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Interaction of Metal Ions with Humic-like Models. Part VII*. Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) Complexes of 2,5-Dihydroxybenzoic Acid

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Abstract

Complexes of formula $M(2,5\text{-DHB})_2 4H_2O$ (M = Mn, Co, Ni, Zn, Cu and Cd; 2,5-DHB = 2,5-dihydroxybenzoate) were prepared and characterized by means of infrared and electronic spectroscopy, and by electron spin resonance. For the Zn complex the crystal and molecular structure was also determined by single-crystal X-ray diffraction analysis. The crystal is orthorhombic, space group *Pbca* (No. 61), with a = 18.503(4), b = 13.536(3), c = 6.900(2) Å, and Z = 4. The final refinement used 877 reflections and gave a residual R value of 0.041. The complex has slightly compressed octahedral coordination, with the zinc atom bound to two monodentate carboxylate groups lying in *trans* positions and four water molecules. X-ray data and infrared spectra show the Mn, Co, Ni, Zn and Cd complexes to be isostructural with the Zn compound. The electronic, infrared and ESR spectra of the copper(II) complex are consistent with a CuO_4-based chromophore involving two water molecules and two monodentate carboxylate groups in the metal plane, and long axial contacts.

Introduction

It is widely accepted that metal binding to soil humic matter involves the participation of polyhydroxybenzoate units [1]. In this connection we have carried out comparative structural investigations on the metal complexes formed by 2,6-dihydroxybenzoic and 2,6-dimethoxybenzoic acids [2–5] in order to show the influence of phenolic substitutions on the coordination behaviour of this type of ligand. It has been found that the ion surrounding and the molecular arrangement in the complexes are largely dependent on the presence of free phenolic functions which are responsible for strong hydrogen bond interactions within the structure.

In order to investigate further the effects of phenolic substitutions on the stereochemistry of dihydroxybenzoate complexes, we have now prepared some metal complexes of 2,5-dihydroxybenzoate (2,5-DHB). This paper describes the synthesis and the spectral properties of M(II) 2,5-dihydroxybenzoates (M = Mn, Co, Ni, Cu, Zn and Cd), as well as the crystal and molecular structure of the Zn-complex.

Experimental

Materials

2,5-Dihydroxybenzoic acid (Merck) was recrystallized twice from water. Very pure metal salts (purchased from Merck) were used without further purification.

Preparation of Complexes

The complexes were prepared by adding 1.5 mmol of the appropriate metal salt ($Cu(NO_3)_2 \cdot 3H_2O$, $Ni(CH_3COO)_2 \cdot 4H_2O$, $Co(CH_3COO)_2 \cdot 4H_2O$, $ZnSO_4 \cdot 7H_2O$, $MnSO_4 \cdot H_2O$ or $CdSO_4 \cdot 8/3H_2O$) to a warm solution of acid. On standing at room temperature crystalline or powder-like compounds precipitated. Analytical data for the compounds and the sodium salt are given in Table I. Crystals suitable for X-ray analysis were only obtained in the case of the Zn complex.

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TABLE I. Analytical Data.[a]

Compound	%C	%H	%H_2O[b]
$[Mn(2,5\text{-}DHB)_2(H_2O)_4]$	38.44(38.81)	4.15(4.19)	16.5(16.63)
$[Co(2,5\text{-}DHB)_2(H_2O)_4]$	38.55(38.46)	4.05(4.15)	16.5(16.48)
$[Ni(2,5\text{-}DHB)_2(H_2O)_4]$	37.95(38.48)	4.18(4.15)	16.0(16.49)
$[Zn(2,5\text{-}DHB)_2(H_2O)_4]$	38.51(37.90)	4.08(4.09)	16.5(16.24)
$[Cd(2,5\text{-}DHB)_2(H_2O)_4]$	34.79(34.27)	3.49(3.70)	14.5(14.69)
$[Cu(2,5\text{-}DHB)_2(H_2O)_2]\cdot 2H_2O$	37.49(38.06)	4.05(4.11)	16.0(16.31)
$Na(2,5\text{-}DHB)\cdot 2H_2O$	39.62(39.63)	4.17(4.28)	17.0(16.98)

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

Analytical and Spectroscopic Measurements

The techniques and the instrumentation used in obtaining analytical and spectroscopic data have been described previously [2].

