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Mo(VI)-OXALATE DERIVATIVES: THERMAL BEHAVIOUR OF THE $|Co(en)_3|^{3+}$ SALTS OF THREE DIFFERENT OXOANIONIC COMPLEXES

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ABSTRACT

Molybdenum(VI) dimeric complexes containing an oxo bridge group are long known. Suggestions on the probable existence of doubly bridged(μ-oxo-μ-hydroxo)dimolybdenum(VI) complex species have been advanced, lacking direct structural confirmation. The study of the thermal behaviour of three different molybdo-oxalate complexes previously described, namely $|MoO_2(OH)_2(C_2O_4)_2|^{4-}$ and the dimers $|Mo_2O_5(OH)_2(C_2O_4)_2|^{4-}$ and $|Mo_2O_5(OH)(C_2O_4)_2|^{3-}$, has provided evidence regarding the existence of significant structural differences between both dimeric species that support the above hypothesis. On the other hand, a new monomeric trioxo species, $|MoO_3(C_2O_4)_2|^{4-}$, has been identified and characterized.

INTRODUCTION

In a previous publication [1] the synthesis and a preliminary characterization of the $|Co(en)_3|^{3+}$ salts of three different crystalline oxalato derivatives of Mo(VI) were reported. The oxo-anionic complexes were formulated as $|MoO_2(OH)_2(C_2O_4)_2|^{4-}$, $|Mo_2O_5(OH)_2(C_2O_4)_2|^{4-}$ and $|Mo_2O_5(OH)(C_2O_4)_2|^{3-}$. Structural proposals were advanced and it was stressed that the last species probably involves a μ-oxo-μ-hydroxo bridged dimolybdenum core. Lack of direct structural confirmation of this seemingly striking fact * is related to the difficulty in obtaining single crystals of these types of compounds. Thus, although Cotton et al. [4] have described the structure of the related potassium salt $K_2\{|MoO_2(C_2O_4)(H_2O)|_2O\}$ by X-ray diffraction

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* Whereas double bridges are usually found in the Mo(V) chemistry, they are practically unknown in the Mo(VI) coordination chemistry [2].

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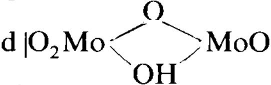
on a single crystal supplied by Lucas and Sandor [3] (who were convinced that the compound was the Mo(V) derivative $K_2|Mo_2O_4(C_2O_4)_2(H_2O)_2|$), they were not able to crystallize this salt again [4].

More recently, new evidence suggesting the existence of these three different molybdenum–oxygen core types, namely $|MoO_2|^{2+}$ (in monomeric $|MoO_2L_2|$ species, where L = bidendate ligand) and the corresponding dinuclear complexes, $|O_2Mo{-}O{-}MoO_2|^{2+}$ and  $|O_2Mo\langle{}^{O}_{OH}\rangle MoO_2|^{+}$, has been provided for other related Mo(VI) complexes containing polyhydroxylic ligands [5–7].

While at the present time we are engaged in the resolution of the difficulties in the synthesis hindering the obtention of single crystals, and consequently the elucidation of the structures, it was considered of interest to obtain additional information on these types of compounds. Accordingly, a study of the thermal behaviour of the reported $|Co(en)_3|^{3+}$ salts of the oxalate compounds has been made, attempting to show the existence of structural differences among the oxo-anionic complexes.

EXPERIMENTAL

The hydrates of the $|Co(en)_3|^{3+}$ salts of the oxalate anionic complexes $|MoO_2(OH)_2(C_2O_4)_2|^{4-}$, $|Mo_2O_5(OH)_2(C_2O_4)_2|^{4-}$ and $|Mo_2O_5(OH)(C_2O_4)_2|^{3-}$ (see Table 1) were prepared as described previously [1].

The thermal analyses were made using a Setaram 870 simultaneous TGA–DTA thermobalance at a heating rate of 4.4°C min^{-1} under a dynamic air atmosphere. Calcined Al_2O_3 was used as reference. In the non-isothermal kinetic study of the dehydration processes, a heating rate of 2.4°C min^{-1} was maintained.

