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Synthesis and structural characterization of mixed transition metal derivatives of maleic acid: $(M^{2+}_{0.5}\,Fe^{2+}_{0.5})(C_4H_3O_4)^-_2{\cdot}4H_2O$ (with M^{2+}=Mn, Co, Ni, and Zn) using powder diffraction data

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Abstract. Four mixed metal derivatives of maleic acid with general formula, $(M^{2+}_{0.5}\,Fe^{2+}_{0.5})(C_4H_3O_4)^-_2{\cdot}4H_2O$ (M^{2+}=Mn, Co, Ni, and Zn) were prepared by slow evaporation at room temperature of the aqueous solutions containing the metal carbonates and maleic acid. The X-ray powder diffraction data of the prepared materials, collected with a SIEMENS D5005 diffractometer, showed that they are isostructural and crystallize in a triclinic unit cell similar to the cell of the parent single cation maleates. The unit cell volume of the synthesized mixed metal derivatives varies linearly between that of the Ni complex (V = 319.15(8) Å^3: *a*=5.213(1) Å, *b*=7.349(2) Å, *c*=9.194(2) Å, α=108.77(2)º, β=104.65(3)º, γ=93.11(2)º) and that of the Mn-derivative (V=327.8(1) Å^3: *a*=5.296(2) Å, *b*=7.371(2) Å, *c*=9.326(4) Å, α=109.59(3)º, β=104.70(2)º, γ=93.35(3)º). Rietveld refinements confirmed the isostructural nature of this family of compounds.

Introduction

Transition metal carboxylates have been extensively studied because they exhibit a great variety of structural arrangements and interesting physical and chemical properties. When the parent carboxylic acid is unsaturated, potentially interesting reactivity patterns may be observed upon heating and/or irradiation of the materials in the solid state, as has been reported over the years [1-8]. Additionally, mixed metal carboxylates can be used as precursors to mixed metal oxides with catalytic activity. In particular, maleates of the type (Cu_XZn_{1-X})

$C_4H_2O_4 \cdot 2H_2O$ have been used in the preparation of solid solutions of $Cu_XZn_{1-X}O$ [9]. Thermal decomposition of iron containing mixed metal maleates has also been used as a route for the preparation of several ferrites [10]. Thus, the possibility of having metal derivatives with an important fraction of paramagnetic elements prompted us to prepare and structurally characterize mixed transition metal complexes of maleic acid, with general chemical composition $(M^{2+}_{0.5}\ Fe^{2+}_{0.5})(C_4H_3O_4)^-_2 \cdot 4H_2O$; M^{2+}=Mn, Co, Ni and Zn. In this contribution, we report the X-ray powder diffraction patterns of these materials. It must be mentioned that they are isostructural with the single metal complexes $(M^{2+}(C_4H_3O_4)^-_2 \cdot 4H_2O$; M^{2+} = Mn, Fe, Co, Ni and Zn) which crystallize in space group $P\bar{1}$ with $Z = 1$ [11-14]. As expected, these materials show different magnetic behavior depending on the nature of the M^{2+} atom. The results of these studies will be reported elsewhere.

Synthesis

The syntheses of the materials under study were carried out by combining maleic acid ($C_4H_4O_4$) with the two metal carbonates of interest (MCO_3, where M^{2+} = Mn, Fe, Co, Ni and Zn) in molar proportions 4:1:1, respectively, in warm aqueous solutions. These mixtures were continuously stirred for 2 to 3 hours. Then, they were filtered and the filtrates were allowed to evaporate slowly at ambient temperature over a period of 2 to 3 weeks. The resulting crystals were separated from the solutions and dried over filter paper at room temperature. The color of the crystals varied from light yellow for the Fe-Mn and Fe-Zn complexes, to olive-green for the Fe-Ni complex, to light purple for the Fe-Co complex.

Diffraction data collection

A small fraction of each sample was carefully ground in an agate mortar and passed through a sieve to obtain a grain size less than 53 μm. They were dusted on top of a Si (510) single crystal specimen support (The Gem Dogout), which had been previously coated with a very thin layer of Vaseline grease. This support was allowed to rotate at 15 rpm during the data collection. The diffraction patterns were recorded at 293K in θ-θ configuration on a SIEMENS D5005 diffractometer equipped with a secondary graphite monochromator and a scintillation detector, using CuKα radiation (λ = 1.5418 Å) and operated at 40 kV and 30 mA. Fixed scatter and divergence slits of 1° and a 0.1 mm receiving slit were used. The data were registered in the interval of 5-70° (2θ), in steps of 0.01° with a counting time of 24 s/step. The profile fit of each pattern was carried out with the MDI JADE 5 software [15]. The positions of the diffraction maxima were established after profile fitting the pattern using split Pearson funtions.

