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Interaction of Metal-ions with Humic-like Models. Part 8*. Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) Complexes of 2,4-Dihydroxybenzoic Acid

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Interest in model compounds of metal complexes of humic acids prompted us to investigate the metal derivatives of 2,x-dihydroxybenzoic acids. Previous investigations on metal dihydroxybenzoates (DHB) gave direct evidence that the phenolic groups, unless deprotonated, are never involved as primary binding sites toward metal ions (Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+} and UO_2^{2+} with 2,6-DHB; Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+} and Cd^{2+} with 2,5-DHB) [1–3]. Only in the case of copper(II) the phenolic groups have been found to be responsible for long intermolecular axial contacts toward the metal ion [1, 3].

Nevertheless, the presence and the position of the phenolic functions in the phenyl ring have a remarkable effect on the coordination set and the geometry of the corresponding metal complexes.

Further support to these findings has been given by the comparative examination of the structure of the complexes formed by 2,6-dimethoxybenzoic acid [4–5].

The purpose of this report was to investigate the effects produced by 2,4-phenolic substitutions in the above class of ligands. Complexes with Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) have been synthesized and, based on structural and spectroscopic analysis, characterized as $[Mn(2,4\text{-}DHB)_2(H_2O)_4]$, $[Co(2,4\text{-}DHB)_2(H_2O)_4]\cdot 4H_2O$, $[Ni(2,4\text{-}DHB)_2(H_2O)_4]\cdot 4H_2O$, $[Cu(2,4\text{-}DHB)_2(H_2O)_2]\cdot 5H_2O$ and $[Zn(2,4\text{-}DHB)_2(H_2O)_4]$, respectively.

Experimental

Materials

2,4-Dihydroxybenzoic acid (Merck) was recrystallized twice from water.

Preparation of Complexes

All the compounds were prepared by adding stoichiometric amounts of metal salts (acetate or sulphate) to 2,4-dihydroxybenzoic acid in water at pH 4–5. The resulting solutions were allowed to evaporate at room temperature or cooled. Solid compounds separated, which were filtered, washed with water and air-dried.

Analytical and Spectroscopic Measurements

The instrumentation and techniques used in obtaining analytical and spectroscopic data are those described previously [1]. Analytical data are listed in Table I.

Results

Preliminary results of single X-ray diffraction analysis show that in the nickel complex the metal ion is six-coordinate, being surrounded by four water molecules and two *trans* monodentate carboxylate groups. Except the copper complex, all the other compounds are assigned coordination geometries and donor sets similar to those for the nickel complex, as inferred from the examination of the spectral results summarized below.

TABLE I. Analytical Data[a].

Compound	%C	%H	$\%H_2O^b$
$[Mn(2,4\text{-}DHB)_2(H_2O)_4]$	38.43(38.81)	4.21(4.19)	16.5(16.63)
$[Co(2,4\text{-}DHB)_2(H_2O)_4]\cdot 4H_2O$	33.12(33.02)	5.01(5.14)	28.0(28.30)
$[Ni(2,4\text{-}DHB)_2(H_2O)_4]\cdot 4H_2O$	32.91(33.03)	4.97(5.15)	28.0(28.31)
$[Cu(2,4\text{-}DHB)_2(H_2O)_2]\cdot 5H_2O$	33.85(33.91)	4.78(4.88)	25.0(25.43)
$[Zn(2,4\text{-}DHB)_2(H_2O)_4]$	37.83(37.90)	4.02(4.09)	16.0(16.24)
$Na(2,4\text{-}DHB)\cdot H_2O$	43.27(43.31)	3.74(3.63)	9.0(9.28)

[a] Calculated values are in parentheses. [b] Thermogravimetric determination.

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*For part 7 see Ref. 3.

