



STRUCTURAL AND SPECTROSCOPIC BEHAVIOR OF DOUBLE METAL OXALATES FROM THE FIRST TRANSITION METAL SERIES

María C. D'Antonio^{1,2}, María M. Torres^{1,2}, Daniel Palacios^{1,2},
Ana C. González-Baró³, Vicente L. Barone³ and Enrique J. Baran^{3,*}

¹ Dto. de Cs. Exactas y Naturales, Un. Nac. de la Patagonia Austral, 9400-Río Gallegos, Argentina.

² Dto. de Cs. Básicas, UTN-Facultad Regional Santa Cruz, 9400-Río Gallegos, Argentina.

³ Centro de Química Inorgánica (CEQUINOR, CONICET/UNLP), Fa. de Cs. Exactas, UNLP, 1900-La Plata, Argentina.

* Autor Corresponsal: baran@quimica.unlp.edu.ar

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Resumen

Se preparó y caracterizó una serie de oxalatos dobles de estequiometría $MM'(C_2O_4)_2 \cdot 4H_2O$ (con $MM' = MnCo, MnNi, MnZn, CoNi, CoCu, CoZn, NiCu, NiZn$ y $CuZn$). Su comportamiento estructural fue investigado por medio de difracción de rayos X en polvos, mostrando una fuerte analogía estructural con la fase ortorrómbica, llamada forma- β , de los oxalatos complejos simples de composición $MC_2O_4 \cdot 2H_2O$. El comportamiento espectroscópico vibracional de estos oxalatos dobles fue investigado por espectroscopía de infrarrojo y Raman. Los resultados obtenidos confirmaron claramente las fuertes analogías estructurales existentes entre las series de complejos $MM'(C_2O_4)_2 \cdot 4H_2O$, $\beta-MC_2O_4 \cdot 2H_2O$ y $\alpha-MC_2O_4 \cdot 2H_2O$.

Abstract

A series of double metal oxalates of stoichiometry $MM'(C_2O_4)_2 \cdot 4H_2O$ (with $MM' = MnCo, MnNi, MnZn, CoNi, CoCu, CoZn, NiCu, NiZn$ and $CuZn$) have been prepared and characterized. Their structural behavior was investigated by means of X-ray powder diffractometry, showing a strong structural analogy to the orthorhombic, so-called β -modification, of the related simple oxalate complexes of composition $MC_2O_4 \cdot 2H_2O$. The vibrational spectroscopic behavior of the double metal oxalates was investigated by infrared and Raman spectroscopy. The results clearly confirmed the close structural analogies between the $MM'(C_2O_4)_2 \cdot 4H_2O$, $\beta-MC_2O_4 \cdot 2H_2O$ and $\alpha-MC_2O_4 \cdot 2H_2O$ series of complexes.

Palabras clave: Oxalatos metálicos dobles; difracción de rayos X en polvos; características estructurales; espectros de IR y Raman; comportamiento vibracional.

Keywords: Double metal oxalates; X-ray powder diffractometry; structural characteristics; IR and Raman spectra; vibrational behavior.

1. Introduction

In previous papers, we have investigated the vibrational-spectroscopic behavior of different oxalate complexes of the type $M^{II}C_2O_4 \cdot 2H_2O$ [1-4]. The complexes 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 Fig. 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 metal center. The two polymorphic forms originate in small differences of the three-dimensional pile up of successive sheets, which causes a rearrangement of the hydrogen bonds between the sheets [5,6].

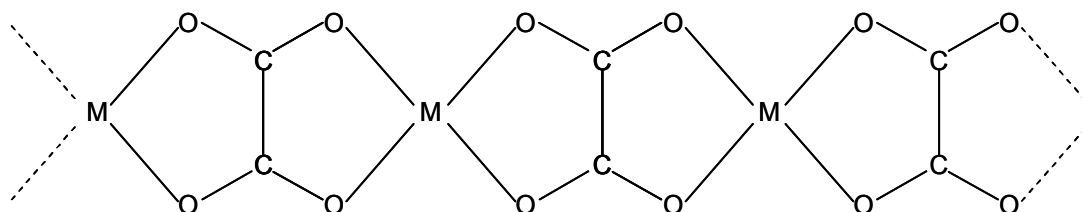


Figure 1. Schematic drawing of the infinite chain arrangement present in M^{II} -oxalates of composition $MC_2O_4 \cdot 2H_2O$.