Crystal Data

$ZnO_{12}C_{14}H_{18}$, M = 443.7, orthorhombic, space group *Pbca* (No. 61), a = 18.503(4), b = 13.536(3), c = 6.900(2) Å, V = 1728.1 Å^3, Z = 4, D_c = 1.70 g cm^{-3}, $F(000)$ = 912, Mo-K$_\alpha$ radiation, λ = 0.71069, (Mo-K$_\alpha$) = 3.17 cm^{-1}.

Intensity Measurements

Data were collected on a Philips PW1100 four-circle diffractometer using graphite monochromatized Mo-K$_\alpha$ radiation. A crystal of dimensions 0.30 × 0.15 × 0.10 mm was used. A θ–2θ scan mode was employed and 2200 reflections in one octant (h, k. l) within the θ range of 3–27° were examined. Weak reflections which gave $I_t - 2(I_t)^{1/2} < I_b$ on the first scan were not recorded (I_t = count rate at the top of the reflection and I_b = the mean count rate of two preliminary 5 s background measurements on either side of the peak). Of the remaining 888 reflections those for which the total intensity recorded in the first scan (I_i) was <500 counts were scanned, up to four times, to reach such a value. A constant scan rate of 0.05° s^{-1} and a scan width of 1.0° were used, with a background measuring time proportional to I_b/I_i. Three standard reflections were measured every 3 h during data collection, and showed no significant variation in intensity. The standard deviation of the intensity (I) was taken as $[\sigma_c(I)^2 + (0.04\ I)^2]^{1/2}$, where $\sigma_c(I)$ is the standard deviation from counting statistics and the term in I^2 was introduced to allow for other sources of error. I and $\sigma(I)$ were corrected for Lorentz and polarization factors by a program written for the PW 1100 diffractometer, and equivalent reflections were averaged, giving a total of 877 data with $I(\sigma(I)) > 3$. Absorption corrections were not applied.

Structure Solution and Refinement

The zinc atom was located from Patterson syntheses in special position (a center of symmetry *a* in Wyckoff notation) from subsequent difference syntheses. All non-hydrogen atoms were assigned anisotropic thermal parameters in the final cycles of refinement in which the reflections were weighted as $1/\sigma^2(F_o)$. The hydrogen atoms were refined using isotropic thermal parameters. The final R and R' were 0.041 and 0.045 respectively, where $R' = \Sigma||F_o| - |F_c||w^{1/2}/\Sigma|F_o|w^{1/2}$. The SHELX-76 programs [6] were used and the scattering factors were those of Cromer and Mann [7]. Corrections for the real and imaginary parts of the anomalous dispersion were applied. The final atomic co-ordinates are given in Table II, while Tables of structure amplitudes are available as Supplementary Material.

Results

Molecular Structure of Tetraaquabis(2,5-dihydroxybenzoato)zinc(II)

The complex show a *trans* coordination geometry (Fig. 1), with the zinc atom, lying on a crystallographic inversion centre, bound to four water molecules and to two monodentate 2,5-DHB ligands. Selected bond lengths and angles are given in Table III. The six oxygen atoms of the Zn coordination define a slightly compressed octahedron, the Zn–O-(carboxylate) distances being shorter than the Zn–O-(water) ones (mean values 2.051 and 2.125 Å, respectively). This range of distances is usual for Zn–O interactions in an octahedral environment. For instance, in $[Zn(H_2O)_6](2,6\text{-}DHB)_2\cdot 2H_2O$ [2] we have found four Zn–O(water) distances with a mean value of 2.122 Å and two with a mean value of 2.050 Å.

Some kind of distortion is often present in the octahedral geometry of such compounds and can be ascribed to packing forces, because of the presence of many intra- and intermolecular hydrogen-bonds.

For the present compound the relevant O····O interactions are reported in Table IV. Of the four water molecules, two are involved in both intermolecular and intramolecular hydrogen-bonds (the

TABLE II. Fractional Atomic Coordinates and Anisotropic Thermal Parameters (Å^2).