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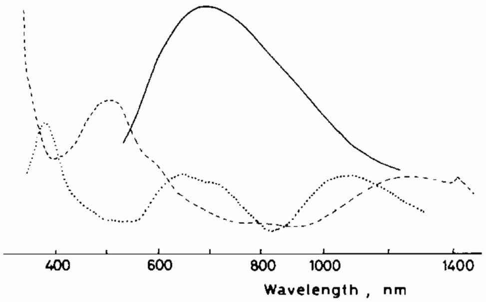

Fig. 1. Reflectance absorption spectra of [Cu(2,4-DHB)$_2$-(H$_2$O)$_2$]·5H$_2$O (——), [Ni(2,4-DHB)$_2$(H$_2$O)$_4$]·4H$_2$O (·····) and [Co(2,4-DHB)$_2$(H$_2$O)$_4$]·4H$_2$O (-----).

TABLE II. IR Absorptions (cm^{-1})^a.

Compound	ν_s(COO)	ν_{as}(COO)	$\Delta\nu$
Na(2,4-DHB)·H$_2$O	1420s	1575s	155
[Co(2,4-DHB)$_2$(H$_2$O)$_4$]·4H$_2$O	1420s	1560s	140
[Ni(2,4-DHB)$_2$(H$_2$O)$_4$]·4H$_2$O	1420s	1560s	140
[Mn(2,4-DHB)$_2$(H$_2$O)$_4$]	1425s	1565s	140
[Zn(2,4-DHB)$_2$(H$_2$O)$_4$]	1425s	1565s	140
[Cu(2,4-DHB)$_2$(H$_2$O)$_2$]·5H$_2$O	1380sh	1575s	195

[a] s = strong, sh = shoulder.

The reflectance absorption spectra of the Co and Ni compounds are indicative of an almost regular O$_6$ coordination around the metal ion (Fig. 1). The spectra show also striking resemblance to those of the analogous 2,5-dihydroxybenzoate complexes [3], where coordination environments similar to that observed for [Ni(2,4-DHB)$_2$(H$_2$O)$_4$]·4H$_2$O take place. On the other hand, the energy value of the d–d absorption maximum of the copper(II)–2,4-DHB complex rules out an approximately regular octahedral geometry and supports a marked distortion. Really, both the electronic absorption maximum (710 nm) and the g values of the powder ESR spectrum (g_1 = 2.326, g_2 = 2.131, g_3 = 2.066) of the complex compare rather well to those for [Cu-(2,6-DHB)$_2$(H$_2$O)$_2$] [1], where copper is surrounded by two water molecules and two monodentate carboxylate groups in the plane and forms long axial contacts with phenolic oxygens of adjacent molecules.

Also, the overall features of the IR spectra distinguish the Cu complex from the Mn, Co, Ni and Zn analogues. Instead, comparison of the spectra of Co and Ni with those of Mn and Zn shows only minor differences, which may be related to the presence of lattice water molecules in the former complexes. All the compounds display carboxylate absorptions typical for monodentate coordination (Table II). However, the $\Delta(\nu_{as} - \nu_s)$ value for the Cu complex is higher than for the other compounds thus indicating dissimilar bonding (and/or non bonding) interactions involving the carboxylate groups.

Conclusion

From the comparative examination of the solid-state structures of metal complexes formed by 2,x-dihydroxybenzoic acids (x = 4, 5 and 6) it appears that phenolic groups show a tendency to be involved in hydrogen-bonding rather than in metal coordination.

On the other hand, depending on the relative position of the phenolic groups, the ligands have different tendencies when taking part in the inner coordination sphere of metal ions, probably due to the different stability of the resulting hydrogen-bonding networks. Indeed, metal–ligand interactions of outer-sphcre nature are allowed with 2,6-DHB [1], whereas the shift of a phenolic group from the position x = 6 to x = 4 or 5 restores coordinative properties more typical for carboxylate ligands.

Finally, in these complexes copper(II) always displays a different coordination behaviour in comparison with Mn, Co, Ni and Zn divalent ions, which all exhibit very similar, ligand-dependent, coordination geometries.

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