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Hydrogen-Bonding in Two Pyridinium Salts of $[Mo_2O_4Cl_4(\mu_2\text{-dmsH})]^{3-}$ Complex (dmsH$^-$ = a Half-Neutralized Form of 2,2-Dimethylsuccinic Acid)

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Abstract: Reactions of a mononuclear molybdenum(V) starting material, $(PyH)_5[MoOCl_4(H_2O)]_3Cl_2$, with 2,2-dimethylsuccinic acid in the presence of base afforded two products, $(PyH)_3[Mo_2O_4Cl_4(\mu_2\text{-dmsH})]\cdot1/2CH_3CN$ (**1**) and $(PyH)_4[Mo_2O_4Cl_4(\mu_2\text{-dmsH})]Cl$ (**2**). As revealed by the X-ray structure analysis, the half-neutralized form of the dicarboxylic acid, the dmsH$^-$ ion, coordinated to the well-known $\{Mo_2O_4\}^{2+}$ core in the *syn-syn* bidentate bridging manner. In both compounds, the non-ionized terminus of the ligand, the COOH function, participated in hydrogen-bonding interactions. The incorporation of the chloride counteranion in **2**, prevented the formation of the common "carboxylic acid dimer" which was observed for **1**. Instead, a hydrogen-bonded linkage of the COOH function with the chloride occurred.

Keywords: molybdenum; $\{Mo_2O_4\}^{2+}$ core; carboxylate complexes; hydrogen-bonding; carboxylic acid dimer

1. Introduction

The singly metal−metal bonded $\{Mo_2(\mu_2\text{-O})_2O_2\}^{2+}$ structural fragment, shortly denoted as $\{Mo_2O_4\}^{2+}$, pervades the chemistry of molybdenum(V) [1–4]. Its ability to retain its structural integrity upon coordination of various ligands to its peripheral sites makes it a suitable candidate for the construction of metal-organic frameworks. The designed synthesis of such compounds has been an area of active research over the past two decades [5]. For example, the appropriately designed Mo_2^{4+} dimetal units served as preformed molecular building blocks in the formation of higher order structures [6–8].

We hoped that the combination of the $\{Mo_2O_4\}^{2+}$ building blocks with multidentate ligands such as di- or tricarboxylates would under favourable conditions result either in discrete clusters or polymeric materials. Our goal was realized by the reaction system of a mononuclear molybdenum(V) starting material, $(PyH)_5[MoOCl_4(H_2O)]_3Cl_2$, and 1,3,5-benzenetricarboxylic acid. In the presence of a weak base, pyridine, a dinuclear anionic complex $(PyH)_4[Mo_2O_4Cl_4(\mu_2\text{-}btcH_2)]Cl$ and a tetranuclear neutral complex $[\{Mo_2O_4(Py)_3\}_2(\mu_3\text{-}btcH)_2]\cdot6Py$ (where PyH^+ is pyridinium cation, whereas $btcH_2^-$ and $btcH^{2-}$ stand for anionic forms of the acid with one or two ionized functions, respectively) were prepared [9]. Only the ionized functions of the acid were seen to participate in bonding interactions with the metal atoms. In both compounds, a carboxylate function coordinated to the $\{Mo_2O_4\}^{2+}$ core in a *syn-syn* bidentate bridging manner with the carboxylate oxygens occupying the positions which were *trans* to the terminal oxides (Figure 1). The carboxylate ligand of $[\{Mo_2O_4(Py)_3\}_2(\mu_3\text{-}btcH)_2]\cdot6Py$ possessed another ionized function which employed a different binding mode: it coordinated in a monodentate manner to a metal ion in an adjacent dinuclear unit and a discrete tetranuclear cluster formed. Since the reaction outcome depends upon the number of the ionized functions in the acid, other bases apart from pyridine were used. At first, reactions of an acid with two carboxylic groups, 2,2-dimethylsuccinic acid, hereafter designated as $dmsH_2$, were investigated. The structural formula of the acid is shown in Figure 2. Following similar procedures to those employed with 1,3,5-benzentricarboxylic acid, the reactions with $dmsH_2$ in the presence of triethylamine or tetrabutylammonium hydroxide afforded two products, $(PyH)_3[Mo_2O_4Cl_4(\mu_2\text{-}dmsH)]\cdot1/2CH_3CN$ (**1**) and $(PyH)_4[Mo_2O_4Cl_4(\mu_2\text{-}dmsH)]Cl$ (**2**). Herein, their solid state structures are presented with the emphasis on the differences in the intermolecular interactions.

Figure 1. A typical coordination of the carboxylate ligand to the $\{Mo_2O_4\}^{2+}$ structural core.
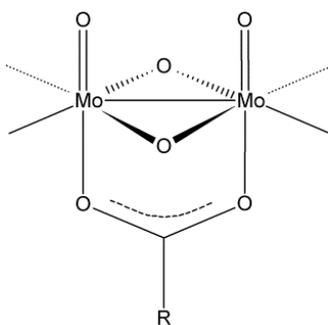
Figure 2. A molecular formula of 2,2-dimethylsuccinic acid, $dmsH_2$.
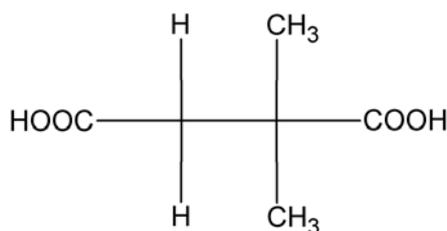
2. Results and Discussion

2.1. Solid State Structures

The X-ray structure analysis revealed that compounds **1** and **2** are pyridinium salts of the $[Mo_2O_4Cl_4(\mu_2\text{-dmsH})]^{3-}$ complex anion. A dinuclear $[Mo_2O_4Cl_4(\mu_2\text{-dmsH})]^{3-}$ ion of **2**, depicted in Figure 3, occupies a general position within the unit cell of the monoclinic space group $P\,2_1/n$. Four protonated pyridinium cations and a chloride counteranion are associated with each dinuclear anion. Compound **1** crystallizes in the same space group. Its composition is different: the asymmetric unit contains two $[Mo_2O_4Cl_4(\mu_2\text{-dmsH})]^{3-}$ complex anions, six pyridinium cations and an acetonitrile solvent molecule.