Atom	x	y	z	U_{iso} or U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Zn	0.00000	0.00000	0.00000	0.0240(4)	0.0022(1)	0.014(1)	0.036(1)	0.001(1)	0.002(1)	0.003(1)
Ow(1)	−0.0758(3)	−0.0801(4)	0.1688(8)	0.044(3)	0.046(3)	0.023(2)	0.062(3)	−0.000(2)	0.022(3)	0.006(2)
Ow(2)	0.0432(3)	0.0760(4)	0.2443(9)	0.046(3)	0.042(3)	0.033(3)	0.061(3)	−0.016(3)	−0.019(3)	0.018(3)
O(1)	0.0737(2)	−0.1125(3)	0.0244(7)	0.030(2)	0.023(2)	0.014(2)	0.052(3)	0.009(2)	−0.001(2)	0.004(1)
C(1)	0.0637(3)	−0.2060(4)	0.0542(9)	0.024(3)	0.022(3)	0.020(3)	0.031(4)	−0.002(2)	0.004(2)	−0.000(2)
O(2)	0.0046(2)	−0.2426(3)	0.1092(9)	0.038(2)	0.022(2)	0.025(2)	0.068(3)	0.004(2)	0.010(3)	0.001(2)
C(2)	0.1278(3)	−0.2714(4)	0.0255(9)	0.019(3)	0.018(2)	0.019(2)	0.019(4)	0.000(3)	−0.002(3)	0.003(2)
C(3)	0.1977(3)	−0.2318(3)	0.0024(13)	0.024(3)	0.026(2)	0.018(2)	0.029(3)	−0.001(4)	0.000(4)	−0.001(2)
C(4)	0.2566(3)	−0.2946(4)	−0.0163(13)	0.033(3)	0.018(2)	0.022(3)	0.059(5)	−0.001(4)	−0.001(4)	−0.002(2)
C(5)	0.2472(3)	−0.3962(4)	−0.0179(12)	0.032(3)	0.020(3)	0.021(2)	0.056(4)	0.001(4)	0.003(4)	0.004(2)
C(6)	0.1778(3)	−0.4355(3)	−0.0023(11)	0.024(3)	0.023(2)	0.012(2)	0.037(3)	0.002(4)	−0.003(4)	−0.000(2)
C(7)	0.1192(3)	−0.3735(4)	0.0198(11)	0.024(3)	0.014(2)	0.017(2)	0.041(4)	0.007(3)	0.001(3)	−0.001(2)
O(3)	0.2089(2)	−0.1319(3)	−0.0042(9)	0.036(2)	0.023(2)	0.015(2)	0.071(3)	0.004(3)	0.001(3)	−0.004(1)
O(4)	0.1639(2)	−0.5359(3)	−0.0085(9)	0.036(2)	0.022(2)	0.015(2)	0.071(3)	−0.001(3)	−0.002(3)	0.006(2)
HC(4)	0.301(3)	−0.260(4)	−0.048(8)	0.04(1)						
HC(5)	0.289(3)	−0.438(4)	−0.018(7)	0.03(1)						
HC(7)	0.076(3)	−0.396(4)	0.021(7)	0.03(1)						
HO(3)	0.167(4)	−0.107(4)	−0.008(8)	0.04(1)						
HO(4)	0.198(4)	−0.559(5)	0.017(9)	0.06(1)						
Hw(11)	−0.071(3)	−0.059(4)	0.297(5)	0.08(1)						
Hw(12)	−0.062(3)	−0.143(3)	0.178(8)	0.06(1)						
Hw(21)	0.091(2)	0.072(5)	0.247(7)	0.06(1)						
Hw(22)	0.028(3)	0.139(3)	0.263(8)	0.09(1)						

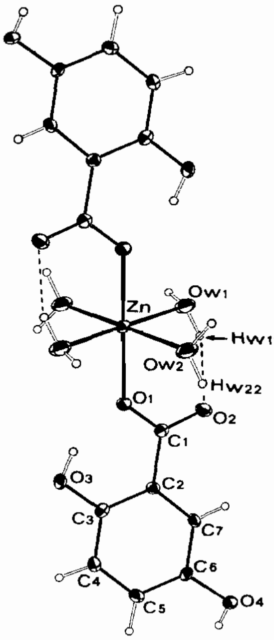

Fig. 1. Perspective view of [$Zn(2,5\text{-}DHB)_2(H_2O)_4$].

