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Novel molybdenum(V) squarato complexes based on the dinuclear metal–metal bonded unit: syntheses and structural characterization of dinuclear $[Mo_2O_4(C_4O_4)(R\text{-}Py)_4]$ and tetranuclear $[Mo_4O_8(C_4O_4)_4]^{4-}$

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Received 17th September 2003, Accepted 28th October 2003
First published as an Advance Article on the web 11th November 2003

Reactions of mononuclear oxohalomolybdates(V) with squaric acid (3,4-dihydroxycyclobut-3-ene-1,2-dione) afforded two types of $\{Mo_2O_4\}^{2+}$ containing species with the squarato ligand engaged in a μ_2-1,2-bis(monodentate) binding mode. In the presence of pyridine (Py) or 3,5-lutidine (3,5-Lut) neutral, dinuclear complexes $[Mo_2O_4(C_4O_4)(Py)_4]\cdot 2MeOH\cdot 0.5Py$ **1a**, $[Mo_2O_4(C_4O_4)(Py)_4]\cdot 2Py$ **1b** and $[Mo_2O_4(C_4O_4)(3,5\text{-Lut})_4]\cdot 2(3,5\text{-Lut})$ **1c** were obtained. A pair of nitrogen donor ligands and a squarate oxygen occupy the three coordination sites of each metal in the $\{Mo_2O_4\}^{2+}$ unit in **1a**, **1b** and **1c**. The squarate functions as a third, auxiliary bridge between a pair of molybdenum atoms at an average distance of 2.55 Å. Using 2,4,6-collidine (Col) afforded $(ColMe)_4[Mo_4O_8(C_4O_4)_4]\cdot 2MeOH\cdot 2Col$ **2a** ($ColMe^+$ = *N*-methylcollidinium cation, $NC_9H_{14}^+$) and $(ColH)_4(PyEt)[Mo_4O_8(C_4O_4)_4]Br$ **2b** ($ColH^+$ = protonated 2,4,6-collidine, $NC_8H_{12}^+$; $PyEt^+$ = *N*-ethylpyridinium cation, $NC_7H_{10}^+$). The tetranuclear anions of **2a** and **2b** consist of a rare, cube-like $\{Mo_4O_4(\mu_3\text{-}O)_4\}^{4+}$ core with four squarato ligands attached to its periphery. The squarato ligands in the $[Mo_4O_8(C_4O_4)_4]^{4-}$ anions bridge pairs of molybdenum atoms from neighbouring $\{Mo_2O_4\}^{2+}$ units, spanning an average distance of 3.43 Å. The compounds were fully characterized by infrared vibrational spectroscopy, NMR spectroscopy, elemental analyses and X-ray diffraction studies.

Introduction

Research involving polyoxometalates is driven by their remarkable structural and electronic properties, and by their potential and also realized applications in many areas, especially catalysis.[1] In particular, the chemistry of coordination compounds of polyoxomolybdates(VI) with organic ligands provides knowledge about the interactions of small organic molecules with catalytic oxide surfaces.[2] Recently, the well-known polyoxomolybdate(VI) anions, such as $[Mo_6O_{19}]^{2-}$ and $[Mo_8O_{26}]^{4-}$, were incorporated into extended arrays by covalent linkages with complexes of multidentate nitrogen donor ligands and secondary transition metals.[3] With no secondary transition metal introduced, the multidentate ligand failed to adopt the anticipated bridging role.[4] Furthermore, the highly oxophilic nature of the rare earth cations was exploited in the linkage of mixed-valence polyoxomolybdate(V,VI) entities into polymeric materials.[5] The linkers consisted of multidentate oxygen donor ligands coordinated to two or more rare earth cations which capped the metal oxide cores.

The structural chemistry of oxomolybdenum(V) compounds is limited mostly to molecular compounds with either $\{Mo_2O_2(\mu_2\text{-}O)_2\}^{2+}$ fragment, denoted $\{Mo_2O_4\}^{2+}$, in which a pair of molybdenum atoms is connected by a single metal–metal bond or to assemblies of two, three, four or more dinuclear units as recurring structural patterns.[6,7] The vast majority are dinuclear species with diverse ligands completing five- or six-fold coordination environments of molybdenum. Not so numerous are the higher nuclearity clusters whose formation may be envisioned as stepwise condensation of dinuclear units,[6] enabled by oxygen donor ligands which can participate in bridging interactions with two, three or even four metal centres. The self-assembly of dinuclear units to produce discrete oligonuclear cores was observed to take place also in the presence of multidentate oxygen donor ligands as illustrated by a few selected examples, *i.e.*, $\{Na[(Mo_2O_4)_3(\mu_2\text{-}O)_3(\mu_6\text{-}SO_3)(\mu_2\text{-}SO_3)_3]_2\}^{15-}$, $[(Mo_2O_4)_3(\mu_2\text{-}OH)_3(\mu_6\text{-}CO_3)(\mu_2\text{-}CO_3)_3]^{5-}$, $[(Mo_2O_4)_3(Mo^{VI}O_4)(O_3PCH_2PO_3)_3]^{8-}$ and $[(Mo_2O_4)_{10}(P_2O_7)_{10}(CH_3COO)_8(H_2O)_4\}]^{28-}$.[8–11] In only three cases were the $\{Mo_2O_4\}^{2+}$ units covalently linked *via* bridging ligands into infinite arrays. In the earliest example, $[Mo_2O_4(PO_4)(HPO_4)]_n^{3n-}$, the tetrahedral phosphates connect in a complicated manner the dinuclear building blocks into a two-dimensional layered structure.[12] The phosphate assisted polymerization of dinuclear blocks also resulted in $[Mo_2O_4(H_2PO_4)(C_2O_4)_2]_n^{3n-}$ with an infinite chain structure.[13] Chains of alternating dinuclear blocks and bisbidentate oxalates were observed for $[Mo_2O_4Cl_2(C_2O_4)]_n^{2n-}$.[14] Polymeric phosphomolybdates(V) reveal two other building blocks, both consisting of $\{Mo_2O_4\}^{2+}$ units. The repeating pattern in $[Mo_8O_{12}(PO_4)_4(HPO_4)_2]$ is a single $\{Mo_2O_4\}^{2+}$ moiety with two additional molybdenum(V) centres attached through the bridging oxo groups.[15] In $[Mo_4O_8(PO_4)(H_{1.5}PO_4)_2]_n^{2n-}$ and $[Mo_4O_8(PO_4)_2]_n^{2n-}$ the tetrahedral phosphates connect the cube-like $\{Mo_4O_4(\mu_3\text{-}O)_4\}^{4+}$ entities, which are compact associations of two $\{Mo_2O_4\}^{2+}$ subunits, into infinite 1D or 2D structures, respectively.[16,17]

Prior to this, we reported on a series of oxalato $\{Mo_2O_4\}^{2+}$ complexes, ranging from discrete dinuclear, tetranuclear and octanuclear species to 1D-polymer with the oxalate engaged in different binding modes.[14,18] With the hope that the speciation and the structural diversity among the squarato complexes would parallel that encountered among the oxalato complexes, a similar synthetic strategy was undertaken. Due to geometric constraints the squarate was not expected to adopt a bidentate binding mode, but rather monodentate to one or more metal centres.[19] Hitherto unknown species, a dinuclear $[Mo_2O_4(C_4O_4)(R\text{-}Py)_4]$ and a tetranuclear $[Mo_4O_8(C_4O_4)_4]^{4-}$, based on a cube-like $\{Mo_4O_4(\mu_3\text{-}O)_4\}^{4+}$, were obtained. In both, the squarate binds as a μ_2-1,2-bis(monodentate) ligand, in $[Mo_2O_4(C_4O_4)(R\text{-}Py)_4]$ to one dinuclear unit only, forming a third

DOI: 10.1039/b311348e

bridge between a pair of metal–metal bonded molybdenum atoms, while in $[Mo_4O_8(C_4O_4)_4]^{4-}$ to pairs of molybdenum atoms not connected by metal–metal bonds.