Figure 3. ORTEP drawing of $[Mo_2O_4Cl_4(\mu_2\text{-dmsH})]^{3-}$, the anionic part of **2**. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms are shown as spheres of arbitrary radii.
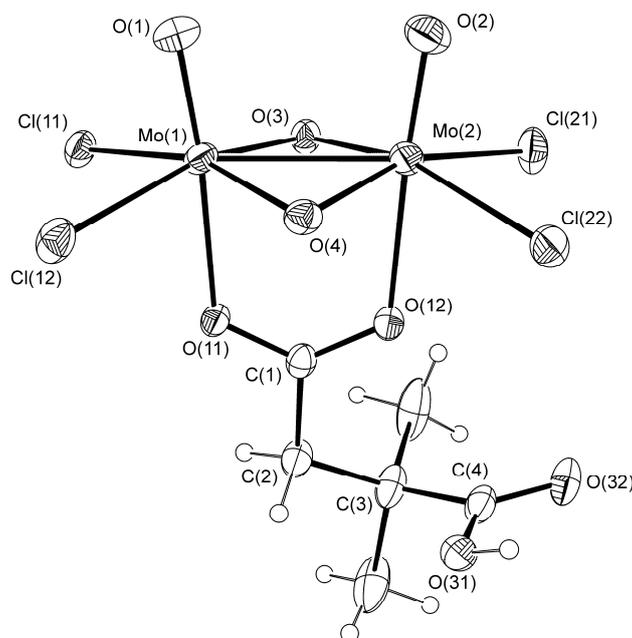
The geometric properties of the $[Mo_2O_4Cl_4(\mu_2\text{-dmsH})]^{3-}$ anions of **1** and **2** do not show significant differences (see Table 1). The overall features of the $\{Mo_2O_4\}^{2+}$ cores in the $[Mo_2O_4Cl_4(\mu_2\text{-dmsH})]^{3-}$ anions are non-exceptional: (i) a short distance between a pair of molybdenum atoms, 2.5713(4) and 2.5827(4) Å in **1** and 2.5929(7) Å in **2**, and (ii) a non-planar $Mo(\mu_2\text{-O})_2Mo$ rhombus whose deviation from planarity is given by a dihedral angle between two $Mo(\mu_2\text{-O})_2$ planes. The latter angle is known also as a fold angle. The larger the fold angle, the more planar moiety. The fold angles in compounds **1** and **2** fall in the interval of values observed for other $\{Mo_2O_4\}^{2+}$ complexes with the carboxylate serving as a third bridging ligand. Geometric parameters of a series of such complexes are summarized in Table 2. The series displays with no exception larger fold angles than the $\{Mo_2O_4\}^{2+}$ complexes without a third bridging ligand. For example, in a dinuclear $[Mo_2O_4Cl_4(MeOH)_2]^{2-}$ anion an angle of 146.0(1)° was observed [10]. Nevertheless, the puckering of the $Mo(\mu_2\text{-O})_2Mo$ moiety is a means of allowing a close approach of the metal atoms [11]. Therefore a somewhat more flattened $Mo(\mu_2\text{-O})_2Mo$

moiety in **2** is accompanied by a longer metal−metal bond length. A distorted octahedral coordination of each metal center of the $\{Mo_2O_4\}^{2+}$ core in the complex anions of **1** and **2** is completed by a pair of chlorides and an oxygen from the carboxylate group. In both compounds, the dmsH⁻ ion, an anionic form of the parent acid with one ionized COOH function, is bound to the metal ions of the $\{Mo_2O_4\}^{2+}$ core in a *syn-syn* bidentate bridging manner. The carboxylate group occupies a pair of *trans* positions relative to the Mo=O bonds and is, therefore, subjected to their well-documented *trans* influence [12]. The molybdenum-to-the-carboxylate bond lengths listed in Table 2 are seen to span a wide range. Furthermore, in some complexes a non-equivalence in the pair of molybdenum-to-the-carboxylate bond lengths is displayed. In the case of $[Mo_2O_4Cl_4(\mu_2\text{-}dmsH)]^{3-}$ anions, a more pronounced asymmetry in the carboxylate coordination occurs only for one of the two complex anions in the asymmetric unit of **1**. The corresponding bond distances are 2.286(2) *vs.* 2.344(2) Å. In this case, the asymmetry can be traced also to the involvement of the particular carboxylate oxygen in another bonding interaction, *i.e.*, a hydrogen bond with pyridinium cation. It is to be noted that the main difference in the two complex anions of the asymmetric unit in **1** is in the relative orientation of the dmsH⁻ ligand [13]. The similarities and the differences can be seen in Figure 4 which shows an overlay of the two complex anions.

