VIBRATIONAL SPECTRA OF THE α-$M^{II}C_2O_4 \cdot 2H_2O$ OXALATO COMPLEXES, WITH M^{II} = Co, Ni, Zn

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Abstract

The infrared and Raman spectra of the α-$M^{II}C_2O_4 \cdot 2H_2O$ oxalate complexes with M^{II} = Co, Ni and Zn were recorded and briefly discussed on the basis of their structural peculiarities. The IR spectrum of a partially deuterated sample of α-$ZnC_2O_4 \cdot 2H_2O$ is also discussed, reinforcing some of the performed assignments in the lower energy spectral region.

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Resumen

Se registraron los espectros de infrarrojo y Raman de los oxalato-complejos α-$M^{II}C_2O_4 \cdot 2H_2O$ con M^{II} = Co, Ni, Zn y se los discute brevemente en base a sus peculiaridades estructurales. Asimismo, se discute el espectro IR de una muestra parcialmente deuterada de α-$ZnC_2O_4 \cdot 2H_2O$ el que permitió reforzar algunas de las asignaciones realizadas en la zona espectral de baja energía.

Palabras clave: complejos de oxalato; complejos de Co(II), Ni(II), Zn(II); espectros de infrarrojo; espectros Raman.

Introduction

The dihydrated metallic oxalates of the type $M^{II}C_2O_4 \cdot 2H_2O$ with M^{II} = Mg, Fe, Co and Ni present two polymorphic forms, called α-modification (monoclinic, space group C2/c, Z = 4) and β-modification (orthorhombic, space group Cccm, Z = 8), generated from the bidimensional structural arrangement depicted in Figure 1, with the oxalate anions acting as tetradentate ligands. The structure is completed with two water molecules, above and below each cation, generating an approximately octahedral $M^{II}O_6$ coordination sphere around each metallic center [1-4]. The two polymorphic forms originate in small differences of the three-dimensional piling up of these structural blocks in the crystallographic unit cell.
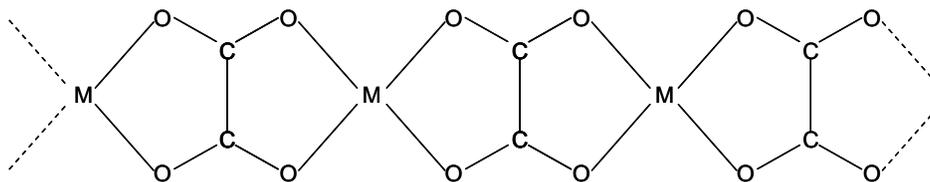
Figure 1. Schematic drawing of the infinite chain arrangement present in M^{II}-oxalates of composition $M^{II}C_2O_4 \cdot 2H_2O$.

In the case of M^{II} = Mn, two other complex species (γ-$MnC_2O_4 \cdot 2H_2O$ and $MnC_2O_4 \cdot 3H_2O$), together with the characteristic α-modification are known [3,5] and, in the case of M^{II} = Zn only this α-form has been characterized [2,3]. On the other hand, the related Cu(II) complex, $CuC_2O_4 \cdot nH_2O$ (synthetic moolooite), basically presents the structure depicted in Figure 1 [6], containing only a small proportion of water, of zeolitic nature [7].

In previous papers, we have investigated the vibrational-spectroscopic behavior of the oxalato complexes of Cu(II) [8] Fe(II) and Fe(III) [9], Mn(II) [10] and Mg(II) [11] and we have now investigated that of the α-modifications of Co(II), Ni(II) and Zn(II in order to extend these studies as well as to complete the spectroscopic characterization of the α-$M^{II}C_2O_4 \cdot 2H_2O$ species belonging to the first row transition metal cations.

The structures of the three complexes were determined a long time ago by X-ray powder diffractometry [2] and, in the case of α-$CoC_2O_4 \cdot 2H_2O$, recently confirmed by single-crystal diffractometric studies [12]. As mentioned above, the three complexes crystallize in the monoclinic C2/c crystal system, with four formula units in the crystallographic unit cell.

Experimental

Synthesis of the complexes

The synthesis of these complexes is relatively simple and can be performed by direct reaction of aqueous solutions of a salt of the respective metallic cation with a slight excess of an alkaline oxalate. In the case of Zn(II) the reaction can be performed directly at room temperature, whereas for Co(II) the preparation is performed at 50-60 °C, under continuous stirring, during 3 hours. For Ni(II), it is necessary to boil the reaction mixture at reflux, during 15 hours. After completion of the reaction, the precipitated micro crystalline powders (violet-pink α-CoC$_2$O$_4$·2H$_2$O, light green α-NiC$_2$O$_4$·2H$_2$O and white α-ZnC$_2$O$_4$·2H$_2$O) were separated by filtration, washed with small portions of hot water and finally air dried [2]. The purity of the generated samples was confirmed by X-ray powder diffractometry [2], employing a Philips PW 1710 diffractometer, and Ni-filtered Cu-K$_α$ radiation (λ = 1.5425 Å).