Experimental

General techniques

Acetonitrile, ethanol, methanol, 2,4,6-collidine, 3,5-lutidine, pyridine and squaric acid were purchased from Aldrich and used without further purification. $(PyH)_2[MoOCl_5]$ and $(PyH)[MoOBr_4]$ were prepared by minor modification of a published procedure.[20] The solvothermal reactions were carried out in sealed glass tubes under autogenous pressure. The infrared spectra were measured on solid samples as Nujol or poly(chlorotrifluoroethylene) mulls using a Perkin Elmer 2000 Fourier Transform infrared spectrometer. ^1H spectrum was recorded on a Bruker Avance DPX 300 spectrometer (^1H, 300 MHz) referenced to the solvent. Elemental analyses were carried out by the Chemistry Department service at the University of Ljubljana.

Preparations

$[Mo_2O_4(C_4O_4)(Py)_4]\cdot 2MeOH\cdot 0.5Py$ 1a. $(PyH)[MoOBr_4]$ (0.469 mmol, 240 mg) or $(PyH)_2[MoOCl_5]$ (0.469 mmol, 210 mg) and $H_2C_4O_4$ (0.263 mmol, 30 mg) were added to a mixture of pyridine (2 cm^3), methanol (2.5 cm^3) and acetonitrile (0.5 cm^3). The reaction mixture was allowed to stand in a closed Erlenmeyer flask at ambient conditions for three days. Large, red crystals were collected by filtration and washed with the hexanes. Yield 41% (76 mg). Calc. for $C_{28.5}H_{30.5}Mo_2N_{4.5}O_{10}$: C, 43.44; H, 3.90; N, 8.00. Found: C, 43.20; H, 3.74; N, 7.88%.

IR (cm^{-1}): 3435m, 2920w, 1787s, 1729w, 1660vvs, 1606vvs, 1571m, 1519vvs, 1485vs, 1445vvs, 1222vvs, 1156m, 1066vs, 1044vs, 1015vs, 945vvs, 928vs, 760s, 742vvs, 692vvs, 640s, 605w, 495m, 481m, 450m, 434s, 409m, 348w, 305m, 278s, 199w.

$[Mo_2O_4(C_4O_4)(Py)_4]\cdot 2Py$ 1b. A mixture of $(PyH)[MoOBr_4]$ (0.235 mmol, 120 mg), $H_2C_4O_4$ (1 mmol, 114 mg) and pyridine (4 cm^3) was placed in a glass tube which was sealed and subsequently heated for 120 h in an electric oven maintained at 115 °C. The tube was allowed to cool slowly to room temperature. The solid product in the orange solution consisted of two phases: colourless, crystalline $(PyH)HC_4O_4$ and orange crystals of **1b** which decomposed when taken out from the mother-liquor.

$[Mo_2O_4(C_4O_4)(3,5\text{-Lut})_4]\cdot 2(3,5\text{-Lut})$ 1c. *Procedure a.* $(PyH)_2[MoOCl_5]$ (0.445 mmol, 200 mg) or $(PyH)[MoOBr_4]$ (0.445 mmol, 228 mg) and $H_2C_4O_4$ (0.307 mmol, 35 mg) were added to a mixture of 3,5-lutidine (2 cm^3), methanol (2.5 cm^3) and acetonitrile (0.5 cm^3). The reaction mixture was allowed to stand in a closed Erlenmeyer flask at ambient conditions for three days. Orange, microcrystalline product was collected by filtration and washed with hexanes. Yield 68% (154 mg).

Procedure b. A mixture of $(PyH)_2[MoOCl_5]$ (0.235 mmol, 106 mg) or $(PyH)[MoOBr_4]$ (0.235 mmol, 120 mg), $H_2C_4O_4$ (1 mmol, 114 mg) and 3,5-lutidine (4 cm^3) was placed in a glass tube which was sealed and subsequently heated for 120 h in an electric oven maintained at 115 °C. The tube was allowed to cool slowly to room temperature. Large, orange crystals of **1c** were separated manually from unidentified crystalline material of a light yellow colour, probably the 3,5-lutidinium salt of squaric acid.

The elemental analysis was performed on a dried sample. Calc. for $C_{32}H_{36}Mo_2N_4O_8$: C, 48.25; H, 4.56; N, 7.03. Found: C, 47.98; H, 4.67; N, 6.91%.

IR (cm^{-1}): 3435m, 3015 w, 2921s, 2857m, 1786s, 1673vs, 1599s, 1524vvs, 1428vvs, 1250m, 1184m, 1152vs, 1074m, 1050m, 953vs, 927s, 867m, 768vs, 739vs, 699s, 651w, 539m, 486m, 467m, 449m, 426w, 408m, 350w, 317m, 300m, 274vs, 219w, 181m.

$(ColMe)_4[Mo_4O_8(C_4O_4)_4]\cdot 2MeOH\cdot 2Col$ 2a. A glass tube was charged with $(PyH)[MoOBr_4]$ (0.117 mmol, 60 mg), $H_2C_4O_4$ (0.439 mmol, 50 mg), 2,4,6-collidine (4 cm^3), methanol (0.5 cm^3) and acetonitrile (0.5 cm^3). The tube was sealed and heated for 120 h in an electric oven maintained at 115 °C. Over a period of two weeks, a few orange crystals of **2a** grew from a dark brown solution. The crystals decomposed quickly when removed from the mother-liquor.

$(ColH)_4(PyEt)[Mo_4O_8(C_4O_4)_4]Br$ 2b. A glass tube was charged with $(PyH)[MoOBr_4]$ (0.782 mmol, 400 mg), $H_2C_4O_4$ (3.07 mmol, 350 mg), 2,4,6-collidine (1 cm^3), ethanol (3 cm^3) and acetonitrile (0.5 cm^3). The tube was sealed and heated for 120 h in an electric oven maintained at 115 °C. Over a period of two weeks, large, dark orange crystals of **2b** grew from a brown solution. The crystals of **2b** were separated manually from unidentified, crystalline material of a light yellow colour. Yield 34% (108 mg). Calc. for $C_{55}H_{58}BrMo_4N_5O_{24}$: C, 40.36; H, 3.57; N, 4.28. Found: C, 40.15; H, 3.39; N, 4.06%.

IR (cm^{-1}): 2708m, 1807w, 1799m, 1687vs, 1670s, 1652m, 1633s, 1542vs, 1485vs, 1438vs, 1335w, 1281w, 1247w, 1179m, 1173m, 1145w, 1095w, 1081w, 1053s, 1037vs, 1000w, 968vs, 895w, 865m, 857m, 787m, 746vs, 721w, 713w, 684s, 671s, 658w, 622m, 518m, 497m, 434s, 412vs, 355w, 275m, 235m, 201m, 160w, 136w, 121w.