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 [6] and, in the case of $M^{II} = Zn$ only the α -form has been characterized [4,6]. On the other hand, the related $Cu(II)$ complex, $CuC_2O_4 \cdot nH_2O$ (synthetic moolooite), basically presents the structure depicted in Fig. 1, containing only a small proportion of water, of zeolitic nature [5-7].

Also, some double metal oxalates of the type $MM'(C_2O_4)_2 \cdot 4H_2O$ (with $MM' = MnCo, MnNi, MnCu, MnZn, CoNi, CoCu, CoZn, NiCu, NiZn$ and $CuZn$ have been described some years ago [8]. Therefore, it appears interesting to prepare these species and compare their general structural and spectroscopic behavior with those of the previously investigated simple oxalates.

2. Materials and Methods

Synthesis of the compounds

The investigated double oxalates, of composition $MM'(C_2O_4)_2 \cdot 4H_2O$ were prepared according to the methodology of ref. [8], as follows: To 20 mL of an aqueous 0.2 M solution of $MCl_2 \cdot nH_2O$ at $\sim 90^\circ C$, 20 mL of a hot (*ca.* $90^\circ C$) 0.8 M solution of oxalic acid was added with stirring. To this

solution, 20 mL of a hot aqueous solution of 0.2 M $M'Cl_2 \cdot nH_2O$ was dropwise added. After a few minutes the complexes precipitated out. They were separated by filtration, washed with hot water and finally dried in vacuum over H_2SO_4 . The purity of the obtained complexes was checked by elemental analysis (C and H) using a Carlo Erba model EA 1108 elemental analyzer. The water content was determined by heating a known sample amount to a constant weight at 100 °C, 120 °C, and 150 °C and determining the loss of weight.

In this way, all of the previously described double metal oxalates were obtained, except $CuMn(C_2O_4)_2 \cdot 4H_2O$ which could not be prepared despite the numerous attempts and variations in the synthetic procedure that were performed. As shown by the X-ray powder diagrams the main product in this case was always $CuC_2O_4 \cdot nH_2O$ (clearly identified by its characteristic powder diagram [9]) accompanied by traces of other, not identified, by-products.

Structural studies

The obtained complexes were characterized by X-ray powder diffractometry, using a continuous step scanning procedure (step size: 0.020° (in 2 θ); time per step: 0.5 s), with a Philips PW 1710 diffractometer and monochromatic (Ni-filtered) Cu- K_α radiation ($\lambda = 1.5418 \text{ \AA}$), using NaCl as an external calibration standard. The indexation of the powder diagrams and calculation of unit cell parameters were carried out using a locally modified version of the program PIRUM of Werner [10].

Vibrational spectra

The infrared spectra, in the spectral range between 4000 and 400 cm^{-1} , were recorded with a FTIR-Bruker-EQUINOX-55 spectrophotometer, using the KBr pellet technique. Raman spectra were obtained in the same spectral range with a Thermo Scientific DXR Raman microscope, using the 532 nm line of a Thermo Scientific solid-state laser diode pump for excitation.

3. Results and Discussion

3.1. Structural characteristics

As mentioned in the Introduction, the dihydrated metal oxalates of stoichiometry $M^{II}(C_2O_4) \cdot 2H_2O$, with $M^{II} = Mg, Fe, Co$ and Ni present two polymorphic forms, called α - and β -modifications. Thermodynamically, the α -modification is the most stable form and the $\beta \rightarrow \alpha$ transformation is irreversible [6,11].

The structural characteristics of the now prepared double-metal oxalates were derived from the analysis of the corresponding X-ray powder diffractograms. These diagrams are practically identical for the full series of complexes, and show a close relationship to that of the β -modification of the $M^{II}(C_2O_4) \cdot 2H_2O$ complexes.

