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Interaction of Metal Ions with Humic-Like Models. Part. I. Synthesis, Spectroscopic and Structural Properties of Diaquabis-(2,6-dihydroxybenzoato) Copper(II) and HexaaquaM(II) Bis(2,6-dihydroxybenzoate) Dihydrate (M = Mn, Fe, Co, Ni, Cu and Zn)

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Compounds of the type $M(2,6\text{-}DHB)_2\cdot 8H_2O$ ($M = Mn, Fe, Co, Ni,$ and Zn; 2,6-DHB = 2,6-dihydroxybenzoate ion) and $Cu(2,6\text{-}DHB)_2(H_2O)_2$ were prepared and characterized by means of infrared and electronic spectroscopy, electron spin resonance and thermal analysis. For $Cu(2,6\text{-}DHB)_2(H_2O)_2$ (1) and $Zn(2,6\text{-}DHB)_2\cdot 8H_2O$ (2) the crystal structure was also determined by single-crystal X-ray diffraction methods.

The compound (1) has a polymeric nature, the coordination around each copper atom being tetragonally-distorted octahedral, with two water oxygens [Cu–O, 1.966(3) Å] and two carboxyl oxygens [Cu–O, 1.935(2) Å] from 2,6-DHB molecules about the square plane and two phenolic groups from adjacent units in the axial positions.

The structure of (2) consists of almost regular octahedral $[Zn(H_2O)_6]^{2+}$ cations surrounded by 2,6-DHB anions. The remaining two water molecules are involved in hydrogen bonding with the coordinated water molecules.

X-ray data show that all the $M(2,6\text{-}DHB)_2\cdot 8H_2O$ are isomorphous with (2).

The thermal, spectroscopic and magnetic properties are interpreted on the basis of the crystal structures. In particular, the ESR and absorption data of the copper(II) compounds are compared with those of the salicylate complexes.

Introduction

Interaction of hydroxybenzoic acids with common metal ions is of particular interest for a basic understanding of metal complexation in the environment. A large portion of the soil organic matter consists of polymeric molecules, referred to as humic and fulvic acids, whose core is thought to contain aromatic nuclei bearing, as main substituents, carboxylic and phenolic groups [1]. Hydroxybenzoic acids are thus, of the simple models, the most appropriate to investigate the ligand behaviour of the soil organic matter.

Due to the complex structure of the naturally occurring polyelectrolytes, it is conceivable that, depending on both the nature and the position of the substitutents in the aromatic rings, different structural units can be found. Thus, dissimilar complexation mechanisms could occur resulting in heterogeneous binding of metal ions.

As regards the ligand behaviour of salicylic acid, detailed structural information is available for some metal complexes [2–7]. No structural investigation has been carried out on the complexes formed by 2,x (x = 3,4,5,6)-dihydroxybenzoic acids which are better representatives of humic and fulvic substances [1].

As part of our continuing research on complexes formed upon interaction of metal ions with soil ligands, we have undertaken the study of 2, x (x = 3,4,5,6)-dihydroxybenzoate complexes to ascertain the effect of ring substitutions on the ligand properties of salicylic-like acids. This paper reports the crystal and molecular structures of diaquabis-(2,6-dihydroxybenzoato)copper(II) and hexaaquazinc(II) bis(2,6-dihydroxybenzoate) dihydrate, together with the spectroscopic and thermal analysis of these compounds and of the hexaaquametal(II) bis(2,6-dihydroxybenzoate) dihydrate complexes (metal = Mn, Fe, Co, Ni and Cu) which, as revealed

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by X-ray diffraction, are isomorphous and isostructural with the zinc complex.

Experimental

Reagents

2,6-Dihydroxybenzoic acid (Merck, 97%) was twice recrystallized from water and dried *in vacuo.* Commercially very pure metal salts (Merck) were used without further purification.

Preparation of the Complexes

All the complexes were prepared by adding stoichiometric amounts of metal salts (sulphate, nitrate or acetate) to hot aqueous solutions of the acid and adjusting the pH with NaOH. On standing crystals appeared after slow cooling. They were filtered off, washed with hot water and air-dried. From acid solutions containing Mn(II), Fe(II), Co(II), Ni(II) and Zn(II) only complexes of stoichiometry $M(2,6\text{-}DHB)_2 \cdot 8H_2O$ were obtained. In contrast, from the copper(II) solutions two complexes, $Cu(2,6\text{-}DHB)_2 \cdot 2H_2O$ and $Cu(2,6\text{-}DHB)_2 \cdot 8H_2O$ were obtained at pH 3–3.5 and 4–5, respectively. By reaction in D_2O medium complexes containing deuterated water molecules and phenolic groups were isolated. Analytical data concerning the metal complexes and the sodium salt are given in Table I.