^1H NMR (CD_3OD, 300 MHz), δ 1.66 (3H, t, J = 7.4 Hz, $CH_3CH_2NC_5H_5$), 2.51 (12H, s, 4-$CH_3NC_5H_2(CH_3)_2$), 2.64 (24H, s, 2,6-$(CH_3)_2NC_5H_2(CH_3)$), 4.70 (2H, q, J = 7.4 Hz, $CH_3CH_2NC_5H_5$), 7.43 (8H, s, $H_{3,5}$ ($ColH^+$)), 8.11 (2H, m, $H_{3,5}$ ($PyEt^+$)), 8.57 (1H, t, J = 7.9 Hz, H_4 ($PyEt^+$)), 9.01 (2H, d, J = 6.0 Hz, $H_{2,6}$ ($PyEt^+$)).

$[Mo_4O_8(OMe)_2Cl_2(Py)_4]\cdot CH_3CN$ 3. An analogous procedure as for the preparation of **1a** was used with $(PyH)_2[MoOCl_5]$ as a starting material and a smaller amount of $H_2C_4O_4$. $(PyH)_2[MoOCl_5]$ (225 mg, 0.5 mmol) and $H_2C_4O_4$ (15 mg, 0.13 mmol) were added to the mixture of pyridine (2 cm^3), methanol (2.5 cm^3) and acetonitrile (0.5 cm^3). The Erlenmeyer flask was stoppered and allowed to stand at ambient conditions overnight. Large, red prismatic crystals formed. The crystals were collected by filtration and washed with the hexanes. Later the synthesis of **3** was carried out in a rational way without the addition of squaric acid. Yield 62% (78 mg).

Calc. for $C_{24}H_{29}Cl_2Mo_4N_5O_{10}$: C, 28.76; H, 2.92; N, 6.99. Found: C, 28.81; H, 2.85; N, 6.90%.

IR (cm^{-1}): 2922m, 2851m, 1607vs, 1487m, 1451s, 1221vs, 1155m, 1075vs, 1045vs, 1018vs, 957vvs, 933vvs, 757vs, 742vvs, 690vvs, 666vvs, 645s, 505vs, 473s, 434m, 422w, 355m, 321m, 278m. The compound was subjected to the X-ray structure analysis.[21]

Crystallography

The crystals were mounted on the tip of a glass fibre with a small amount of silicon grease and transferred to a goniometer head. Data for **1a**, **2b** and **3** were collected on a Nonius Kappa CCD diffractometer using graphite monochromated Mo-Kα radiation. Data reduction and integration were performed with the software package DENZO-SMN.[22] Specific absorption corrections were not applied since the crystals were nearly equidimensional and averaging of the symmetry-equivalent reflections largely compensated for any absorption effects. Crystallographic data for compounds **1b**, **1c** and **2a** were collected on a Bruker P4 diffractometer equipped with a SMART CCD system. Data processing was accomplished with the SAINT program.[23] Absorption corrections were made using SADABS.[24] For all compounds, the coordinates of some

Table 1 Crystallographic data for compounds **1a**, **1b**, **1c**, **2a** and **2b**

	1a	**1b**	**1c**	**2a**	**2b**
Empirical formula	$C_{28.5}H_{30.5}Mo_2N_{4.5}O_{10}$	$C_{34}H_{30}Mo_2N_6O_8$	$C_{46}H_{54}Mo_2N_6O_8$	$C_{70}H_{86}Mo_4N_6O_{26}$	$C_{55}H_{58}BrMo_4N_5O_{24}$
Formula weight	787.9	842.5	1010.8	1811.2	1636.7
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P2_1/m$
T/K	150(2)	90(2)	90(2)	90(2)	150(2)
a/Å	10.3502(2)	17.1101(7)	9.9594(5)	14.2914(6)	11.05280(10)
b/Å	10.97220(10)	11.1614(5)	11.8057(6)	17.1820(8)	22.6688(2)
c/Å	14.9631(2)	35.7999(15)	21.0573(11)	30.5418(14)	12.1180(2)
α/°	70.3901(6)	90	90.3260(10)	90	90
β/°	79.9458(6)	91.3470(10)	92.4660(10)	100.0820(10)	96.0427(4)
γ/°	86.4850(6)	90	111.8640(10)	90	90
V/Å^3	1576.13(4)	6834.9(5)	2295.0(2)	7383.9(6)	3019.34(6)
Z	2	8	2	4	2
μ/mm^{-1}	0.858	0.794	0.605	0.749	1.560
Collected reflections	13037	89080	29617	95337	10451
Unique reflections, R_{int}	7198, 0.0165	24054, 0.0307	14929, 0.0192	24562, 0.0758	5462, 0.0168
Observed reflections	6423	20517	13130	16327	4925
$R1$ [$I > 2\sigma(I)$]	0.0258	0.0340	0.0312	0.0514	0.0255
$wR2$ (all data)	0.0704	0.0767	0.0805	0.1163	0.0665

or all of the non-hydrogen atoms were found *via* direct methods using the structure solution program SHELXS.[25] The positions of the remaining non-hydrogen atoms were located by use of a combination of least-squares refinement and difference Fourier maps in the SHELXL 97 program.[25] With the exception of **1a** all non-hydrogen atoms were refined anisotropically. One of the two methanol solvent molecules in **1a** was disordered over two positions with occupancies of 0.656(6) and 0.344(6), respectively. Carbon atoms of the disordered methanol were refined with isotropic displacement parameters. Pyridine solvent molecule was found on a crystallographic inversion centre, its disorder was resolved using PART-1 instruction. The hydrogen atoms were included in the structure factor calculations at idealized positions. Figures depicting the structures were prepared by SHELXTL.[26] Cell parameters and refinement results are summarized in Table 1.

CCDC reference numbers 219865–219870.

See http://www.rsc.org/suppdata/dt/b3/b311348e/ for crystallographic data in .CIF or other electronic format.

Results and discussion

Structural studies

The crystal structures of $[Mo_2O_4(C_4O_4)(Py)_4]\cdot 2MeOH\cdot 0.5Py$ 1a, $[Mo_2O_4(C_4O_4)(Py)_4]\cdot 2Py$ 1b and $[Mo_2O_4(C_4O_4)(3,5\text{-Lut})_4]\cdot 2(3,5\text{-Lut})$ 1c. In the crystalline state all three compounds are composed of discrete $[Mo_2O_4(C_4O_4)(R\text{-}Py)_4]$ molecules, shown in Fig. 1, and solvent molecules, methanol and pyridine in **1a**, pyridine in **1b** and 3,5-lutidine in **1c**.[27] Listings of pertinent bond distances and angles are given in Table 2. The dinuclear molecules consist of the well-known $\{Mo_2O_4\}^{2+}$ core whose structural parameters are essentially identical to those previously reported:[6] (i) a relatively short distance between a pair of molybdenum atoms, 2.5405(2) Å for **1a**, 2.5416(2) and 2.5479(2) Å for **1b** and 2.5519(2) Å for **1c**, typical for a single metal–metal bond, and (ii) the non-planar $\{Mo_2(\mu_2\text{-}O)_2\}$ bridge. The deviation of the bridge from planarity is given by the dihedral angle between the two $Mo(\mu_2\text{-}O)_2$ planes, 149.04(7)° for **1a**, 150.96(4) and 151.29(5)° for **1b** and 151.03(5)° for **1c**. A distorted octahedral environment of each molybdenum atom is completed by a pair of *cis* equatorial pyridine ligands and a squarato oxygen atom in *trans* position to the terminal oxo group. The observed coordination mode of the squarate merits comment. The squarate acts as a μ_2-1,2-bis(monodentate) ligand forming an auxiliary bridge between a pair of metal centres, spanning an average distance of 2.55 Å. The significantly longer distance between a pair of coordinated squarate oxygen atoms, 3.3161(20) Å for **1a**, 3.2891(18) Å and 3.3040(17) for **1b** and 3.3209(16) Å for **1c**, suggests that the ligand is more suitable to bridge pairs of metal atoms at larger separations. The squarate is slightly tilted away from the plane of molybdenum atoms and terminal oxo groups. The molybdenum to squarato-oxygen bonds experience a *trans* influence of the terminal oxo groups, with lengths of 2.1736(14) and