Infrared spectra (KBr pellet) were recorded in a Pye-Unicam SP 2000 spectrophotometer.

X-Ray powder diffraction patterns were obtained by means of a Kristalloflex 810 Siemens diffractometer using CuK_α radiation.

Mo and Co analyses were performed by means of atomic absorption using a Perkin-Elmer 300 spectrophotometer. C was determined by elemental analysis using a Coleman analyzer.

RESULTS AND DISCUSSION

The TGA and DTA curves of the complexes are given in Fig. 1. The analytical data calculated from the curves in Fig. 1 are summarized in Table 1.

TABLE 1

Thermal analysis data

	Complex I $M_4|MoO_2(OH)_2(C_2O_4)_2|_3 \cdot 7\ H_2O$ [a]		Complex II $M_4|Mo_2O_5(OH)_2(C_2O_4)_2|_3 \cdot 6\ H_2O$ [a]		Complex III $M|Mo_2O_5(OH)(C_2O_4)_2| \cdot 9/2\ H_2O$ [a]	
	TGA [b]	DTA [c]	TGA [b]	DTA [c]	TGA [b]	DTA [c]
Dehydration	7.50 ($n = 8$) [d]	80, endo 107, endo	5.60 ($n = 7$) [d]	108, endo 165, endo	10.1 ($n = 9/2$) [d]	92, endo 114, endo
Decarboxylation (oxalate removal)	Obsd. 24.20	225, endo 253, endo	19.50	230, endo	20.27	220, exo
	Calcd. 24.98		20.89		21.40	
Counter ion decomposition	Obsd. 29.30	450, exo 540, exo	24.76	450, exo 520, exo	21.36	426, exo 483, exo
	Calcd. 31.00		25.96		20.89	

[a] $M = |Co(en)_3|^{3+}$.

[b] Percent weight loss.

[c] Temperature in °C.

[d] Total number of water molecules lost.

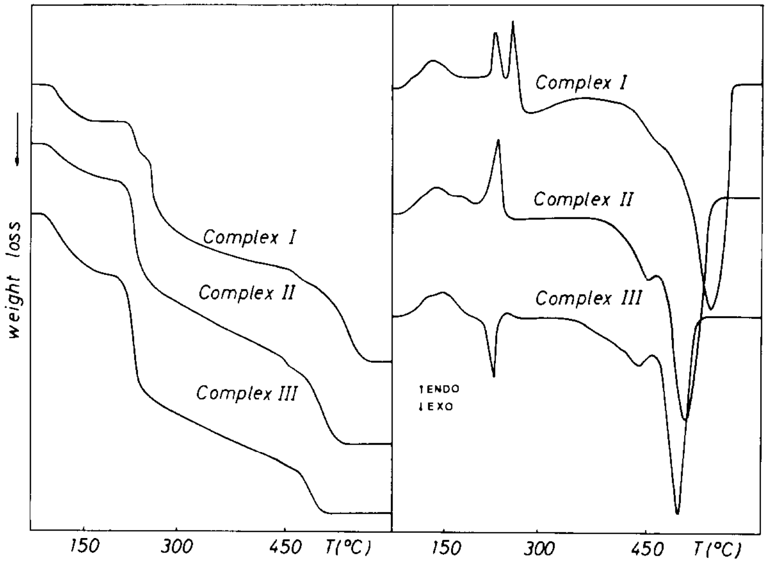


Fig. 1. TGA–DTA plots of the complexes (dynamic air atmosphere, 4.4°C min^{-1}).

Dehydration

In all three cases, the low temperature range of the first endothermic stage in the decomposition process of the complexes allows it to be associated with the dehydration of the compounds [8]. The two peaks in the DTA curves, showing that dehydration occurs through two partially overlapping steps, suggest that the overall weight loss observed involves the removal of all the molecules of water of hydration and also, in the case of complexes I and II, the dehydroxylation of the oxo-anions. In this sense, it can be pointed out that the dehydration of the tartrate derivatives analogous to complexes I and II, which lack OH ligand groups, occurs in a single step [7]. On the other hand, it can be noted that the DTA curve of complex II exhibits its endothermic effects at 108 and 165°C, i.e. at temperatures appreciably higher than complex III (92 and 114°C), thus supporting our assumption regarding the dehydroxylation of complex II. The fact that complex I loses all its water at a relatively low temperature (endothermic effects at 80 and 107°C) can be understood on the basis of the appearance of a plateau in the TGA curve which implies the formation of an anhydrous stable intermediate. We shall insist on this intermediate later on.