Results and discussion

The X-ray powder diffraction patterns recorded for the mixed transition metal complexes of maleic acid prepared are shown in figure 1.

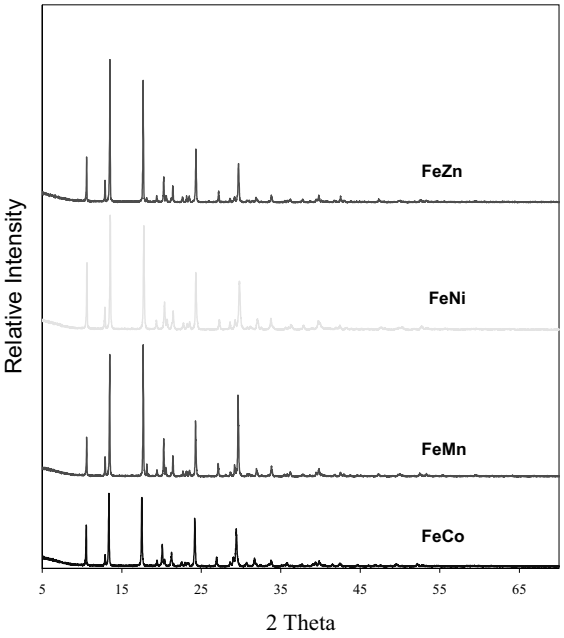

Figure 1. X-Ray Powder Diffraction Patterns obtained for the series ($M^{2+}_{0.5}$ $Fe^{2+}_{0.5}$)$(C_4H_3O_4)^-_2 \cdot 4H_2O$; ($M^{2+}$ = Mn, Co, Ni and Zn)

The similary of the patterns clearly indicates the isostructural nature of these materials. They exhibit the same structure type as the single metal complexes (Mn, Fe, Co, Ni, and Zn). The positions of the diffraction maxima were established from the fit of the diffraction profiles using a Pearson VII function. The four complete diffraction datasets were reviewed by means of the program NBS*AIDS83 [16] using the structural data previously reported for single metal complexes [11-14]. All the observed maxima were indexed in their reported triclinic unit cells. The unit cell parameters obtained are presented in Table I, together with the de Wolf [17] and Smith-Snyder [18] figures of merit.

Figure 2 shows the plot of the unit cell volume *versus* the average ionic radius ($r^{2+}_{av.}$) of the transition metals for the different mixed metal maleate complexes prepared. The average ionic radius has been defined as $r^{2+}_{av.} = (r^{2+}_{M} + r^{2+}_{Fe.})/2$. The effective ionic radii for the M^{2+} cations (Mn, Fe, Co, Ni and Zn) were obtained from Shannon [19], considering octahedral coordinations for all the cations and high spin configurations for the Mn^{2+}, Fe^{2+}, and Co^{2+} ions.

*Table 1. Crystal Data obtained for ($M^{2+}_{0.5}$ $Fe^{2+}_{0.5}$)$(C_4H_3O_4)^-_2 \cdot 4H_2O$;($M^{2+}$ = Mn, Co, Ni and Zn) after NBS*AIDS83.*

	(FeMn)HMal	(FeCo)HMal	(FeNi)HMal	(FeZn)HMal
a (Å)	5.296(2)	5.235(1)	5.213(1)	5.243(1)
b (Å)	7.371(2)	7.352(2)	7.349(2)	7.340(2)
c (Å)	9.326(4)	9.246(2)	9.194(2)	9.240(2)
α(°)	109.59(3)	109.28(2)	108.77(2)	108.94(2)
β(°)	104.70(2)	104.72(2)	104.65(3)	104.69(2)
γ(°)	93.35(3)	93.29(3)	93.11(2)	93.30(2)
V(Å)	327.8(1)	321.4(1)	319.15(8)	321.47(9)
M_{20}	21.7	45.7	50.5	33.2
F_{30}	28.4 (0.0082,54)	52.9 (0.0123,43)	28.0 (0.0098,58)	47.4 (0.0093,40)