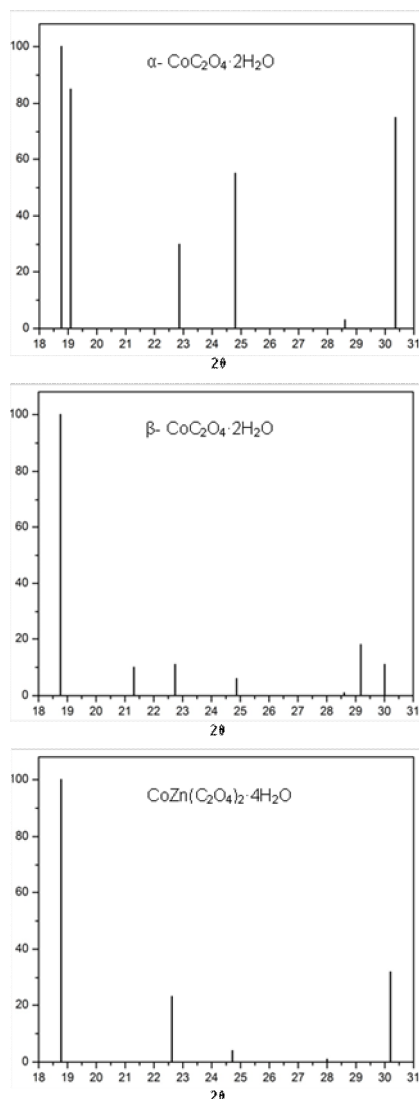


Figure 2. Comparison of the powder diagrams of $\alpha\text{-CoC}_2\text{O}_4\cdot 2\text{H}_2\text{O}$, $\beta\text{-CoC}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ and $\text{CoZn}(\text{C}_2\text{O}_4)_2\cdot 4\text{H}_2\text{O}$ in the 2θ range between 18 and 30° .

To emphasize these relationships, in Fig. 2 we present a comparison of the powder diagrams of $\alpha\text{-Co}(\text{C}_2\text{O}_4)\cdot 2\text{H}_2\text{O}$ [12], $\beta\text{-Co}(\text{C}_2\text{O}_4)\cdot 2\text{H}_2\text{O}$ [12], and $\text{CoZn}(\text{C}_2\text{O}_4)_2\cdot 4\text{H}_2\text{O}$. All the double oxalates could be indexed in the orthorhombic system, but with an indexing difference from that of $\beta\text{-Co}(\text{C}_2\text{O}_4)\cdot 2\text{H}_2\text{O}$, suggesting a different but closely related space group which, unfortunately, could not be established with certainty. In Table 1 we present the unit cell parameters calculated for all the investigated double metal oxalates.

An analysis of the presented data shows that the unit cell parameters of all the oxalates appear in relatively restricted ranges (a between 12.03 and 12.25 Å; b between 5.44 and 5.94 Å, and c between 15.07 and 15.81 Å) whereas the volumes of the unit cell extended between 1036.53 and 1092.09 Å³.

Table 1. Unit cell parameters determined for the $MM'(C_2O_4)_2 \cdot 4H_2O$ oxalate complexes.

MM'	<i>a</i> [Å]	<i>b</i> [Å]	<i>c</i> [Å]	Vol. [Å³]
CoCu	12.09(2)	5.44(6)	15.76(3)	1036.53
CoNi	12.06(2)	5.46(1)	15.77(2)	1038.42
MnZn	12.12(3)	5.46(1)	15.78(7)	1044.24
NiZn	12.03(3)	5.51(1)	15.76(7)	1044.66
CuZn	12.14(1)	5.55(1)	15.52(1)	1045.69
MnNi	12.12(2)	5.46(1)	15.81(6)	1046.23
MnCo	12.25(3)	5.58(1)	15.56(2)	1063.60
NiCu	12.24(1)	5.62(1)	15.59(2)	1072.42
CoZn	12.20(3)	5.94(1)	15.07(3)	1092.09

Experimental densities determined pycnometrically, using benzene as the working liquid, varied between 2.20 and 2.40 g/cm³, supporting that the number of formulas in the unit cell (*Z*) is always *Z* = 4.

On the other hand, it is interesting to remark that it was not possible to find any direct relationship between the ionic radii of the involved cations and the unit cell parameters, suggesting a certain degree of disorder in the cationic distribution. The effective ionic radii in octahedral coordination, and high-spin electronic configuration, follow the order $Mn^{2+}(0.97 \text{ Å}) > Co^{2+}(0.88 \text{ Å}) \sim Zn^{2+}(0.88 \text{ Å}) > Cu^{2+}(0.87 \text{ Å}) > Ni^{2+}(0.83 \text{ Å})$ [13], but this order is not reflected in any way in the data presented in Table 1.

3.2. Vibrational spectra

In our previous papers we have demonstrated that the vibrational (IR and Raman) spectra of the α - and β -modifications of the $M(C_2O_4) \cdot 2H_2O$ complexes are totally identical, confirming the close structural relationship between them [1-3]. Therefore, this methodology is not useful to distinguish between these two polymorphic forms.