Table 1. Relevant bonding parameters (Å, deg) of $[Mo_2O_4Cl_4(\mu_2\text{-}dmsH)]^{3-}$ ions in **1** and **2**.

Bond	**1**[a]		**2**
Mo–Mo	2.5827(4)	2.5713(4)	2.5929(7)
Fold angle[b]	157.9(1)	156.6(1)	160.7(3)
Mo–Cl	2.4407(9)−2.4718(9)	2.4522(9)−2.4722(9)	2.438(2)−2.472(2)
Mo–O(carboxylate)	2.286(2), 2.344(2)	2.324(2), 2.366(2)	2.236(4), 2.287(4)
C–O(carboxylate)	1.258(4), 1.288(4)	1.255(4), 1.275(4)	1.265(6), 1.271(6)
C–O(COOH)	1.254(4), 1.293(4)	1.245(4), 1.291(4)	1.223(7), 1.312(8)

[a] Two sets of parameters, one for each complex anion in the asymmetric unit; [b] Defined as a dihedral angle between two $Mo(\mu_2\text{-}O)_2$ planes.

Table 2. Dimensions (Å, deg) of $\{Mo_2O_4\}^{2+}$ units in carboxylate complexes.

Species	L[a]	Mo–O(L)	Mo–Mo	Fold angle	Ref.
1	dmsH⁻	2.286(2), 2.344(2)	2.5827(4)	157.9(1)	-
		2.324(2), 2.366(2)	2.5713(4)	156.6(1)	
2	dmsH⁻	2.236(4), 2.287(4)	2.5929(7)	160.7(3)	-
$[Mo_2O_4Cl_4(\mu_2\text{-}OOCCH_3)]^{3-}$	acetate	2.354(1), 2.366(1)	2.5727(2)	157.01(9)	[14]
$[Mo_2O_4Cl_4(\mu_2\text{-}Hmal)]^{3-}$	Hmal⁻	2.330(2), 2.357(2)	2.5859(3)	160.08(5)	[15]
$[Mo_2O_4Cl_4(\mu_2\text{-}Hmale)]^{3-b}$	Hmale⁻	2.380(2), 2.438(2)	2.5916(3)	156.49(9)	[16]
		2.371(2), 2.377(2)	2.5951(3)	158.3(1)	
$[Mo_2O_4Cl_4(\mu_2\text{-}btcH_2)]^{3-}$	btcH₂⁻	2.269(2), 2.281(2)	2.5962(4)	159.85(5)	[9]

[a] In all, the carboxylate ligand L is coordinated in a bidentate bridging manner to a pair of *trans* sites in the $\{Mo_2O_4\}^{2+}$ unit. Abbreviations used: Hmal⁻ = hydrogen malonate, Hmale⁻ = hydrogen maleate, btcH₂⁻ = an anion of 1,3,5-benzenetricarboxylic acid with one ionized function; [b] Two sets of parameters, one for each complex anion in the asymmetric unit.

Figure 4. An overlay of the crystallographically independent complex anions in **1**.
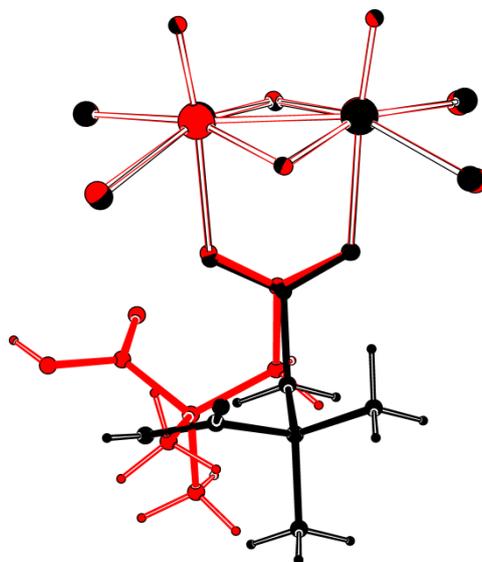
In both compounds, the non-ionized COOH termini of the dmsH⁻ ligands participate in hydrogen-bonding. Illustrations of hydrogen bonds and packing diagrams for **1** and **2** are given in Figures 5−8. For neither compound could the positions of the carboxylic hydrogen atoms be located from the electron density maps. The sites of protonation were thus established from the hydrogen-bonding pattern. In the case of **2**, a non-equivalent pattern of C−O bond lengths within the COOH function corroborates the formulation. Lists of hydrogen bonds in **1** and **2** are provided in Tables 3 and 4. In **1**, the COOH group of one $[Mo_2O_4Cl_4(\mu_2\text{-dmsH})]^{3-}$ ion is linked with the agency of two O–H···O hydrogen bonds with the COOH group of another complex ion (Table 3). The corresponding O···O distances, 2.609(3) and 2.630(3) Å, are significantly shorter than the sum of the van der Waals radii, 3.04 Å [17]. Such a linkage, known also as a "carboxylic acid dimer" and is illustrated in Figure 9, is a dominant recognition motif in the structures of carboxylic acids [18]. As will be shown presently, the molybdenum(V) complexes with multicarboxylate ligands which possess at least one non-ionized COOH function reveal several other connectivity patterns. The explanation for a displayed diversity lies in the presence of structural entities which can participate in interactions with the COOH entity. Typically, these are pyridine solvent molecules and chloride counteranions. The outcome of the unavoidable competition between the several hydrogen bond donors and acceptors is unpredictable. Compound **2** exemplifies the case when the incorporation of the chloride counteranion into the structure interferes with the formation of the carboxylic acid dimer. In **2**, the COOH function is engaged in a hydrogen bond with chloride, $O(31)\cdots Cl(5)^{iii} = 3.044(4)$ Å [(iii) symmetry code: $x + 0.5$, $-y + 0.5$, $z + 0.5$] which forms another hydrogen bond of a comparable length with protonated pyridine, *i.e.*, $N(3)^{iii}\cdots Cl(5)^{iii} = 3.047(5)$ Å (Table 4). The other three pyridinium cations in **2** interact with the μ_2-oxides of the $\{Mo_2O_4\}^{2+}$ core. The resulting N···O contacts are in the 2.620(8)−2.807(7) Å range. This type of hydrogen-bonding appears as a recurrent structural motif among the anionic $\{Mo_2O_4\}^{2+}$ complexes with protonated pyridine molecules as countercations [10]. Similarly, four out of six pyridinium cations in the asymmetric unit of **1**, participate in the same type of the interaction, whereas the remaining two cations form hydrogen bonds with the carboxylate oxygens.