For the synthesis of the partially deuterated samples of α-Zn(C$_2$O$_4$)·2H$_2$O the same procedure was used as described above, but working directly in 5 mL of D$_2$O at a micro scale level. In this case, the obtained sample was rapidly dried in vacuum over H$_2$SO$_4$.

Spectroscopic measurements

The infrared spectra in the range 4000-400 cm^{-1} were recorded with a FTIR-Bruker-EQUINOX-55 instrument, using the KBr pellet technique. Spectra measured with suspensions of the compounds in Nujol mulls, gave identical results. Raman spectra in the same spectral range were measured on powdered samples using the FRA 106 Raman accessory of an IF66 Bruker spectrophotometer. Radiation from a Nd:YAG solid-state laser (1064 nm) was used for excitation.

Only in the case of α-Ni(C$_2$O$_4$)·2H$_2$O it was impossible to obtain good quality Raman spectra, even using KBr dilution of the sample and/or modifying the number of accumulated scans during measurement.

Results and discussion

The obtained FTIR and FT-Raman spectra of all the investigated samples present characteristic and totally comparable spectral patterns, as expected from their structural analogy. Obviously, they also resemble those of α-Fe(C$_2$O$_4$)·2H$_2$O [9], α-Mn(C$_2$O$_4$)·2H$_2$O [10] and α-Mg(C$_2$O$_4$)·2H$_2$O [11]. As a representative example of the now measured spectra, Figure 2 shows those of α-Zn(C$_2$O$_4$)$_2$·2H$_2$O.

The spectral assignments, based on those discussed in our previous papers [8-11], are presented in Tables 1 and 2. The comparison of the presented results clearly confirms that there is a strong analogy in the band distribution and their intensity among the different investigated complexes.

Some brief additional comments on the performed assignments are given, as follows:

 - The band related to the stretching motions of water is very strong and well-defined (cf. again Figure 2). Its position suggests that the water hydrogen atoms are involved in relatively strong H-bonds [13,14]. As suggested in the previously investigated cases, it is assumed that the bending mode of water, δ(H$_2$O), is overlapped with the strong IR band at 1620-1630 cm^{-1}. In the lower IR frequency range we have also tentatively assigned two "rocking" modes of these water molecules.

 - The weak features observed in all cases at the lower energy side of the strong ν(O-H) band are probably originated in combinations or overtone modes.

 - The fact that certain bands are only observed in the IR spectrum and others only in the Raman spectrum is in perfect agreement with the local structure of the oxalate ligands in these complexes.

Considering only the two oxalate groups bonded to the cation in a planar arrangement (cf. again Figure 1), the molecular point group of the 13 atoms unit will be D_{2h} and the irreducible representation is given by $\Gamma = 6A_g + 2B_{1g} + 2B_{2g} + 5B_{3g} + 3A_u + 6B_{1u} + 6B_{2u} + 3B_{3u}$. Due to the presence of a symmetry center, the exclusion principle becomes operative and, therefore, phonons with g-parity are only Raman active and those with u-parity are only IR active [11,15].

 - The proposed assignment ν_{as} (COO) > ν_s(COO) is in agreement with the results of former solution studies [16,17] as well as with our recent studies of other metallic oxalates [10,11] and with those of an important number of natural oxalates [15,18].
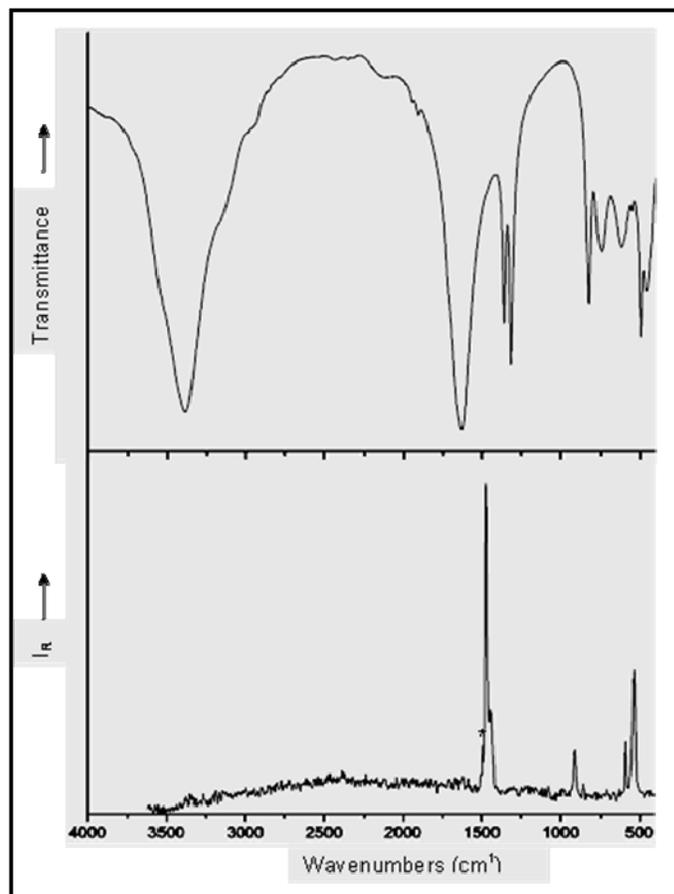
Figure 2. FTIR (above) and FT-Raman spectra (below) of α-ZnC$_2$O$_4$·2H$_2$O in the spectral range between 4000 and 400 cm^{-1} (*this band (1492 cm^{-1})) originates in an instrumental noise).