Non-isothermal kinetic analyses of these processes were carried out using the Satava integral method [9]. In all three cases, dehydration takes place by means of a nucleation mechanism, controlled by monodimensional diffusion, which corresponds to the F_1 model (Sharp notation [10]). The calculated activation energies and pre-exponential factors are listed in Table 2. These results suggest that the structural role played by the water molecules is not essentially different.

TABLE 2

Calculated kinetic parameters

	Kinetic model	E_a [a]	Z [b]
Complex I	F_1	10.5	$10^{3.0}$
Complex II	F_1	7.6	$10^{1.3}$
Complex III	F_1	10.5	$10^{3.2}$

[a] Activation energy in kcal mol^{-1}.

[b] Pre-exponential factor in s^{-1}.

Oxalate removal

The observed weight losses in the TGA curves of the complexes indicate that, following the dehydration reactions, decarboxylation (oxalate removal) of the solids occurs (see Table 1). The DTA curves of all three compounds show, in the temperature ranges associated with these processes, remarkable dissimilarities that can be related to the existence of significant differences among the basic structures of the anhydrous solids.

Thus, complex I loses the oxalate groups through two well-defined endothermic consecutive steps (peaks at 225 and 253°C). One oxalate molecule per molybdenum atom is lost in each step (ca. 12.5% weight loss). This result suggests the presence of two distinctively coordinated oxalate ligands in the stable anhydrous intermediate mentioned above.

On the contrary, decarboxylation of the dimeric complexes II and III occurs in a single step. Nevertheless, whereas this process is accompanied, as expected, by an endothermic effect (peak at 230°C) in the case of complex II, the DTA curve of complex III exhibits an exothermic peak (at a similar temperature, 220°C). These same types of behaviour have been observed for the ligand removal processes of the tartrate derivative analogues [7]. Two main conclusions may be inferred from this similarity. First, there must be a basic resemblance between the structural cores of the oxalate compounds and those of their respective analogous tartrate derivatives. Second, the exothermic character of the decarboxylation in the case of complex III must imply that oxo-anion bonding breakdown must be accompanied by a rearrangement of the atomic skeleton which overcomes the required energy for breaking bonds, and this behaviour should be consistent with the existence of an important difference between the structures of both dimeric 1/1 species (complexes II and III) as previously suggested by IR spectroscopy [1].

The decarboxylation of complex I deserves a more detailed comment. Extensive spectrophotometric and cryoscopic studies in solution, as well as the analysis and IR spectroscopy of its $|Co(en)_3|^{3+}$ salt, led to the proposed formulation for the monomeric oxoanion, $|MoO_2(OH)_2(C_2O_4)_2|^{4-}$ [1]. Oxalate groups must act as monodentate ligands in this species and, given that all the Mo(VI) dioxocomplexes have both oxo groups located in the *cis* position [11], its stability has been explained on the basis of the probable formation of hydrogen-bonded six-membered chelate pseudo-rings involving the terminal (non-coordinated) carboxylate groups of the oxalate ligands and the respective *cis* located OH groups [5]. As stated above, the dehydration of $|Co(en)_3|_4|MoO_2(OH)_2(C_2O_4)_2|_3 \cdot 7\ H_2O$, which occurs through two steps, must involve the removal of all the seven hydration water molecules and also the dehydroxylation of the oxo-anion leading to a stable anhydrous intermediate. This last species of low crystallinity has been isolated by prolonged heating in an oven (24 h at 170°C) of a sample of the hydrate and stored in a desiccator over P_4O_{10}. Its composition has been determined by chemical analysis: 15.3% Mo, 12.0% Co and 21.9% C ($C_{36}H_{96}N_{24}O_{33}Co_4Mo_3$ calcd.: Mo 15.0, Co 12.3 and C 22.6%).