Figure 5. Hydrogen-bonding pattern in **1**. (**a**) O–H···O bonds link two $[Mo_2O_4Cl_4(\mu_2\text{-dmsH})]^{3-}$ ions into a dimer. Molybdenum atoms are drawn as large cross-hatched circles, chlorine atoms as large striped spheres, oxygen and carbon atoms as medium-sized open and shaded spheres; (**b**) Six pyridinium cations are attached via hydrogen bonds to the dimer.

(**a**)

(**b**)
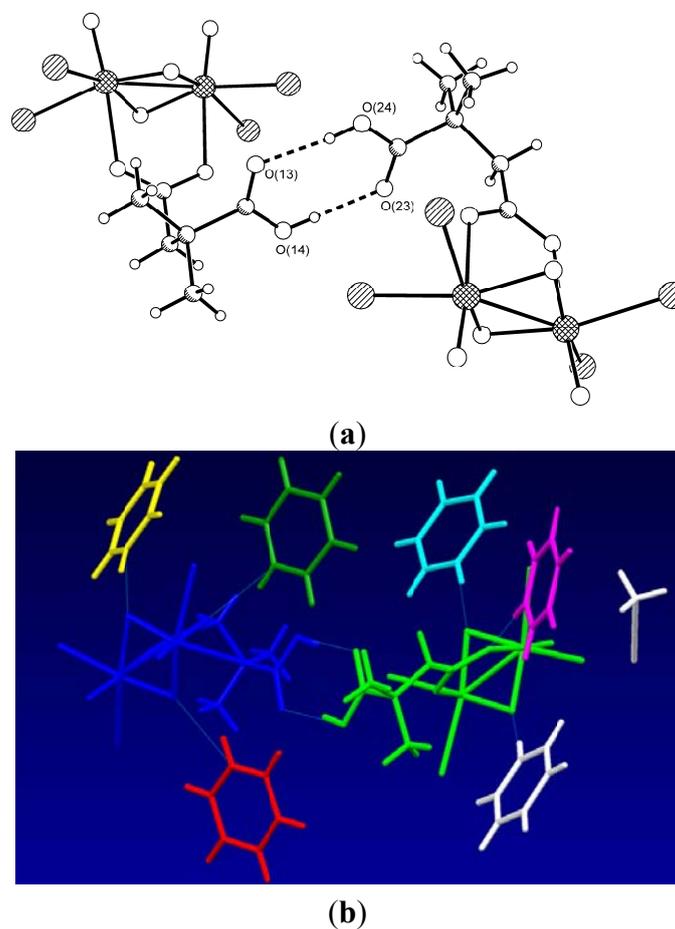
Figure 6. Hydrogen-bonding pattern in **2**. (**a**) COOH function of the dmsH⁻ ligand is hydrogen-bonded to the chloride counteranion which is engaged also in interaction with pyridinium cation; (**b**) The remaining pyridinium cations are attached to the μ_2-oxides of the $\{Mo_2O_4\}^{2+}$ core.

(**a**)
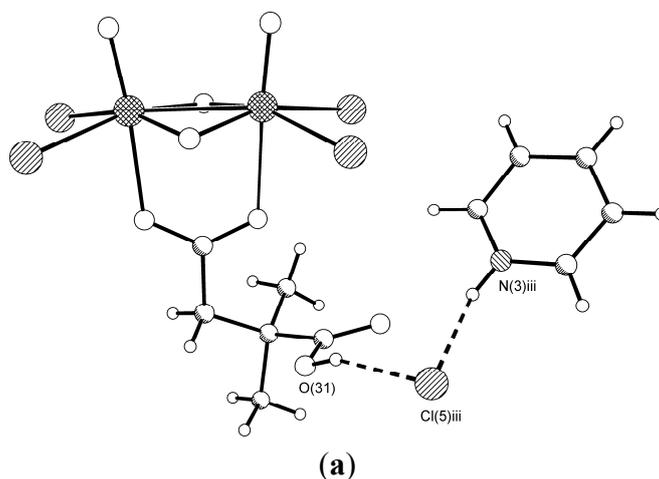
Figure 6. Cont.
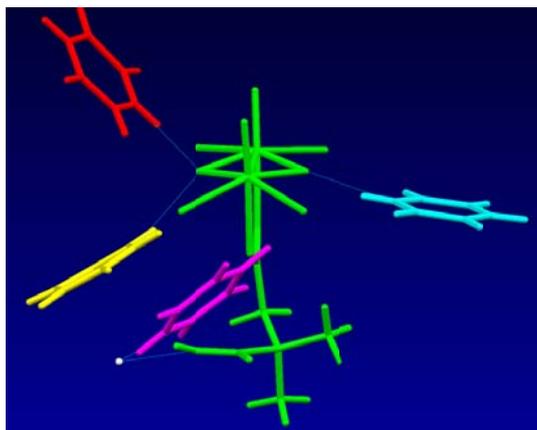
(**b**)