Analytical and Spectroscopic Measurements

The chemical analysis for C and H was performed on a Perkin-Elmer 240 B Elemental Analyzer. Thermal analyses were carried out under either nitrogen or oxygen flow at a heating rate of 5 °C min^{-1} on a Perkin-Elmer TGS-2 thermogravimetric apparatus. IR spectra were recorded on a Perkin-Elmer 683 B spectrophotometer. Since the use of either mulls between alkaline halide plates or potassium halide disks could result in anion exchange, IR spectra were obtained on powdered samples spread on NaCl plates. Electronic diffuse reflectance spectra were obtained on a Beckman Acta MIV spectrophotometer equipped with a reflectance sphere using $BaSO_4$ as reference sample. ESR spectra of polycrystalline samples were obtained with a Varian E9 spectrometer. DPPH was the standard field marker.

Crystal Data

Compound (*1*). $C_{14}H_{14}CuO_{10}$, $M = 405.8$, monoclinic, $a = 5.246(1)$, $b = 10.709(1)$, $c = 13.134(1)$ Å, $\beta = 94.49(1)^\circ$, $V = 735.5$ Å^3, $D_c = 1.83$ g cm^{-3} for $Z = 2$, $F(000) = 414$, λ(Mo-Kα) = 0.71073 Å, μ(Mo-Kα) = 16.0 cm^{-1}, space group $P2_1/n$ (N. 14). Compound (*2*). $C_{14}H_{26}O_{16}Zn$, $M = 515.7$, triclinic, $a = 6.586(1)$, $b = 7.938(1)$, $c = 9.884(1)$ Å, $\alpha = 96.29(1)$, $\beta = 93.19(1)$, $\gamma = 100.05(1)^\circ$, $V = 504.3$ Å^3, $D_c = 1.70$ g cm^{-3} for $Z = 1$, $F(000) = 268$, λ(Mo-Kα) = 0.71073 Å, μ(Mo-Kα) = 13.4 cm^{-1}, space group $P\bar{1}$ (N. 2).

Intensity Data

Accurate crystal parameters were measured and data collections made on a Nonius CAD-4 diffractometer using graphite monochromatized Mo-Kα radiation. For compound (*1*) a single crystal of dimensions 0.10 X 0.15 X 0.29 mm was used and 1285 reflections ($\pm h, k, l$) in the range $3^\circ < \vartheta < 25^\circ$ were collected. For compound (*2*) 1758 intensities ($\pm h, \pm k, l$) were measured up to a ϑ_{max} value of 25° from a crystal of dimensions 0.14 X 0.20 X 0.22 mm. In both cases the data collection was made at the constant scan speed of 2.5° min^{-1} by using the ω-scan method and a scan range of $(\alpha + 0.35 \tan\vartheta)^\circ$ ($\alpha = 0.8$ and 1.2 for compound (*1*) and (*2*), respectively) with a 25% extension at each end for background determination. The intensities of three standard reflections were measured every two hours of X-ray exposure and no decay was observed for either of the crystals.

Data Reduction, Structure Resolution and Refinements

The Lorentz and polarization corrections were applied to the measured data. We also applied an empirical absorption correction based on ψ-scans on reflections with χ values near to 90°. The maximum, minimum and average relative transmission values were 1.00, 0.95, 0.97 for compound (*1*) and 1.00, 0.91, 0.95 for (*2*), respectively. A total of 945 independent reflections with $I > 2\sigma(I)$ for compound (1) and of 1623 with $I > 3\sigma(I)$ for compound (2) were used in the structure resolutions (by the heavy atom method) and refinements.

In both cases, after location of the atoms from Fourier difference maps, we refined the parameters by full-matrix least squares assigning anisotropic thermal factors to the non-hydrogen atoms and isotropic thermal factors to hydrogens.

Weights were assigned according to the formula $w = 1/[\sigma(F_o)]^2$, where the σ of the reflections were judged by a factor $p \cdot F_o^2$ (p = 0.02 and 0.03 for (*1*) and (*2*), respectively). The final conventional R and R_w factors were 0.039 and 0.033 for compound (*1*) and 0.021 and 0.028 for compound (*2*), respectively. Final difference Fourier maps were flat, the remaining peaks being no greater than 0.3 eÅ^{-3}.