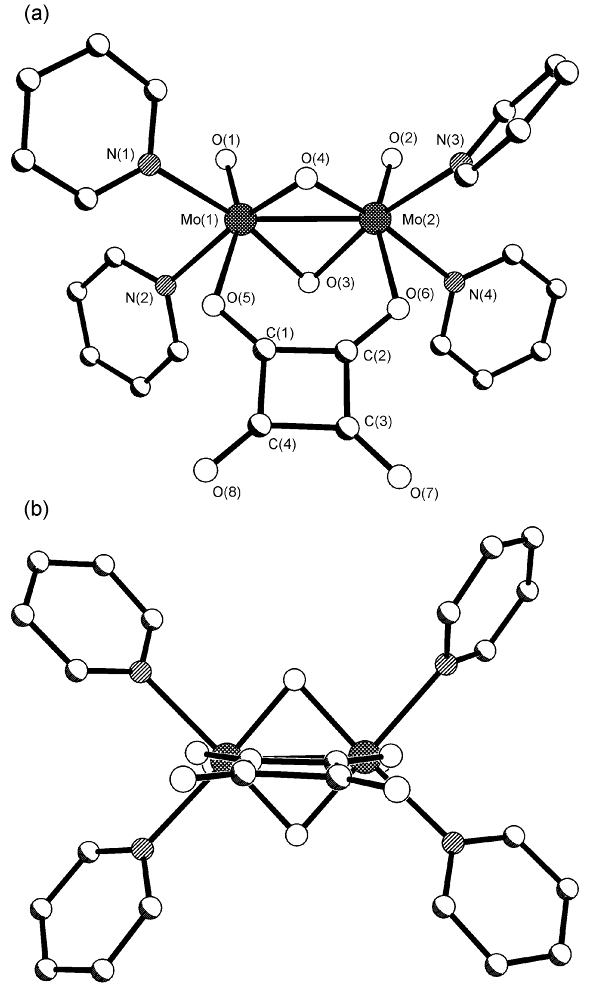

Fig. 1 (a) A molecular structure of $[Mo_2O_4(C_4O_4)(Py)_4]$. Molybdenum atoms are cross-hatched; nitrogen atoms are lined bottom left to top right; oxygen atoms are unshaded and carbon atoms shaded, small sized spheres, respectively. (b) A view perpendicular to the $Mo_2(\mu_2\text{-}O)_2$ rhombus, emphasizing the almost coplanar arrangement of the squarate and the terminal oxo groups.

Table 2 Bond lengths (Å) and angles (°) in $[\mathrm{Mo_2O_4(C_4O_4)(R\text{-}Py)_4}]$[a]

	1a	**1b**[b]		**1c**
Mo(1)–O(1)	1.6913(14)	1.6901(13)	1.6917(13)	1.6978(12)
Mo(1)–O(3)	1.9303(14)	1.9333(12)	1.9387(12)	1.9355(11)
Mo(1)–O(4)	1.9370(14)	1.9361(12)	1.9325(12)	1.9423(11)
Mo(1)–O(5)	2.1736(14)	2.1608(13)	2.1531(13)	2.1616(11)
Mo(2)–O(2)	1.6913(15)	1.6909(13)	1.6945(11)	1.6962(11)
Mo(2)–O(3)	1.9375(14)	1.9338(12)	1.9417(12)	1.9413(11)
Mo(2)–O(4)	1.9330(14)	1.9386(12)	1.9332(12)	1.9402(11)
Mo(2)–O(6)	2.1800(14)	2.1854(13)	2.1782(13)	2.1573(11)
Mo(1)–Mo(2)	2.5405(2)	2.5416(2)	2.5479(2)	2.5519(2)
Mo(1)–N(1)	2.2599(17)	2.2540(15)	2.2542(15)	2.2641(13)
Mo(1)–N(2)	2.2557(17)	2.2495(15)	2.2723(15)	2.2634(13)
Mo(2)–N(3)	2.2606(17)	2.2241(15)	2.2544(15)	2.2680(13)
Mo(2)–N(4)	2.2577(18)	2.2521(15)	2.2313(15)	2.2699(13)
O(3)–Mo(1)–O(4)	94.15(6)	94.63(5)	94.52(5)	94.47(5)
O(3)–Mo(2)–O(4)	94.05(6)	94.54(5)	94.40(5)	94.36(5)
O(1)–Mo(1)–O(5)	157.23(6)	157.13(6)	155.21(6)	158.22(5)
O(2)–Mo(2)–O(6)	157.50(6)	159.19(6)	159.54(6)	158.40(5)
O(5) ··· O(6)	3.3161(20)	3.2891(18)	3.3040(17)	3.3209(16)
O(7) ··· O(8)	3.2609(24)	3.2681(20)	3.2666(20)	3.2991(20)
C(1)–O(5)	1.288(2)	1.283(2)	1.289(2)	1.2889(19)
C(2)–O(6)	1.285(3)	1.280(2)	1.282(2)	1.2866(19)
C(3)–O(7)	1.230(3)	1.227(2)	1.230(2)	1.226(2)
C(4)–O(8)	1.226(3)	1.225(2)	1.222(2)	1.228(2)
C(1)–C(2)	1.438(3)	1.434(2)	1.433(2)	1.433(2)
C(2)–C(3)	1.472(3)	1.477(2)	1.471(2)	1.474(2)
C(3)–C(4)	1.504(3)	1.511(3)	1.510(3)	1.514(2)
C(4)–C(1)	1.464(3)	1.474(2)	1.474(2)	1.478(2)

[a] Same labelling scheme pertains to **1a**, **1b** and **1c**. [b] The asymmetric unit of **1b** contains two independent dinuclear moieties.

Table 3 Selected geometric parameters (Å) of $\{\mathrm{Mo_2O_4}\}^{2+}$ units with metal centres bridged by a third ligand L[a]

	Mo–Mo	L[b]	Mo–O[c]	Ref.
1a	2.5405(2)	$\mu_2\text{-}\mathrm{C_4O_4}^{2-}$	2.1736(14), 2.1800(14)	This work
1b[d]	2.5416(2), 2.5479(2)	$\mu_2\text{-}\mathrm{C_4O_4}^{2-}$	2.1608(13), 2.1854(13) 2.1531(13), 2.1782(13)	This work
1c	2.5519(2)	$\mu_2\text{-}\mathrm{C_4O_4}^{2-}$	2.1573(11), 2.1616(11)	This work
$\mathrm{(NH_4)_8[Mo_2O_4(\mu_2\text{-}SO_3)(SO_3)_4]\cdot 2H_2O}$	2.5872(18)	$\mu_2\text{-}\mathrm{SO_3}^{2-}$	2.27(1)	8
$\mathrm{(NH_4)_3[Mo_2O_4(\mu_2\text{-}OOCH)(OOCH)_4]}$	2.5490(5)	$\mu_2\text{-}\mathrm{OOCH}^{-}$	2.302(2)	31
$\mathrm{[Mo_2O_4(acac)_2(\mu_2\text{-}thala)]\cdot 3EtOH}$[e]	2.5631(5)	$\mu_2\text{-}\mathrm{OOCR}$[e]	2.319(2), 2.365(2)	32
$\mathrm{(NH_4)_5[(Mo_2O_4)_3(\mu_2\text{-}OH)_3(\mu_6\text{-}CO_3)(\mu_2\text{-}CO_3)_3]\cdot 0.5MeOH}$	2.5884(6)	$\mu_6\text{-}\mathrm{CO_3}^{2-}$	2.355(3)	9
$\mathrm{(H_3O)Cs_2K_8Na[(Mo_2O_4)_3(\mu_2\text{-}OH)_3(\mu_6\text{-}AsO_3)(\mu_2\text{-}SO_4)_3]_2\cdot 12H_2O}$	2.6011(9)	$\mu_6\text{-}\mathrm{AsO_3}^{3-}$	2.157(5)–2.206(5)	33
$\mathrm{(NH_4)_{15}\{Na[(Mo_2O_4)_3(\mu_2\text{-}O)_3(\mu_6\text{-}SO_3)(\mu_2\text{-}SO_3)_3]_2\}\cdot 5H_2O}$	2.597(5)	$\mu_6\text{-}\mathrm{SO_3}^{2-}$	2.36(2)	8