Figure 7. A projection of the unit cell content of **1** along *a*-axis.
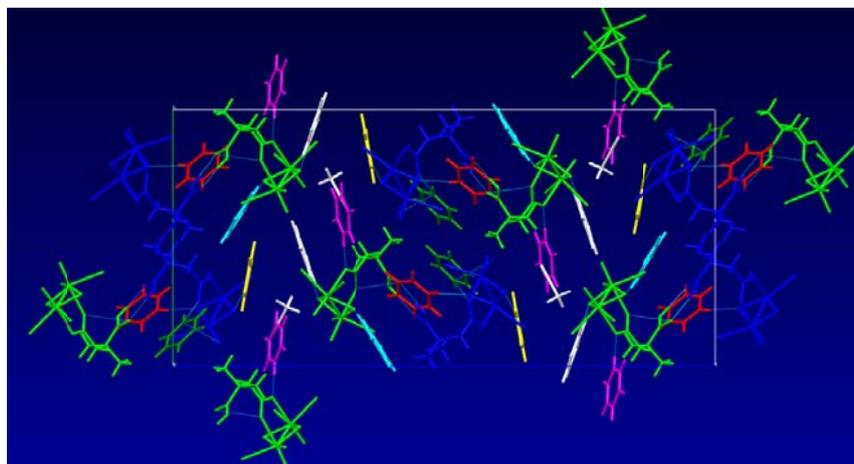
Figure 8. A projection of the unit cell content of **2** along *a*-axis.
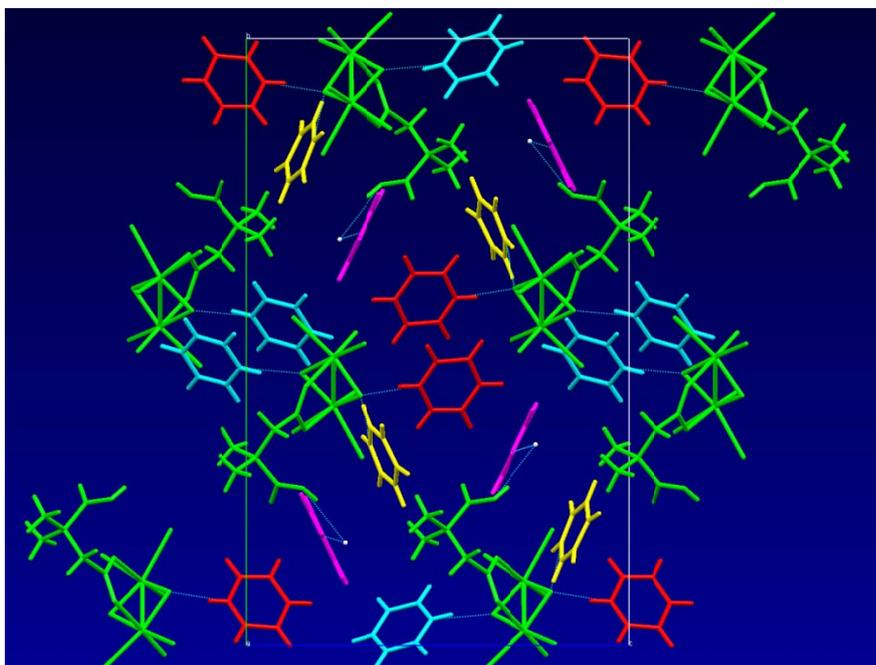
Table 3. Hydrogen bonds in **1**.

Type	Donor atom···acceptor atom [a]	Length (Å) [b]
COOH···COOH	O(14)···O(23)	2.630(3)
COOH···COOH	O(24)···O(13)	2.609(3)
PyH$^+$···μ_2-O	N(1)···O(7)	2.767(5)
PyH$^+$···μ_2-O	N(2)···O(8)	2.716(4)
PyH$^+$···μ_2-O	N(4)···O(5) [i]	2.620(4)
PyH$^+$···μ_2-O	N(5)···O(6) [ii]	2.722(4)
PyH$^+$···COO$^-$ [c]	N(3)···O(11) [ii]	2.737(4)
PyH$^+$···COO$^-$ [c]	N(6)···O(22) [i]	2.833(4)

[a] Symmetry codes: (i) $x + 1, y, z$; (ii) $-x + 1, -y + 1, -z + 1$; [b] The distances may be compared to the sums of the corresponding van der Waals radii: 3.04 Å for O+O, and 3.07 Å for N+O [17]; [c] COO$^-$, the carboxylate group coordinated to the $\{Mo_2O_4\}^{2+}$ core.

Table 4. Hydrogen bonds in **2**.