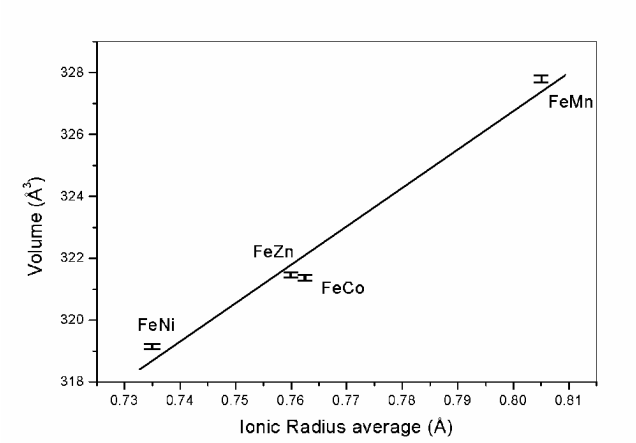

Figure 2. Unit cell volume as a function of $r^{2+}_{av.}$ *in the (* $M^{2+}_{0.5}$ $Fe^{2+}_{0.5}$ *)*$(C_4H_3O_4)^-_2 \cdot 4H_2O$*; system.*

The observed linear dependence of the unit cell volume as a function of $r^{2+}_{av.}$ is consistent with the formation of solid solutions in the ($M^{2+}_{0.5}$ $Fe^{2+}_{0.5}$)$(C_4H_3O_4)^-_2 \cdot 4H_2O$ system. It must be mentioned that single crystal studies carried out in some of these mixed complexes have confirmed that both metal atoms occupy the crystallographic positions assigned to the metal positions in the single $M^{2+}(C_4H_3O_4)^-_2 \cdot 4H_2O$ complexes.

As an example of the Rietveld refinements carried out with WinMProf [20], figure 3 shows the final plot for ($Ni^{2+}_{0.5}$ $Fe^{2+}_{0.5}$)$(C_4H_3O_4)^-_2 \cdot 4H_2O$. Reasonable residuals were obtained: R_{EXP}=14.82; R_I=5.07; R_P=16.90; R_{WP}=18.68; S=1.590. The similarity of the structural parameters obtained in the refinement with those previously reported for the single metal complexes confirmed the isostructural nature of these materials. In this structure, the metal atoms coordinate six oxygen atoms: two from two maleate ligands and four from water molecules

(figure 4). The oxygen atoms are arranged in a slightly distorted octahedral environment. Inspection of the figure also shows that the maleate moiety behaves as a monodentate ligand.

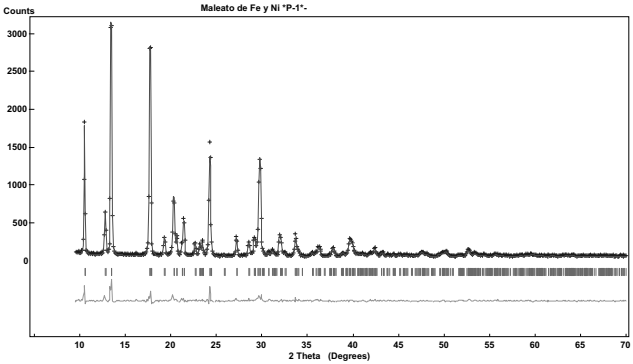

Figure 3. Final Rietveld refinement plot for $(Ni_{0.5}^{2+}\ Fe_{0.5}^{2+})(C_4H_3O_4)^-_2 \cdot 4H_2O$.

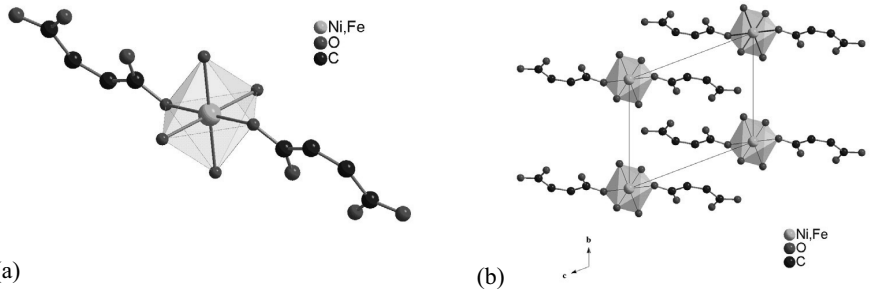

Figure 4. (a) Coordination enviroment of (Ni,Fe) and (b) projection of the structure along the **a**-*axis in* $(Ni_{0.5}^{2+}\ Fe_{0.5}^{2+})(C_4H_3O_4)^-_2 \cdot 4H_2O$.

Conclusion

The mixed metal derivatives of the $(M_{0.5}^{2+}\ Fe_{0.5}^{2+})(C_4H_3O_4)^-_2 \cdot 4H_2O$ (M^{2+}=Mn, Co, Ni and Zn) system are isostructural and exhibit the same crystal structure type as the single metal complexes. The plot of the unit cell volume *vs*. the average of the ionic radii is consistent with the formation of a solid solution in this system. The Rietveld refinement confirms the nature of the structure.

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