The FTIR spectra of the now prepared $MM'(C_2O_4)_2 \cdot 4H_2O$ complexes are also similar to those recorded for the two polymorphs of the simple dihydrated oxalates. On the other hand, the spectra of all these double metal oxalates are practically identical. The only very small difference between them is the structure of the most intense and strong IR band. In the case of the oxalates with $MM' = ZnMn$, $NiCo$, and $NiMn$ this band is somewhat broader as in the other cases, presenting also a weak shoulder on the higher energy side.

As examples of the measured spectra, Fig. 3 shows the FTIR and Raman spectra of $ZnMn(C_2O_4)_2 \cdot 4H_2O$ and Fig. 4 those of $ZnCo(C_2O_4)_2 \cdot 4H_2O$. The assignment of both pairs of spectra is presented in Table 2.

Considering that the vibrational unit conformed by the two oxalate groups bonded to the cations in a planar arrangement, as depicted in Fig. 1, possesses the approximate D_{2h} point group, whose irreducible representation is given by $\Gamma = 6A_g + 2B_{1g} + 2B_{2g} + 5B_{3g} + 3A_u + 6B_{1u} + 6B_{2u}$

+ $3B_{3u}$ (*cf.* also [2-4]). Due to the presence of a symmetry center one may expect the operativity of the so-called exclusion principle and, therefore, phonons with u-parity are only IR active and those with g-parity are only Raman active, a fact that becomes immediately apparent by inspection of the results presented in Table 2.

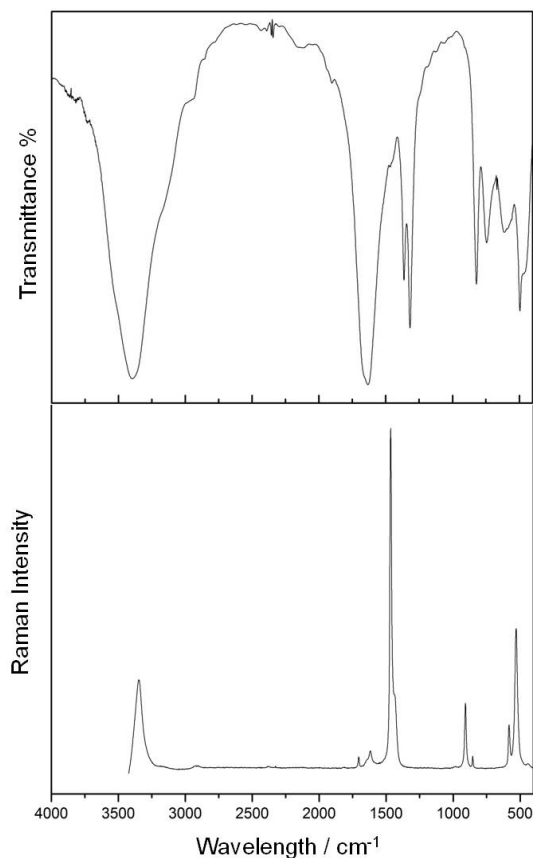


Figure 3. FTIR (above) and Raman spectra (below) of $ZnMn(C_2O_4)_2 \cdot 4H_2O$.

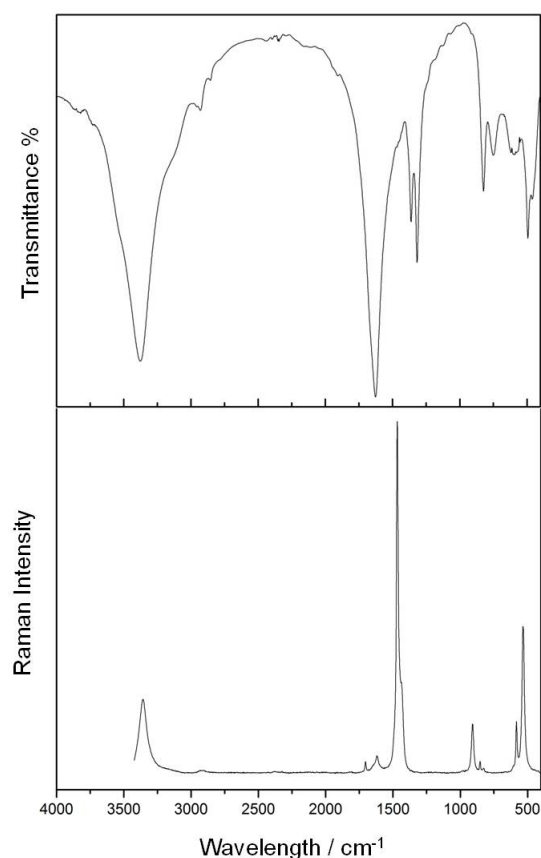


Figure 4. FTIR (above) and Raman spectra (below) of $ZnCo(C_2O_4)_2 \cdot 4H_2O$.