The IR spectrum of the solid (KBr pellet) was recorded and compared with that of the parent material. In Fig. 2 two of their more significant portions are plotted. (The overall spectra are too complex. A complete assignment of the bands cannot be made.) The 900 cm^{-1} region is characteristic of the stretching vibrations of the $Mo{-}O_{terminal}$ multiple bonds [12,13], although the bands can appear complicated by components due to the

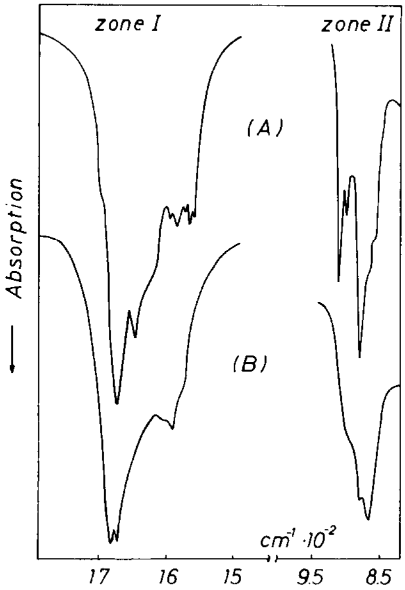
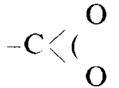


Fig. 2. A partial view of the IR spectra (KBr pellet). Curves A: $|Co(en)_3|_4|MoO_2(OH)_2(C_2O_4)_2|_3 \cdot 7\ H_2O$; curves B: $|Co(en)_3|_4|MoO_3(C_2O_4)_2|_3$. Zone I: asymmetric stretching vibration of the carboxyl groups region; zone II: $\nu(Mo{-}O_{terminal})$ bonds region.

absorption of the stretching C–O vibration (which is strongly coupled with in-plane bending δ(O–C=O) vibration [14a]). The 1500–1700 cm^{-1} region corresponds to the stretching asymmetric vibration of the carboxyl groups [14a–16] (if well bending vibrations of H_2O and –NH entities also appear in this zone [14b]).

An outstanding aspect of the last zone is the greater simplicity in the spectrum of the anhydrous solid as compared to that of the hydrated one. Contributing to this relative simplicity is the absence of the H_2O bending vibration component in the spectrum of the anhydrous material *. However, there are other differences that may be attributed to the stretching vibrations of the carboxyl groups. Thus, in the hydrated solid, the ν_a(COO) band shows two components: that of 1675–1640 cm^{-1} is assignable to a $-CO_2M$ group (i.e., to a covalently combined carboxyl group, and, consequently, to a primarily C=O bond). The component centred at 1580 cm^{-1} can be associated with a free $-CO_2$ group (i.e., to the terminal  $-\mathrm{C}\langle(^{\mathrm{O}}_{\mathrm{O}}$ ionic group). The coupling between the vibrations of the two identical monodentate oxalate ligands should justify the splitting of both components [17]. On the contrary, the bands in the spectrum of the anhydrous solid are, as stated, more simple. The band at 1685 cm^{-1}, slightly split, is characteristic of a single bidentate oxalate group [14a–17]. The definite peak at lower frequency, 1590 cm^{-1}, could be assigned to the asymmetric stretching vibration of one monodentate oxalate ligand [19]. The hypothesis of the different character of the two oxalate groups (i.e., one monodentate and the remainder bidentate) in the anhydrous material is supported, as suggested above, by its behaviour during the thermal decarboxylation process. Nevertheless, the more significant evidence in this sense is provided, besides the chemical analysis of the material, by the observed evolution of the Mo–O_{terminal} stretching frequencies on heating the hydrated compound. In the spectrum of this last solid, the two narrow bands at 925 and 910 cm^{-1} are clearly assignable to the molybdenum-to-oxygen multiple bond stretching frequencies of a *cis*-MoO_2 core (C_{2v} local symmetry) [12,13]. The band at ca. 880 cm^{-1} is essentially due to $\nu_s(CO) + \delta(O\text{–}C{=}O)$ [14a]. This band is present as a shoulder, at the same frequency, on the broad band that occupies the same zone in the spectrum of the anhydrous intermediate. However, in this case, the main ν(Mo–O_t) absorption appears at a remarkably lower frequency, 865 cm^{-1}, than in the parent compound. This decrease indicates a Mo–O_t bond order