[a] L = multidentate oxygen donor ligand. [b] See text for description of the coordination of L. [c] A distance between molybdenum and oxygen belonging to L. [d] Two sets of distances, for each independent molecule of the asymmetric unit one. [e] thala = 3-(2-thienyl)-DL-alanine. The zwitter ionic form of thala coordinates through the carboxylate moiety.

2.1800(14) Å for **1a**, 2.1531(13)–2.1854(13) Å for **1b** and 2.1573(11) and 2.1616(11) Å for **1c**. Their values are longer than those observed in $[\mathrm{Mo_2O_3Cl_3(C_4O_4)_2}]^{3-}$,[28] 2.022(3)–2.048(3) Å, $[\mathrm{Mo_4O_8(OH)_2(H_2O)_2(C_4O_4)_2}]^{2-}$,[29] 2.086(6) and 2.169(6) Å, and $[\mathrm{Mo_4O_8(OMe)_2(C_4O_4)_2(HC_4O_4)_2}]^{4-}$,[30] 2.063(6) and 2.097(6) Å. In each of these instances, the squarate also adopts μ_2-1,2-bis(monodentate) binding role, but its position is not *trans* to the terminal oxo groups. The lengthening of the *trans* bonds can be even more pronounced as shown by a series of $\{\mathrm{Mo_2O_4}\}^{2+}$ compounds with pairs of molybdenum atoms supported by a third bridging ligand L listed in Table 3. With the exception of the last three examples, the multidentate oxygen donor ligand L is bonded in the same manner as in **1a**, **1b** and **1c**, *i.e.*, as a μ_2-bis(monodentate) ligand in a *trans* position to the terminal oxo groups. The μ_6-ligands, $\mathrm{CO_3}^{2-}$, $\mathrm{AsO_3}^{3-}$ or $\mathrm{SO_3}^{2-}$, in the last three examples also coordinate to each $\{\mathrm{Mo_2O_4}\}^{2+}$ unit with two of their oxygen atoms. However, the μ_6-ligand is surrounded by three dinuclear units forming a planar, hexanuclear core. Each oxygen atom of the ligand is thus shared between a pair of molybdenum atoms belonging to adjacent $\{\mathrm{Mo_2O_4}\}^{2+}$ units. The listed molybdenum–oxygen bonds can be as large as 2.36 Å.

The squarato ligands in **1a**, **1b** and **1c** are almost planar. The structural parameters indicate a localized structure. Of the four C–C bonds, one is long (its mean value is 1.510 Å), two are intermediate (1.473 Å) and one with the largest double bond character is short (1.435 Å). The C(1)–O(5) and C(2)–O(6) bonds are longer than the C(3)–O(7) and C(4)–O(8) bonds, confirming the double bond character in the latter. Similar pattern of bond lengths is displayed in the squarato ligands of $[\mathrm{Mo_4O_8(OH)_2(H_2O)_2(C_4O_4)_2}]^{2-}$.[29]

The crystal structures of $\mathrm{(ColMe)_4[Mo_4O_8(C_4O_4)_4]\cdot 2MeOH\cdot 2Col}$ 2a and $\mathrm{(ColH)_4(PyEt)[Mo_4O_8(C_4O_4)_4]Br}$ 2b. The tetranuclear anion of **2a** and **2b**, shown in Fig. 2, consists of a $\{\mathrm{Mo_4O_4(\mu_3\text{-}O)_4}\}^{4+}$ core, a compact association of two $\{\mathrm{Mo_2O_4}\}^{2+}$ units. Four metal centres and four μ_3-bridging oxo groups define the vertices of a highly distorted cube (Fig. 2(a)). The arrangement of metal centres or μ_3-oxo groups is that of a distorted tetrahedron, elongated along its twofold axis. Selected

Table 4 Bond lengths (Å) and angles (°) of $[Mo_4O_8(C_4O_4)_4]^{4-}$ in **2a**

Mo(1)–O(1)	1.677(2)	Mo(3)–O(3)	1.672(2)
Mo(1)–O(5)	1.968(2)	Mo(3)–O(7)	1.983(2)
Mo(1)–O(6)	1.971(2)	Mo(3)–O(8)	1.980(2)
Mo(1)–O(7)	2.354(2)	Mo(3)–O(5)	2.429(2)
Mo(1)–O(132)	2.067(2)	Mo(3)–O(131)	2.030(2)
Mo(1)–O(142)	2.052(2)	Mo(3)–O(232)	2.034(2)
Mo(1)–Mo(2)	2.5904(4)	Mo(3)–Mo(4)	2.5932(4)
Mo(2)–O(2)	1.676(2)	Mo(4)–O(4)	1.673(2)
Mo(2)–O(5)	1.971(2)	Mo(4)–O(7)	1.978(2)
Mo(2)–O(6)	1.973(2)	Mo(4)–O(8)	1.978(2)
Mo(2)–O(8)	2.343(2)	Mo(4)–O(6)	2.379(2)
Mo(2)–O(231)	2.059(2)	Mo(4)–O(141)	2.051(2)
Mo(2)–O(242)	2.055(2)	Mo(4)–O(241)	2.050(2)
O(5)–Mo(1)–O(6)	90.60(8)	O(7)–Mo(3)–O(8)	89.12(9)
O(5)–Mo(2)–O(6)	90.45(8)	O(7)–Mo(4)–O(8)	89.35(8)
Mo(1)–O(5)–Mo(2)	82.22(8)	Mo(3)–O(7)–Mo(4)	81.78(8)
Mo(1)–O(5)–Mo(3)	102.42(9)	Mo(3)–O(7)–Mo(1)	104.62(9)
Mo(2)–O(5)–Mo(3)	102.42(9)	Mo(4)–O(7)–Mo(1)	103.80(9)
Mo(1)–O(6)–Mo(2)	82.11(8)	Mo(3)–O(8)–Mo(4)	81.85(8)
Mo(1)–O(6)–Mo(4)	103.14(9)	Mo(3)–O(8)–Mo(2)	105.25(9)
Mo(2)–O(6)–Mo(4)	103.16(9)	Mo(4)–O(8)–Mo(2)	104.30(9)