TABLE III. Bond Distances and Angles in [$Zn(2,5\text{-}DHB)_2(H_2O)_4$].

Distances (Å)		Angles (°)	
Zn–Ow(1)	2.121(5)	Ow(2)–Zn–Ow(1)	93.5(2)
Zn–Ow(2)	2.130(5)	O(1)–Zn–Ow(1)	90.9(2)
Zn–O(1)	2.051(4)	O(1)–Zn–Ow(2)	92.6(2)
O(1)–C(1)	1.295(6)	C(1)–O(1)–Zn	130.1(4)
C(1)–O(2)	1.260(6)	O(2)–C(1)–O(1)	123.8(5)
C(1)–C(2)	1.493(7)	C(2)–C(1)–O(1)	116.4(5)
C(2)–C(3)	1.409(7)	C(2)–C(1)–O(2)	119.8(5)
C(2)–C(7)	1.392(7)	C(3)–C(2)–C(1)	121.2(5)
C(3)–C(4)	1.388(8)	C(7)–C(2)–C(1)	120.1(5)
C(3)–O(3)	1.369(6)	C(7)–C(2)–C(3)	118.7(5)
C(4)–C(5)	1.386(8)	C(4)–C(3)–C(2)	119.9(5)
C(5)–C(6)	1.394(8)	O(3)–C(3)–C(2)	121.3(5)
C(6)–C(7)	1.380(7)	O(3)–C(3)–C(4)	118.9(5)
C(6)–O(4)	1.384(7)	C(5)–C(4)–C(3)	120.6(6)
Ow(1)–Hw(11)	0.93(4)	C(6)–C(5)–C(4)	119.6(6)
Ow(1)–Hw(12)	0.90(4)	C(7)–C(6)–C(5)	120.0(5)
Ow(2)–Hw(21)	0.89(4)	O(4)–C(6)–C(5)	122.9(5)
Ow(2)–Hw(22)	0.91(4)	O(4)–C(6)–C(7)	117.0(5)
C(4)–HC(4)	0.97(6)	C(6)–C(7)–C(2)	121.1(5)
C(5)–HC(5)	0.96(6)		
C(7)–HC(7)	0.85(6)		
O(3)–HO(3)	0.85(7)		
O(4)–HO(4)	0.73(7)		

latter ones with the uncoordinated carboxylic oxygen atom) while the other two participate only to intermolecular bonding.

TABLE IV. Hydrogen-bond Distances (Å).

O···H–O	O···O	O···H
O(1)···HO(3)–O(3)	2.52	1.74
O(3)···HO(4)–O(4)	2.69	1.99
O(4)···Hw(11)–Ow(1)	2.92	2.28
O(2)···Hw(12)–Ow(1)	2.69	1.88
O(4)···Hw(21)–Ow(2)	2.86	2.12
O(2)···Hw(22)–Ow(2)	2.80	1.92

Tetraaquabis(2,5-dihydroxybenzoato)M(II) (M = Mn and Cd)

Single-crystal measurements showed these compounds to have cell dimensions and space groups similar to those of [$Zn(2,5\text{-}DHB)_2(H_2O)_4$], suggesting that they may be isostructural with the Zn compound.

Electronic and ESR Spectra

The d–d absorption spectra of the Ni and Co complexes (Fig. 2) are typical of nearly octahedral coordination at the metal ion, according to the structural results for the Zn compound. In contrast, the electronic spectrum of the copper complex (Fig. 2), which exhibits a broad band centered at about 675 nm, is clearly indicative of pronounced tetragonal distortion. Indeed, for a complex of the tetraaquabis(carboxylato)Cu(II)-type with a moderate tetragonal distortion, *e.g.* tetraaquabis(β-alaninato)copper(II) [8], an absorption maximum at about 800 nm should be expected. Also the ESR powder spectrum of the compound ($g_{\parallel}$ = 2.339, $g_{\perp}$ = 2.081) agrees with a tetragonal geometry strongly distorted toward the planar one. A comparative examination shows that both the absorption and ESR parameters of the copper(II) 2,5-dihydroxybenzoate are intermediate between those of [Cu-