Type	Donor atom···acceptor atom [a]	Length (Å) [b]
COOH···Cl$^-$	O(31)···Cl(5) [iii]	3.044(4)
PyH$^+$···Cl$^-$	N(3) [iii]··· Cl(5) [iii]	3.047(5)
PyH$^+$···μ_2-O	N(1)···O(4) [iv]	2.620(8)
PyH$^+$···μ_2-O	N(2)···O(4)	2.807(7)
PyH$^+$···μ_2-O	N(4)···O(3)	2.666(6)

[a] Symmetry codes: (iii) $x + 0.5, -y + 0.5, z + 0.5$; (iv) $x, y, z - 1$; [b] The distances may be compared to the sums of the corresponding van der Waals radii: 3.27 Å for O+Cl, 3.30 Å for N+Cl, and 3.07 Å for N+O [17].

Figure 9. Pair-wise association of two carboxylic acids, a common hydrogen bond synthon.
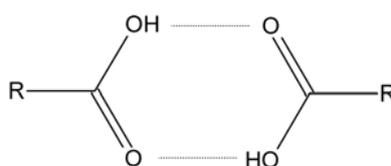
In the absence of other hydrogen bond donors and acceptors in the compound, the COOH function can form an intramolecular interaction as exemplified by the hydrogen malonate complex, $(PyH)_3[Mo_2O_4Cl_4(\mu_2\text{-Hmal})]\cdot CH_3CN$, with the ligand Hmal$^-$ bound in the same manner as dmsH$^-$ in compounds **1** and **2** [15]. The bond is formed between the COOH terminus of the Hmal$^-$ ligand and the carboxylate oxygen (Figure 10a). The respective O···O contact is short, it amounts to 2.552(4) Å. The same motif is observed for the hydrogen maleate complex $(PyH)_3[Mo_2O_4Cl_4(\mu_2\text{-Hmale})]$ with the O···O contacts in the 2.523(3)−2.533(3) Å range [16]. In both examples, the geometry of the ligand favours such an interaction. Consequently, the formation of intramolecular hydrogen bonds is a common feature of the hydrogen malonate or hydrogen maleate coordination chemistry [19]. On the other hand, the example that follows, $(PyH)_2[Mo_2O_4Cl(Py)(\eta^2\text{-mal})(\mu_2\text{-Hmal})]$, shows that even hydrogen malonate can produce other hydrogen-bonding patterns [15]. The latter complex possesses also fully neutralized malonate ions, mal^{2-}. The COOH group is hydrogen-bonded to the

non-coordinated oxygen of the mal^{2-} ligand of an adjacent complex (Figure 10b). The O···O contacts with lengths of 2.558(4) Å link complex ions into infinite chains. A complex with the hydrogen succinate, (PyH)[Mo$_2$O$_4$Cl$_2$(Py)$_2$(μ_2-Hsuc)]·Py, reveals a yet another structural synthon: the COOH group is engaged in an interaction with pyridine molecule, O···N = 2.636(4) Å [15] (Figure 10c). Although the stoichiometry of another example, (PyH)$_4$[Mo$_2$O$_4$Cl$_4$(μ_2-btcH$_2$)]Cl, is highly reminiscent of that of compound **2**, the ligand, the anion of 1,3,5-benzentricarboxylic acid, possesses two non-ionized COOH functions and a different connectivity pattern is displayed [9]. Both of its COOH functions form hydrogen bonds with chloride counteranions and infinite chains are formed (Figure 10d). The O···Cl lengths, 2.920(3) and 2.938(3) Å, are slightly shorter than in compound **2**. In addition, three pyridinium cations are attached to each chloride counteranion. The respective N···Cl distances are in the 3.112(3)−3.291(3) Å range.

Figure 10. Various hydrogen-bonding motifs involving COOH functions in {Mo$_2$O$_4$}$^{2+}$ complexes. **(a)** An intramolecular O–H···O bond in (PyH)$_3$[Mo$_2$O$_4$Cl$_4$(μ_2-Hmal)]·CH$_3$CN; **(b)** COOH terminus of the Hmal$^-$ ligand is bonded to the COO$^-$ moiety of the mal^{2-} ligand in (PyH)$_2$[Mo$_2$O$_4$Cl(Py)(η^2-mal)(μ_2-Hmal)]; **(c)** In (PyH)[Mo$_2$O$_4$Cl$_2$(Py)$_2$(μ_2-Hsuc)]·Py, the COOH group interacts with pyridine solvent molecule [15]; **(d)** O–H···Cl interactions in (PyH)$_4$[Mo$_2$O$_4$Cl$_4$(μ_2-btcH$_2$)]Cl result in infinite chains [9].

(a)

(b)

(c)