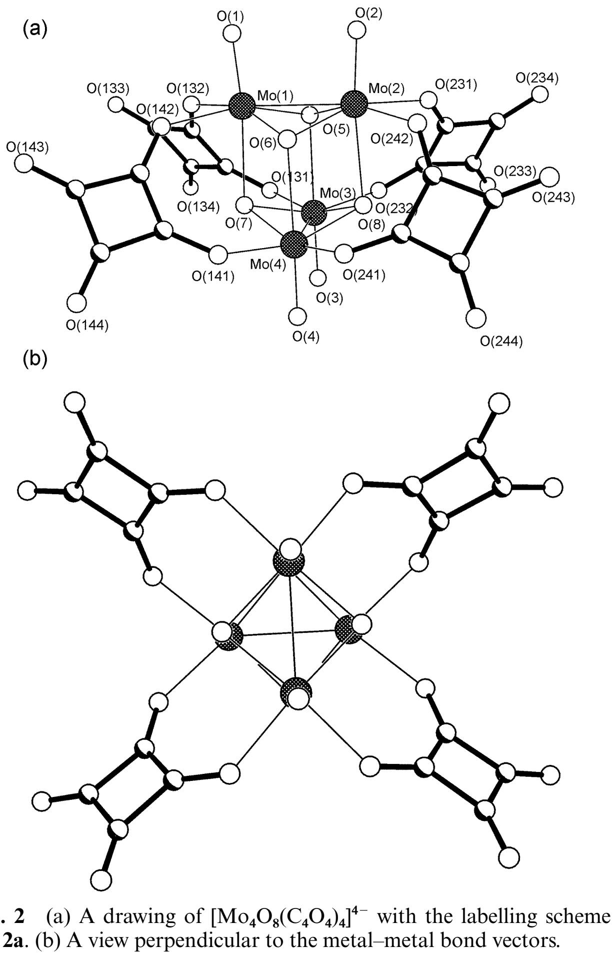

Fig. 2 (a) A drawing of $[Mo_4O_8(C_4O_4)_4]^{4-}$ with the labelling scheme for **2a**. (b) A view perpendicular to the metal–metal bond vectors.

bond distances and angles are given in Tables 4 and 5. The geometric parameters of the tetranuclear anions in **2a** and **2b** do not differ significantly. An octahedral coordination environment of each molybdenum atom consists of six oxygen atoms: a terminal oxo group at an average distance of 1.675 Å, a pair of μ_3-oxo groups at shorter distances, 1.976 Å, a μ_3-oxo group at a longer distance, 2.375 Å, and two squarate oxygen atoms at 2.030(2)–2.067(2) Å for **2a** and 2.0446(18)–2.0615(18) Å for **2b**, each from a different squarate. The lengthening of the bond to the μ_3-oxo group finds its origin in the *trans* influence of the terminal oxo group. The distances between metal atoms are of two types: (i) short ones, 2.5904(4) and 2.5932(4) Å for **2a** and 2.5947(4) and 2.6036(4) Å for **2b**, which occur between molybdenum atoms within the $\{Mo_2O_4\}^{2+}$ units and, (ii) longer ones in the range 3.4167(4)–3.4421(4) Å for **2a** and 3.4292(3)–3.4304(3) Å for **2b**, which occur between molybdenum atoms from neighbouring $\{Mo_2O_4\}^{2+}$ units. Of the six cube faces, four provide binding sites for the squarato ligands. Each squarate binds as a μ_2-1,2-bis(monodentate) ligand to a pair of non-bonded molybdenum atoms, spanning an average distance of 3.43 Å, which is significantly longer than in compounds **1a**, **1b** and **1c**. The virtual symmetry of the tetranuclear anion is C_{2v}. The anion in **2b** has crystallographically imposed symmetry plane which passes through a pair of molybdenum atoms from one dinuclear subunit and bridging oxo groups from the other. The association of two dinuclear units to form the cube-like $\{Mo_4O_4(\mu_3\text{-}O)_4\}^{4+}$ core induces stress upon their internal geometry (Table 6). The values of fold angles, 133.84(6) and 138.02(6)° for **2a**, 136.00(9) and 136.25(11)° for **2b**, are *ca.* 10° smaller than usually observed.[6] With a smaller fold angle a pair of metal atoms should be brought into a closer proximity. However, several factors contribute to the resulting metal–metal bond distance. The internal angles of the $Mo_2(O_b)_2$ rhombus (O_b denotes bridging oxygen atoms in the $\{Mo_2O_4\}^{2+}$ unit), in particular the O_b–Mo–O_b angles, are also subject to changes induced upon the association. The contraction of the O_b–Mo–O_b angles in the anions of **2a** and **2b** counterweighs the effect the smaller fold angle would have upon the metal–metal bond distance. Table 6 lists geometric parameters of another tetranuclear core, $\{Mo_4O_4(\mu_3\text{-}O)_2(\mu_2\text{-}O)_2(\mu_2\text{-}OMe)_2\}^{2+}$ (Fig. 3(b)), observed in $[Mo_4O_8(OMe)_2Cl_2(Py)_4]\cdot CH_3CN$ **3** and which will be discussed presently. Although the changes in the internal geometry of the constituent dinuclear units in the latter are of opposite sign, the metal–metal bond length is found to be similar to those in **2a** and **2b**.

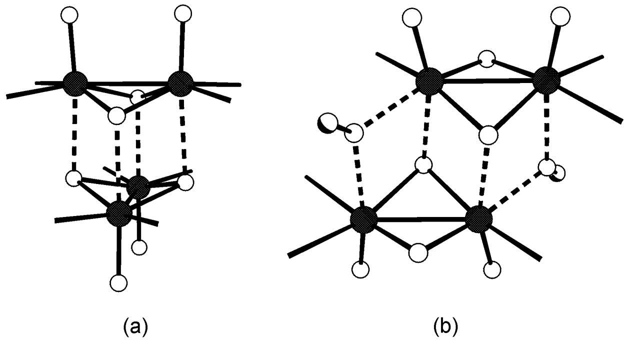
(a) (b)

Fig. 3 The association of two $\{Mo_2O_4\}^{2+}$ units into (a) a cube-like $\{Mo_4O_4(\mu_3\text{-}O)_4\}^{4+}$ and (b) a rhombic $\{Mo_4O_4(\mu_3\text{-}O)_2(\mu_2\text{-}O)_2(\mu_2\text{-}OMe)_2\}^{2+}$ core. The constituent dinuclear units are drawn in bold lines.

The bond pattern in the squarates is the same as observed in **1a**, **1b** and **1c**, revealing pairs of “ketonic” C–O bonds and the largest double bond character in the C–C bonds nearest to the coordinating oxygen atoms.

The countercations in **2a** are *N*-methylated collidine molecules. The crystal structure of **2a** also contains solvent molecules of 2,4,6-collidine and methanol linked by hydrogen bonds, N(1) ··· O(9) 2.800(5) and N(6) ··· O(10) 2.785(5) Å. The crystal structure of **2b** contains apart from the tetranuclear anions, another anionic species, bromide, and two types of cations, protonated collidine and *N*-ethylated pyridine molecules. Relatively strong hydrogen bonds occur between protonated collidine and carbonyl group from the squarate, N(1) ··· $O(134)^i$ 2.751(3) Å ((i) symmetry code: $-x + 1$, $-y + 1$, $-z + 1$). Bromine forms hydrogen bonds in a bifurcated manner with a pair of protonated collidine molecules related through symmetry, x, $-y + 1.5$, z. The corresponding Br ··· N(2) distances are 3.267(2) Å.