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* This greater simplicity is also observed in the 3000–3600 cm^{-1} region. The IR spectra of the solids containing ethylenediamine are very complicated in this higher zone [18]. They present two complex series of bands, of relatively equal intensity, at 3000–3350 cm^{-1} and 3400–3550 cm^{-1}, which should be assignable primarily to the NH and OH bond stretching vibrations. Dehydration does not modify practically the bands in the 3000–3250 cm^{-1} zone (only a slight shift of the peaks toward higher frequencies is observed) but eliminates the components due to OH stretching vibration contributions.

lowering which is consistent with the presence of a molybdenum–oxygen core containing more than two oxo groups per molybdenum atom [4] *. Assuming that the complex anion of the anhydrous intermediate possesses a $|MoO_3|$ core, all our previous results become coherent. Dehydroxylation of the parent material, which contains the anion $|MoO_2(OH)_2(C_2O_4)_2|^{4-}$, involves the removal of one H_2O molecule per molybdenum atom and leads to the trioxocomplex ion, $|MoO_3(C_2O_4)_2|^{4-}$, in which only three coordination sites remain available for occupation by both oxalate groups.

Counter ion decomposition

TGA and DTA curves show that, after complete decarboxylation of the solids, processes involving a smooth (but significant) weight loss occur from ca. 300°C until ca. 400°C (in all three cases). These processes are immediately followed by two sharper overlapping exothermic steps. The overall weight losses in the TGA curves (see Table 1) and DTA affect temperatures, which agree with the literature [21,22], clearly indicate that the counter ion decomposition is implied in these ultimate processes. Counter ion decomposition should proceed by the initial evolution of ethylenediamine and subsequent combustion of the remaining products. The evaluable differences in the temperature of the last exothermic peaks could be related with structural dissimilarities in the parent compounds.

The violet (under normal pressure and room temperature [23]) solid residues resulting from the pyrolysis (which turn green under pressure [23]) were identified by X-ray powder diffraction. They are composed primarily of α-$CoMoO_4$ [24] and also contain CoO (complex I) or MoO_3 (complexes II and III). In this way, the counter ion decomposition implies simultaneously the reduction Co(III) → Co(II).

CONCLUDING REMARKS

The results described in this work are coherent with the previously available data on this system and actually contribute to a better characterization of the molybdo-oxalate complexes under study.

It is worth emphasizing the large differences in the thermal behaviour of both dimeric 1/1 complexes (complexes II and III). Such remarkable dif-

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* In the MoO_3dien complex, the only band which could be assigned as a Mo–O stretch(sic) [12] was found in the IR spectrum at 839 cm^{-1} [20]. A MoO_3 group (C_{3v} symmetry) should have two IR active Mo–O stretching modes. As Cotton has stated, assuming that both modes are accidentally degenerate, the calculated force constants are comparable with those for the MoO_4^{2-} ion (which absorbs at 894 and 833 cm^{-1}) [12]. This way, it is not unreasonable to suggest that, in our case, the shoulder at ca. 890 cm^{-1} could be due to the second Mo–O_t stretching vibration component.

ferences cannot be attributed to a simple protonation of the ligand belonging to the oxo-anion (as formulations might suggest) but must be caused by an essentially different nature of the molybdenum–oxygen cores. The hypothesis of a double, μ-oxo-μ-hydroxo, bridge (complex III) vs. a single μ-oxo bridge (complex II) previously advanced [1]—in agreement with further studies on Mo(VI) polyhydroxylic ligand related compounds [5–7]—seems to find new support.

Lastly, it must be stressed that it has been possible to isolate a trioxo-bisoxalate complex unknown to date. The results concerning this intermediate species fit well into the overall observations referred to the monomeric hydrogen bonded [1,5] $|MoO_2(OH)_2(C_2O_4)_2|^{4-}$ oxo-anion.

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