(d)
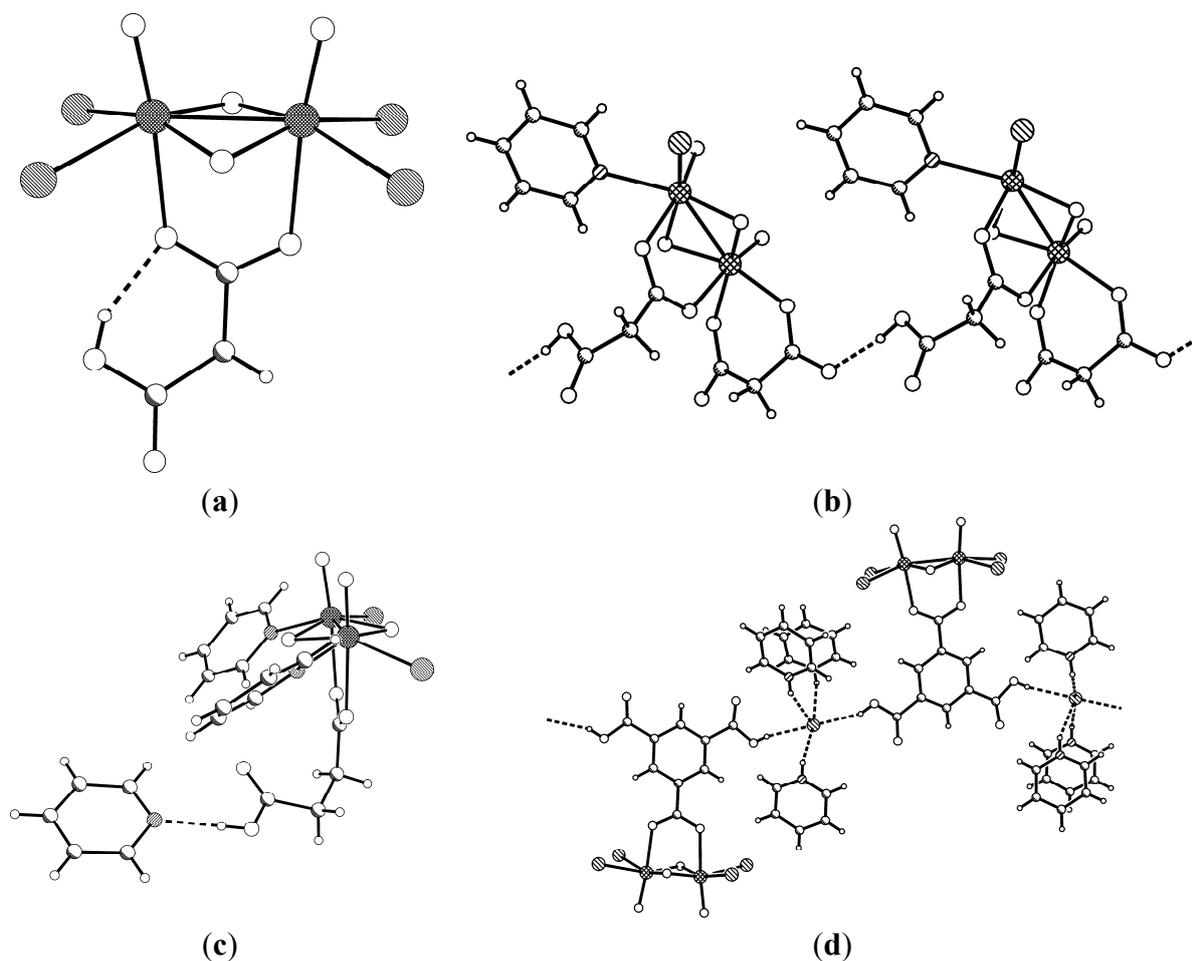
2.2. Infrared Spectroscopy

The positions of the asymmetric and symmetric v(COO) vibrations can be used to diagnose the carboxylate binding mode [20,21]. Due to the presence of two functions in dmsH$^-$ ligands in **1** and **2**, no unambiguous assignation can be made. A group of bands in the region of 1550−1350 cm^{-1} finds its origin in the v_{asym}(COO) and v_{sym}(COO) of the coordinated carboxylate moiety. Strong bands at 1698 cm^{-1} for **1** and at 1710 cm^{-1} for **2** may be assigned to the C=O stretching frequency for the acid end of the dmsH$^-$ ligand [22]. The shift to lower frequency for **1** is in accordance with the involvement of the COOH function in a strong hydrogen-bonding to form a dimer.

3. Experimental Section

3.1. General

All procedures were conducted in air. Most chemicals were purchased from Aldrich Chemical Co., and triethylamine from Fluka. They were used without further purification. (PyH)$_5$[MoOCl$_4$(H$_2$O)]$_3$Cl$_2$ was prepared following the published procedure [10]. The infrared spectra were measured on solid samples as nujol mulls using a Perkin Elmer 2000 series FT-IR spectrometer. Elemental analyses were carried out by the Chemistry Department service at the University of Ljubljana.

3.2. Preparation of (PyH)$_3$[Mo$_2$O$_4$Cl$_4$(μ_2-dmsH)]·1/2CH$_3$CN (1)

2,2-dimethylsuccinc acid (353 mg, 2.415 mmol) was added to the solution of triethylamine (490 mg, 4.84 mmol) in acetonitrile (25 mL). To this solution, (PyH)$_5$[MoOCl$_4$(H$_2$O)]$_3$Cl$_2$ (562 mg, 1.31 mmol of molybdenum) was added. The red solution was left to stand in a closed Erlenmeyer flask at ambient conditions overnight. On the following day, the solution was placed in the refrigerator. Orange crystals of **1** that formed after two days were filtered off. Yield: 248 mg (47%). Calc. for C$_{22}$H$_{28.5}$Cl$_4$Mo$_2$N$_{3.5}$O$_8$: C, 32.88; H, 3.57; N, 6.10. Found: C, 33.05; H, 3.67; N, 6.11. IR (cm^{-1}): 2250 w, 1698 vs, 1634 m, 1611 m, 1546 vs, 1536 vs, 1486 vs, 1418 m, 1402 m, 1366 w, 1324 m, 1300 m, 1222 m, 1201 m, 1168 m, 1054 w, 961 vvs, 937 vs, 887 m, 817 w, 776 m, 751 vvs, 721 vvs, 681 vvs, 605 s.