The ν(C-C) stretching vibrations and the OCO deformational modes are found in ranges which are usual for these vibrations [8-11,17,18].

In order to attain a better insight into the characteristics of the O-H bands and, especially on the origin of some of the lower energy bands, we have measured the IR spectra of partially

deuterated samples of α-Zn(C$_2$O$_4$)$_2$·2H$_2$O, analyzing the observed band shifts using the Teller-Redlich product rule [13]. This analysis is presented in Table 3 and briefly commented, as follows:

- According to the Teller-Redlich product rule, in deuteration experiments the expected ν_H/ν_D ratio must be close to 1.41, although due to coupling and anharmonicity effects this ratio is usually found to lie between 1.2 and 1.4 [13].

- After deuteration the ν(O-H) stretching bands of the water molecules generate a new and strong band centered at 2539 cm^{-1} with a shoulder at 2483 cm^{-1}, which fulfill the above requirement.

- The deformational mode of water appears as a medium intensity band at 1202 cm^{-1}, confirming additionally the assumption that δ(H$_2$O) is overlapped by the intense 1632 cm^{-1} oxalate band.

- The 745 and 618 cm^{-1} bands disappear after deuteration, indicating clearly that they must be related to the proposed librational modes of coordinated water. Besides, the fact that the shift of these bands generates new ones at 554 and 468 cm^{-1}, fulfilling the Teller-Redlich rule, also supports this statement.

- The small shift of the 823 cm^{-1} band, which does not fulfill the mentioned rule, clearly shows that it is not related to water modes. Moreover, the strong 495 cm^{-1} band remains unchanged after deuteration. On the other hand, the 456 cm^{-1} band, assigned to one of the ring modes, could not be identified with certainty in the deuterated samples because it probably suffers a small shift and is overlapped with the new 468 cm^{-1} band which shows some broadening.

Table 1. Assignment of the FTIR and FT-Raman spectra of α-Co(C$_2$O$_4$)$_2$·2H$_2$O and of the FTIR spectrum of α-Ni(C$_2$O$_4$)$_2$·2H$_2$O (Band positions in cm^{-1}).

α-Co(C$_2$O$_4$)$_2$·2H$_2$O		α-Ni(C$_2$O$_4$)$_2$·2H$_2$O	Assignments
Infrared	Raman	Infrared	
3360 vs		3389 vs	ν(OH) (H$_2$O)
3129 sh, 2936 vw		2932 vw	
1627 vs	1620 w	1625 vs	ν_{as}(C-O)
	1472 vs		ν_s (C-O) + ν(C-C)
	1450 w		ν_s(C-O) + δ(OCO)
1359 s, 1315 vs		1360 vs, 1316 vs	ν_s(C-O) + δ(OCO)
	914 m		ν(C-C)
825 s		829 s	ν_s(C-C) + δ(OCO)
745 m, 618 m		752 m, 625 m	ρ(H$_2$O)
	588 w, 531 m		δ_{ring}
492 s, 466 sh		488 s, 453 sh	δ_{ring}

vs, very strong; s, strong; m, medium; w, weak; sh, shoulder.

Table 2. Assignment of the FTIR and FT-Raman spectra of α-Zn$(C_2O_4)_2\cdot2H_2O$ (Band positions in cm^{-1}).

Infrared	Raman	Assignments
3383 vs		ν(OH) (H$_2$O)
3157 sh, 2947 vw		
1632 vs		ν_{as}(C-O)
	1472 vs	ν_s (C-O) + ν(C-C)
	1442 w	ν_s(C-O) + δ(OCO)
1364 s, 1320 vs		ν_s(C-O) + δ(OCO)
	914 m, 855 vw	ν(C-C)
823 s		ν_s(C-C) + δ(OCO)
745 m, 618 m		ρ(H$_2$O)
550 vw	588 m, 536 s	δ_{ring}
495 s, 456 m		δ_{ring}

vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder.

Table 3. Analysis of the band shifts of α-Zn$(C_2O_4)_2\cdot2H_2O$ after partial deuteration (Band positions in cm^{-1})

Normal sample/Table 2	Partially deuterated sample	ν_H/ν_D
3383 vs	2539 vs, 2483 sh	1,33/1,36
ca. 1632 (overlapped)	1202 m	1,36
823 vs	813 vs	1,01
745 m	554 m	1,35
618 m	468 m	1.32
495 s	496 s	
456 m	(see text)	

vs, very strong; s, strong; m, medium; sh, shoulder.

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