spectra of $CHCl_3$/DMF solutions of compound **4** after 30 min recorded at increasing U_c cone voltages (5 V, bottom, 15 V middle and 25 V top).

diphosphane [42,43] complexes of $Mo_3S_4^{4+}$. In the negative scan mode peaks corresponding to the complexes with deprotonated lactates, $[Mo_3S_4(PPh_3)_3(Hlac)lac_2]^-$ and $[Mo_3S_4(PPh_3)_2(Hlac)lac_2]^-$, are observed.

In order to monitor gradual replacement PPh_3 by DMF, stock solutions of **4** in $CHCl_3$/DMF (80:20) were prepared. At different time intervals they were diluted with $CHCl_3$/DMF (80:20) to final concentration of ca. 1×10^{-5} M and then directly introduced in the ESI mass spectrometer. The neutral complex **4** is positively ionized via loss of one lactate ligand, a common ionization mechanism for closely related neutral carboxylate M_3S_4 clusters [30]. Fig. 9 illustrates ESI (+) mass spectrum of compound **4**.

As can be seen, the forms initially present in DMF solution consecutively give rise to the following peaks $[Mo_3S_4(Hlac)(lac)(PPh_3)_2]^+$ (m/z = 1122.0), $[Mo_3S_4(Hlac)(lac)(DMF)(PPh_3)]^+$ (m/z = 930.9), $[Mo_3S_4(Hlac)(lac)(PPh_3)]^+$ (m/z = 857.9), $[Mo_3S_4(Hlac)(lac)(DMF)_3)]^+$ (m/z = 814.9), $[Mo_3S_4(Hlac)(lac)(DMF)_2]^+$ (m/z = 741.9), $[Mo_3S_4(Hlac)(lac)(DMF)]^+$ (m/z = 668.9).

3.3. Formation of cubane-type $Mo_3S_4Cu^{5+}$ clusters featuring lactic acid

Motivated by the interest in preparation of chiral $M_3M'S_4^{4+}$ (M = Mo, W) clusters, we found that complex **4** rapidly adds CuI (color changes from green to red-brown in dichloromethane), according to Eq. (2):

$$[Mo_3S_4(PPh_3)_3(H_2lac)_2lac] + CuI \rightarrow [Mo_3(CuI)_4(PPh_3)_3(Hlac)_2lac] \quad (2)$$

The formation of the cuboidal cluster was confirmed by the observation of the signal from $[Mo_3CuS_4(PPh_3)I(Hlac)lac_2]^-$ (m/z = 1006) in the ESI(−)-MS, and of the daughter peaks resulting from the loss of PPh_3 (m/z = 744), following by the loss of I^- coordinated to copper atom (m/z = 618). Similar behavior was observed for corresponding $W_3S_4^{4+}$ species.

4. Conclusions

Coordination of one or three chiral alfa-oxy or alfa-aminoacids to $M_3S_4^{4+}$ (M = Mo, W) cluster core was achieved. Chirality transfer to the cluster core was detected by circular dichroism. Identified species by ESI-MS and NMR provide complementary information; while the molecular composition can be determined on the basis of ESI mass spectrometry, the presence of a number of isomers can be ascertained as judged by ^{1}H NMR. These chiral triangular clusters can be used for preparation of chiral cuboidal heterometal clusters.

Acknowledgements

S.A.A. thanks the Haldor Topsoe company for a research fellowship. The authors are also grateful to the Serveis Centrals d'Instrumentacio Cientifica (SCIC) of the Universitat Jaume I for providing us with mass spectrometric facilities. The work was supported by Government Contracts GC No. 02.740.11.0628, No. 16.740.11.0273 in the framework of Federal Frame Program "Scientific and Research-Educational Staff for Innovative Russia

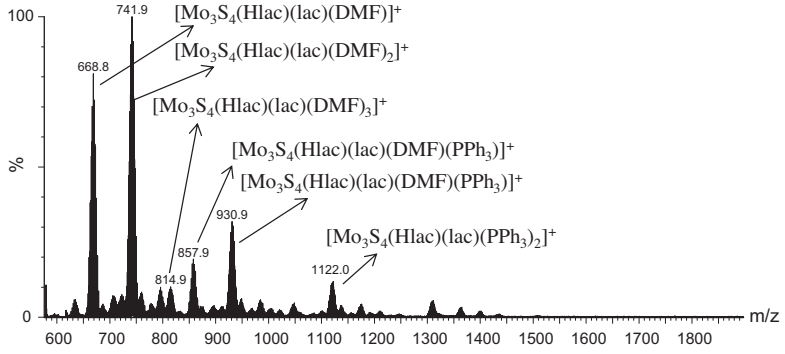


Fig. 9. ESI mass spectrum of $CHCl_3$/dimethylformamide solutions of compound **4**, recorded at a cone voltage U_c = 15 V.

2009–2013" and No. 11.519.11.3021 in the framework of Federal Frame Program "Research and Development of the Science & Technology Complex of Russia in 2007–2013".

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