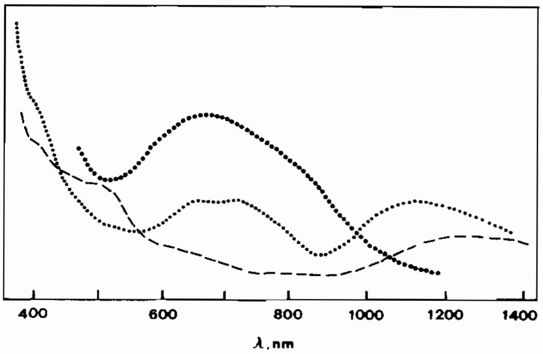

Fig. 2. Diffuse reflectance spectra of [$Cu(2,5\text{-}DHB)_2(H_2O)_2$]·$2H_2O$ (•••••), [$Ni(2,5\text{-}DHB)_2(H_2O)_4$] (····) and [$Co(2,5\text{-}DHB)_2(H_2O)_4$] (-----).

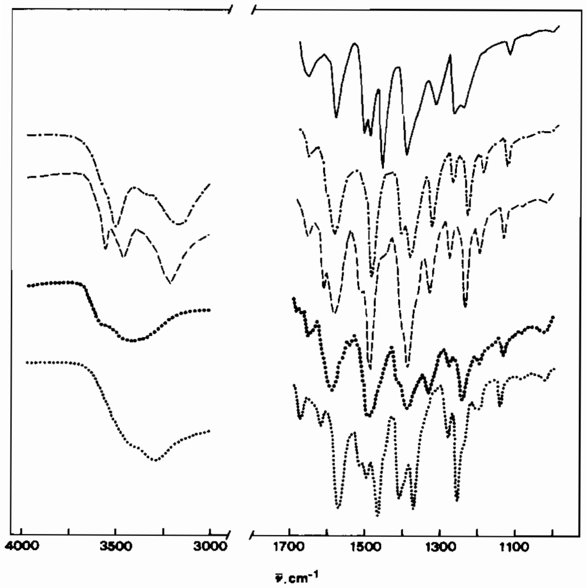

Fig. 3. IR spectra of $Na(2,5\text{-}DHB)2H_2O$ (———), $[Mn(2,5\text{-}DHB)_2(H_2O)_4]$ (–·–), $[Zn(2,5\text{-}DHB)_2(H_2O)_4]$ (----), $[Cd(2,5\text{-}DHB)_2(H_2O)_4]$ (••••) and $[Cu(2,5\text{-}DHB)_2(H_2O)_2]\cdot 2H_2O$ (·····).

$(sal)_2(H_2O)_2]\cdot 2H_2O$ (sal = salicylate) and $[Cu(2,6\text{-}DHB)_2(H_2O)_2]$ [2], which have CuO_4-based chromophores (two water molecules and two monodentate carboxylate groups in the metal plane) with long axial O-contacts (2.8 Å and 2.599(3) Å in the salicylate and 2,6-dihydroxybenzoate complexes, respectively [2, 9]). A similar structure can be proposed for the copper(II) 2,5-DHB complex, which is thus formulated as $[Cu(2,5\text{-}DHB)_2(H_2O)_2]\cdot 2H_2O$.

Infrared Spectra

The assignment of the IR absorptions was made by comparing the spectra of the complexes with those of the corresponding sodium salt and those of the samples after dehydration. The IR features in the range 1700–1000 cm^{-1} (Fig. 3) divide the compounds into three classes: i) M = Cu, ii) M = Mn and Co, iii) M = Ni and Zn, with only minor differences between the classes ii) and iii). The IR spectrum of the cadmium complex is similar, although not coincident, to those of the ii) class. The above analogies, together with the results of X-ray analysis, allow us to assume that the Mn, Co, Ni, Zn and Cd complexes have the same molecular structure. For all the complexes the carboxylate stretching bands fall in the ranges 1580–1595 cm^{-1} (ν_{as}) and 1380–1390 cm^{-1} (ν_s). As to the OH-stretching vibrations (Fig. 3), while in the higher frequency bands ($\nu >$ 3400 cm^{-1}) a large contribution originates from the phenolic group vibration, the absorptions around 3200–3350 cm^{-1} must be ascribed mainly to water. The different form and position of the latter bands indicate that the complexes differ as to the hydrogen bonding involving water.

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