3.3. Preparation of (PyH)$_4$[Mo$_2$O$_4$Cl$_4$(μ_2-dmsH)]Cl (2)

2,2-dimethylsuccinc acid (730 mg, 5.0 mmol) was dissolved in methanol (5 mL), followed by the addition of a methanol solution (1.0 M) of tetrabutylammonium hydroxide (10 mL, 10.0 mmol). Methanol was removed by careful pumping on the vacuum line. Acetonitrile (20 mL) was added to the oily residue. Each gram of thus obtained solution contained 0.319 mmol of (*n*-Bu$_4$N)$_2$dms. This solution (2.19 g, 0.70 mmol of (*n*-Bu$_4$N)$_2$dms) was added to the acetonitrile (20 mL) solution of (PyH)$_5$[MoOCl$_4$(H$_2$O)]$_3$Cl$_2$ (450 mg, 1.05 mmol of molybdenum). The solution of deep yellow colour was left to stand in a closed Erlenmeyer flask at ambient conditions overnight. On the following day, the volume of the solution was reduced to *ca.* one half by pumping on the vacuum line. The resulting solution was placed in the refrigerator. The orange crystals of **2** which formed after two days were filtered off and washed with the hexanes. Yield: 160 mg (34%). Calc. for C$_{26}$H$_{33}$Cl$_5$Mo$_2$N$_4$O$_8$:

C, 34.75; H, 3.70; N, 6.23. Found: C, 34.65; H, 3.62; N, 6.19. IR (cm^{-1}): 1710 vs, 1636 s, 1606 s, 1535 vvs, 1485 vvs, 1429 vs, 1308 m, 1245 w, 1203 vs, 1159 w, 1135 m, 1055 w, 954 vvs, 880 m, 750 vvs, 722 vvs, 683 vvs, 630 w, 604 m.

3.4. X-ray Crystallography

Crystals were mounted on the tip of a glass fibre with a small amount of silicon grease and transferred to a goniometer head. Data were collected on a Nonius Kappa CCD diffractometer. Data reduction and integration were performed with the software package DENZO-SMN [23]. Averaging of the symmetry-equivalent reflections largely compensated for the absorption effects. For both compounds, the coordinates of some or all of the non-hydrogen atoms were found via direct methods using the structure solution program SHELXS [24]. 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. Hydrogen atoms, including the carboxylic hydrogen atoms, were added in calculated positions. All calculations were performed using WinGX System Version 1.80.05 [25]. Figures depicting the structures were prepared using ORTEP3 [26], SHELXTL [27], Mercury [28], and CrystalMaker [29]. Cell parameters and refinement results are summarized in Table 5. Further details on the crystal structure investigations may be obtained free of charge from The Cambridge Crystallographic Data Centre [30]. Cambridge Structural Database deposition numbers: CCDC-917918 (**1**) and -917919 (**2**).

Table 5. Crystallographic data for **1** and **2**.

Compound	1	2
Empirical formula	$C_{22}H_{28.5}Cl_4Mo_2N_{3.5}O_8$	$C_{26}H_{33}Cl_5Mo_2N_4O_8$
Formula weight	803.7	898.7
Crystal system	monoclinic	monoclinic
Space group	$P\,2_1/n$	$P\,2_1/n$
T (K)	150(2)	150(2)
a (Å)	9.9123(1)	9.0254(1)
b (Å)	17.0078(1)	25.7214(4)
c (Å)	36.1401(3)	16.2035(2)
α (deg)	90	90
β (deg)	97.4302(4)	97.0941(7)
γ (deg)	90	90
V (Å^3)	6041.57(9)	3732.78(8)
D_{calcd} (g/cm^3)	1.767	1.599
Z	8	4
λ (Å)	0.71073	0.71073
μ (mm^{-1})	1.233	1.077
Collected reflections	19959	12861
Unique reflections, R_{int}	10966, 0.028	6785, 0.0281
Observed reflections	8997	5449
$R1$ [a] ($I > 2\sigma(I)$)	0.0291	0.0526
$wR2$ [b] (all data)	0.0658	0.1283

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

4. Conclusions

Reactions of $(PyH)_5[MoOCl_4(H_2O)]_3Cl_2$ with 2,2-dimethylsuccinic acid afforded a dinuclear anionic molybdenum(V) complex which crystallized as two pyridinium salts, $(PyH)_3[Mo_2O_4Cl_4(\mu_2\text{-}dmsH)]\cdot1/2CH_3CN$ (**1**) and $(PyH)_4[Mo_2O_4Cl_4(\mu_2\text{-}dmsH)]Cl$ (**2**). In order to deprotonate the acid, triethylamine and tetrabutylammonium hydroxide were used. In either case, products with a $dmsH^-$ ion, a half-neutralized acid, were isolated. The ligand, the $dmsH^-$ ion, coordinated to the $\{Mo_2O_4\}^{2+}$ core in the already observed manner: with both oxygen atoms of the carboxylate to *trans* sites within the $\{Mo_2O_4\}^{2+}$ core. The non-ionized COOH function of the ligand got engaged in hydrogen bonds. In **1**, the COOH groups of two ligands associated to form the well-known "carboxylic acid dimer". Due to the presence of chloride counteranions in **2**, a different intermolecular connectivity was observed. The COOH group formed a hydrogen bond with the chloride. The $[Mo_2O_4Cl_4(\mu_2\text{-}dmsH)]^{3-}$ complex represents a new addition to the growing family of the $\{Mo_2O_4\}^{2+}$-containing complexes with multicarboxylate ligands. In cases when the ligands possess non-ionized functions, diverse hydrogen-bonding motifs which involve the COOH functions are displayed.

Acknowledgments

Conflict of Interest

The author declares no conflict of interest.

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