The $\{Mo_4O_4(\mu_3\text{-}O)_4\}^{4+}$ cubes were observed before in three neutral, discrete complexes, $[Mo_4O_8(OSPMe_2)_4]$,[34] $[Mo_4O_8$-

Table 5 Bond lengths (Å) and angles (°) of $[Mo_4O_8(C_4O_4)_4]^{4-}$ in **2b**

Mo(1)–O(1)	1.675(2)	Mo(3)–O(3)	1.6762(18)
Mo(1)–O(6)	1.9743(18)	Mo(3)–O(4)	1.9766(18)
Mo(1)–O(6)[a]	1.9743(18)	Mo(3)–O(5)	1.9788(19)
Mo(1)–O(4)	2.386(2)	Mo(3)–O(6)	2.3769(17)
Mo(1)–O(132)	2.0550(18)	Mo(3)–O(232)	2.0615(18)
Mo(1)–O(132)[a]	2.0550(18)	Mo(3)–O(131)	2.0446(18)
Mo(1)–Mo(2)	2.5947(4)	Mo(3)–Mo(3)[a]	2.6036(4)
Mo(2)–O(2)	1.676(2)		
Mo(2)–O(6)	1.9800(18)		
Mo(2)–O(6)[a]	1.9800(18)		
Mo(2)–O(5)	2.358(2)		
Mo(2)–O(231)	2.0486(18)		
Mo(2)–O(231)[a]	2.0486(18)		
O(6)–Mo(1)–O(6)[a]	90.17(10)	O(4)–Mo(3)–O(5)	89.54(8)
O(6)–Mo(2)–O(6)[a]	89.84(10)	O(4)–Mo(3)[a]–O(5)	89.54(8)
Mo(1)–O(6)–Mo(2)	82.02(7)	Mo(3)–O(4)–Mo(3)[a]	82.39(9)
Mo(1)–O(6)–Mo(3)	103.68(7)	Mo(3)–O(4)–Mo(1)	103.30(9)
Mo(2)–O(6)–Mo(3)	103.45(7)	Mo(3)[a]–O(4)–Mo(1)	103.30(9)
		Mo(3)–O(5)–Mo(3)[a]	82.28(9)
		Mo(3)–O(5)–Mo(2)	104.16(9)
		Mo(3)[a]–O(5)–Mo(2)	104.16(9)

[a] Related through symmetry: x, $-y + 1.5$, z.

Table 6 Internal dimensions (Å, °) of $\{Mo_2O_4\}^{2+}$ units in a dinuclear species and two types of tetranuclear cores, $\{Mo_4O_4(\mu_3\text{-}O)_2(\mu_2\text{-}O)_2(\mu_2\text{-}OMe)_2\}^{2+}$ in **3** and $\{Mo_4O_4(\mu_3\text{-}O)_4\}^{4+}$ in **2a** and **2b**

	Mo–Mo	Fold angle[a]	Mo–O_b–Mo	O_b–Mo–O_b	Ref.
$[Mo_2O_4Cl_2(4\text{-}EtPy)_4]$[b]	2.5489(5)	144.51(14)	82.29(9), 82.68(10)	92.29(10), 92.50(10)	7
3[c]	2.5854(4)	149.60(13)	80.73(8), 84.28(9)	93.45(9), 94.14(9)	This work
2a	2.5904(4)	138.02(6)	82.11(8), 82.22(8)	90.45(8), 90.60(8)	This work
	2.5932(4)	133.84(6)	81.78(8), 81.85(8)	89.12(9), 89.35(8)	
2b	2.5947(4)	136.25(11)	82.02(7)	89.84(10), 90.17(10)	This work
	2.6036(4)	136.00(9)	82.28(9), 82.39(9)	89.54(8)	

[a] Defined as dihedral angle between two $Mo(O_b)_2$ planes where O_b denotes bridging oxygen atoms in $\{Mo_2O_4\}^{2+}$. New notation is employed because in the tetranuclear cores one or both of these oxygen atoms make bonding interactions to the third metal atom. [b] A dinuclear molecule where chloro and 4-ethylpyridine (4-EtPy) ligands occupy the available sites in the $\{Mo_2O_4\}^{2+}$ unit. [c] See text for the description of its structure.

$(O_2PPh_2)_4]$,[35] $[Mo_4O_8(OSiMe_3)_4(HNMe_2)_4]$,[36] and the aforementioned polymeric phosphomolybdates(V).[16,17] The phosphate and its derivatives coordinate to the metal oxide cubes in the same way as the squarates in **2a** and **2b**: through two oxygen atoms to a pair of metal atoms which belong to two different $\{Mo_2O_4\}^{2+}$ units. However, the phosphate can coordinate with the remaining two oxygen atoms to another cube. When two out of four coordinated phosphates serve as linkages between adjacent cubes, an infinite chain is formed, exemplified by $[Mo_4O_8(PO_4)(H_{1.5}PO_4)_2]_n{}^{2n-}$.[16] When each of the four phosphates is shared between pairs of adjacent metal oxide cubes, a two-dimensional layered structure is obtained, exemplified by $[Mo_4O_8(PO_4)_2]_n{}^{2n-}$.[17] Derivatized phosphates, diphenylphosphate in $[Mo_4O_8(O_2PPh_2)_4]$,[35] and dimethylthiophosphate in $[Mo_4O_8(OSPMe_2)_4]$,[34] possess only two binding sites, so discrete, molecular structures are formed. $[Mo_4O_8(OSiMe_3)_4(HNMe_2)_4]$ is the only example so far with monodentate ligands attached to the periphery of the metal oxide core.[36]

Some general comments on squarate ligation

In the light of the rich coordination chemistry of $\{Mo_2O_4\}^{2+}$ compounds surprisingly few squarato complexes are known. Of the three structurally characterized molybdenum(V) complexes, one, $[Mo_2O_3Cl_3(C_4O_4)_2]^{3-}$, does not possess the $\{Mo_2O_4\}^{2+}$ core, instead a pair of molybdenum atoms at a distance of 3.46 Å is bridged by four ligands: a chloride, an oxo group and two squarates.[28] The other two, $[Mo_4O_8(OH)_2(H_2O)_2(C_4O_4)_2]^{2-}$,[29] and $[Mo_4O_8(OMe)_2(C_4O_4)_2(HC_4O_4)_2]^{4-}$,[30] both possess a well-known $\{Mo_4O_4(\mu_3\text{-}O)_2(\mu_2\text{-}O)_2(\mu_2\text{-}OR)_2\}^{2+}$ (R = H, Me) core with the squarato ligands attached to its periphery. Similarly to **2a** and **2b**, the squarate binds with two of its oxygen atoms to a pair of molybdenum atoms from neighbouring $\{Mo_2O_4\}^{2+}$ units, spanning distances of *ca.* 3.4 Å between the metal centres. $[Mo_4O_8(OMe)_2(C_4O_4)_2(HC_4O_4)_2]^{4-}$ contains another type of the squarato ligand, hydrogensquarate which is bound as a terminal monodentate ligand. Other binding modes where the squarate engages all four oxygen atoms in interactions with metal centres were observed among molybdenum(VI) complexes. A tetramonodentate binding mode occurs in $[Mo_4O_{10}F_6(C_4O_4)]^{4-}$,[28] while the squarates in $[Mo_{12}O_{36}(HC_4O_4)_4]^{4-}$ function as μ_6-ligands.[37]

In spite of the apparent structural similarity with the oxalate, the frequently encountered bidentate or bisbidentate coordination modes of the oxalate have not been found for the squarato complexes with the first- and second-row transition metal ions. Their absence has been explained by the large value of bite parameter in the squarate.[19] 1,2-chelation took place with a related ligand, a dianion of 1,2-dithiosquaric acid, shown by $[Mo_2O_2(\mu_2\text{-}O)(\mu_2\text{-}S)(C_4O_2S_2)_2]^{2-}$.[38] Substituting oxygen atom for sulfur, which is larger, yields a ligand capable of coordination in a bidentate manner. It has been shown by a series of structurally related species, trinuclear $[Mo^{VI}{}_3O_8(OMe)L_2]^{3-}$,[39] dinuclear $[Mo^{VI}{}_2(OR)_2(NNPh)_4L_2]^{2-}$ and tetranuclear $[Mo^{V}{}_4O_8(OMe)_2L_2(HL)_2]^{4-}$,[30] (where L = $C_4O_4{}^{2-}$ or $MoO_4{}^{2-}$, and HL = $HC_4O_4{}^{-}$ or $HMoO_4{}^{-}$) that the squarate functions more as the analogue of tetraoxomolybdate(VI). Furthermore, the direct replacement of tetraoxomolybdate(VI) with the squarate proceeded in all without concomitant structural rearrangements.