Table 2. Assignments of the FTIR and FT-Raman spectra of $ZnMn(C_2O_4)_2 \cdot 4H_2O$ and of $ZnCo(C_2O_4)_2 \cdot 4H_2O$ (Band positions in cm^{-1}).

$ZnMn(C_2O_4)_2 \cdot 4H_2O$		$ZnCo(C_2O_4)_2 \cdot 4H_2O$		Assignments
Infrared	Raman	Infrared	Raman	
3542 sh				
3398 vs	3348 s	3372 vs	3356 s	$\nu(OH) (H_2O)$
3164 sh	3173 sh	3123 sh		
1667sh, 1632vs	1705vw, 1617vw	1627 vs	1704vw, 1619vw	$\nu_{as}(CO)$
	1466 vs		1467 vs	$\nu_s(C-O)+\nu(C-C)$
	1441 sh		1437 sh	$\nu_s(C-O)+\delta(OCO)$
1363s, 1318 vs		1362s, 1318 vs		$\nu_s(C-O)+\delta(OCO)$
	908 m 854 vw		908 m, 852 vw	$\nu(C-C)$
820 s		823 s		$\nu(C-C)+\delta(OCO)$
743 m, 668 m		750 m, 588 m		$\rho(H_2O)$
	582 m, 530 s		582 m, 534 s	δ_{ring}
495 s, 455 sh		493 s, 461 sh		δ_{ring}

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

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

- The strongest IR band corresponds to the antisymmetric carboxylate stretching vibration, $\nu_{\text{as}}(\text{CO})$, whereas the strongest Raman line is assigned to the respective symmetric stretching, partially coupled with one of the $\nu(\text{C-C})$ modes.
- The fact that the $\nu_{\text{as}}(\text{CO})$ vibration generates also two very weak signals in the Raman spectra, suggests the presence of either weak coupling or distortional effects in the unit cell, which partially activate originally forbidden vibrations.
- The proposed assignment $\nu_{\text{as}}(\text{CO}) > \nu_{\text{s}}(\text{CO})$ is in agreement with the results of former solution studies [14,15] as well as with our own studies of other metal oxalate complexes [1-4].
- The $\nu(\text{C-C})$ stretching vibrations and OCO deformation modes are found in ranges that are usual for these vibrations [1-4,15].
- The band related to the stretching motions of the water molecules is very strong and well defined in the IR spectra and somewhat weaker in the Raman spectra. Its position suggests that the water hydrogen atoms are involved in relatively strong H-bonds [16,17]. As suggested in other previously investigated cases, it is assumed that the bending mode of water, $\delta(\text{H}_2\text{O})$, is overlapped by the strongest IR band and attains not enough intensity in the Raman spectra.
- The assignments in the lower-frequency range, and especially that of one of the torsion modes of the bound water molecules, $\rho(\text{H}_2\text{O})$, are also supported by our previous deuteration experiments with related complexes [2-4].

4. Conclusions

A series of double metal oxalates of composition $\text{MM}'(\text{C}_2\text{O}_4)_2 \cdot 4\text{H}_2\text{O}$ ($\text{MM}' = \text{MnCo}, \text{MnNi}, \text{MnZn}, \text{CoNi}, \text{CoCu}, \text{CoZn}, \text{NiCu}, \text{NiZn}, \text{and CuZn}$) were prepared and characterized. X-ray powder diffractometry shows that they present a strong structural analogy to the so-called β -modification of the related simple oxalates of the type $\text{MC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. This fact is highly exciting because in these simple oxalates the α -modification is the thermodynamically most stable form. Besides, the vibrational spectroscopic behavior of both groups of complexes is totally similar, confirming additionally the close structural analogies between the $\text{MM}'(\text{C}_2\text{O}_4)_2 \cdot 4\text{H}_2\text{O}$, α - $\text{MC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and β - $\text{MC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ complexes.

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