Synthetic considerations

Mononuclear oxohalomolybdates(V) prove to be auspicious starting materials for the synthesis of new polyoxomolybdates. In the course of their reaction with alcohol solutions of pyridines, a rapid exchange of halides by the oxygen donor ligands is followed by dimerization reactions.[7,40] Each molybdenum atom in the $\{Mo_2O_4\}^{2+}$ unit has three available sites for the coordination. Provided the reaction medium contains suitable ligands, these coordinate, while in their absence the self-assembly of $\{Mo_2O_4\}^{2+}$ units takes place. In the case of **1a**, **1b** and **1c**, the squarate as μ_2-1,2-bis(monodentate) ligand occupies one site in each metal's environment, the remaining two sites are occupied with pyridine or 3,5-lutidine, which are present in huge excess. Increasing the amount of the squarate, as when the ligand to the metal ratio is raised to over 4, *vide supra* the preparation of **1b** or **1c** (*Procedure b*), does not change the reaction outcome. Reducing the amount of the squarate, *vide supra* the preparation of **3**, fails to produce the anticipated polymeric phase, instead a tetranuclear $[Mo_4O_8(OMe)_2Cl_2(Py)_4]\cdot CH_3CN$ **3** is formed. Apparently, with a smaller amount of the squarate, the self-assembly of $\{Mo_2O_4\}^{2+}$ units through shared bridging oxo groups prevails. One of the two bridging oxo groups in each dinuclear unit coordinates to the metal of the other dinuclear unit, whereupon it becomes a μ_3-ligand. With the agency of two bridging methoxide ions a well-known, centrosymmetric $\{Mo_4O_4(\mu_3\text{-}O)_2(\mu_2\text{-}O)_2(\mu_2\text{-}OMe)_2\}^{2+}$ core with a rhombic, planar arrangement of molybdenum atoms is formed (Fig. 3(b)).[6] Its six terminal positions are distributed among four pyridine and two chloro ligands. When the reaction is run in the solvent with a low-coordinating ability, *i.e.*, in 2,4,6-collidine with bulky methyl substituents in *ortho* positions in the case of **2a** and **2b**, the self-assembly of $\{Mo_2O_4\}^{2+}$ units takes place again, yet in a different way. Although the amount of the squarate is sufficient for the ligand itself to occupy the available coordination sites in the $\{Mo_2O_4\}^{2+}$ unit, pairs of $\{Mo_2O_4\}^{2+}$ units associate into cube-like $\{Mo_4O_4(\mu_3\text{-}O)_4\}^{4+}$ cores (Fig. 3(a)). A description of the association is similar to the one just given, the main difference being that all bridging oxygen atoms change to μ_3-ligands. It is of interest to note that no additional ligands assist in the association. A question arises which factors favour the formation of each of the two tetranuclear cores. It was previously established that the ability of the alkoxide ligands to participate in bridging interactions is responsible for the formation of the $\{Mo_4O_4(\mu_3\text{-}O)_2(\mu_2\text{-}O)_2(\mu_2\text{-}OR)_2\}^{2+}$ core.[36] The amount of the alkoxide ions depends upon the extent of protolytic equilibrium between alcohol and pyridine. With the greater basicity of 2,4,6-collidine relative to pyridine, the latter reaction is more favourable in the case of 2,4,6-collidine, suggesting a tetranuclear compound with the rhombic $\{Mo_4O_4(\mu_3\text{-}O)_2(\mu_2\text{-}O)_2(\mu_2\text{-}OR)_2\}^{2+}$ core as the more likely product. The products obtained, **2a** and **2b**, are not in accord with the above arguments. It appears that the extreme reaction conditions, elevated temperature and prolonged reaction times, favour more the formation of a cube-like $\{Mo_4O_4(\mu_3\text{-}O)_4\}^{4+}$ core. Once the $\{Mo_4O_4(\mu_3\text{-}O)_4\}^{4+}$ core is formed, the squarates coordinate in the usual manner, as μ_2-1,2-bis(monodentate) ligands to its periphery. The coordination sphere of each molybdenum in **2a** and **2b** contains two squarate oxygen atoms, while in **1a**, **1b** and **1c** only one. A "forced" coordination of more than one multidentate ligand to the metal has been already achieved with the oxalate.[18] With no other ligand available but the oxalate, *i.e.*, the reaction medium was also 2,4,6-collidine, rather than adopting a binding mode other than bidentate, a different dinuclear species formed, $\{Mo_2O_2(\mu_2\text{-}O)\}^{4+}$ with four coordination sites per each metal. These were eventually occupied by a pair of bidentate oxalates producing $[Mo_2O_3(\eta^2\text{-}C_2O_4)_4]^{4-}$. The preferential binding modes of the ligands, μ_2-1,2-bis(monodentate) for the squarate and bidentate for the oxalate, coupled with large amounts of the ligands, prove to have a determining influence over the identity of the resulting oxomolybdenum species.

Both compounds with the novel $[Mo_4O_8(C_4O_4)_4]^{4-}$ anions contain *N*-alkylated aromatic molecules, **2a** *N*-methylated 2,4,6-collidine and **2b** *N*-ethylated pyridine, which were generated inadvertently. Their formation is not surprising in view of the previous work.[14,41] Likewise, pyridine *N*-methylation with methanol took place in the presence of oxalic acid at elevated temperature. The current study shows that alkylation proceeds also when squaric acid is used. Moreover, the *N*-ethylated pyridine in **2b** proves the alkylation reaction to be a general one and that it can be applied to other alcohols.

Vibrational spectroscopy

The characteristic absorptions for the squarato ligand are: (i) ν(C=O) vibration which occurs as a band of medium intensity at 1810–1790 cm^{-1}, (ii) ν(C=C) as a strong band at 1690–1630 cm^{-1}, and (iii) the strongly coupled ν(C–C) and ν(C–O) vibrations as a single, intense band at 1560–1470 cm^{-1}.[28,42] The corresponding bands for **1a** are found at 1787, 1660 and 1519 cm^{-1}, for **1c** at 1786, 1673 and 1524 cm^{-1} and for **2b** at 1799, 1670 and 1542 cm^{-1}. Similarly, the μ_2-1,2-bis(monodentate) squarate in $(Et_3N)_3[Mo_2O_3Cl_3(C_4O_4)_2]$ absorbs at 1793, 1674 and 1522 cm^{-1}.[28]

A pair of strong bands at 945 and 928 cm^{-1} for **1a** and at 953 and 927 cm^{-1} for **1c** is associated with the ν(Mo=O) vibrations. A single band at 968 cm^{-1} is displayed in the spectrum of **2b**.

Acknowledgements

We are grateful to the Slovenian Ministry of Education, Science and Sport for supporting this work through research grants PS-0508-0103 and SLO-US-2001/15. We also thank the same agency for funds to purchase the Nonius Kappa CCD diffractometer. The work at Syracuse University was supported by a grant from the National Science Foundation, CHE0242153.

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