Final positional and thermal parameters are given in Tables II and III while Tables of structure amplitudes are available as supplementary material. All the computations were made on a PDP 11/34 computer using the Enraf-Nonius Structure Determination Package (SDP) and the physical constants tabulated therein.

TABLE I. Analytical Data.[a]

Compound	%C	%H	$\%H_2O$ or D_2O[b]
$Cu(2,6\text{-}DHB)_2\cdot 2H_2O$	41.01(41.43)	3.43(3.48)	10.0 (8.87)
$Cu(2,6\text{-}DHB^*)_2\cdot 2D_2O$	39.58(40.60)	–	10.0 (9.67)
$Mn(2,6\text{-}DHB)_2\cdot 8H_2O$	33.47(33.28)	4.79(5.19)	29.0(28.50)
$Mn(2,6\text{-}DHB^*)_2\cdot 8D_2O$	31.82(32.02)	–	30.0(30.70)
$Fe(2,6\text{-}DHB)_2\cdot 8H_2O$	33.26(33.22)	4.87(5.18)	28.0(28.27)
$Co(2,6\text{-}DHB)_2\cdot 8H_2O$	33.18(33.01)	4.98(5.15)	28.0(28.27)
$Ni(2,6\text{-}DHB)_2\cdot 8H_2O$	33.21(33.04)	5.00(5.15)	28.0(28.28)
$Cu(2,6\text{-}DHB)_2\cdot 8H_2O$	32.61(32.72)	4.93(5.10)	28.0(28.05)
$Zn(2,6\text{-}DHB)_2\cdot 8H_2O$	32.50(32.60)	4.91(5.08)	28.0(27.95)
$Na(2,6\text{-}DHB)\cdot 1.5H_2O$	40.92(41.35)	3.86(3.94)	12.5(13.29)

[a] Calculated values in parentheses. $DHB^* = C_6H_3(OD)_2COO^-$. [b] Thermogravimetric determination.

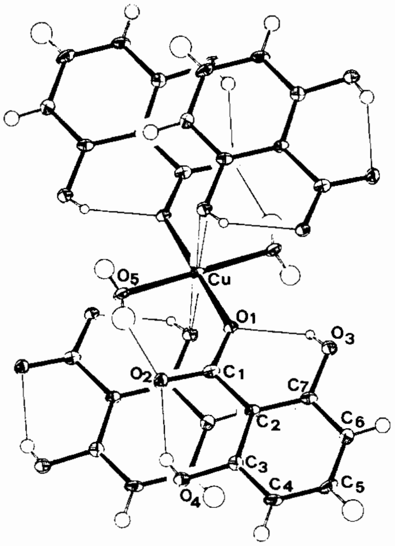

Fig. 1. Perspective view of $Cu(2,6\text{-}DHB)_2(H_2O)_2$.

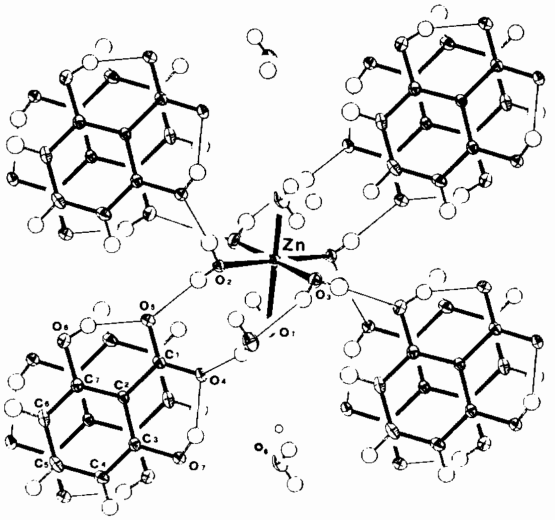

Fig. 2. Perspective view of $Zn(2,6\text{-}DHB)_2\cdot 8H_2O$.

Results

Molecular Structures

Diaquabis(2,6-dihydroxybenzoato)copper(II) (Compound 1)

In Fig. 1 is shown a partial view of the packing of the $Cu(2,6\text{-}DHB)_2(H_2O)_2$ molecule which has, in the solid state, a polymeric nature. The copper atom lies on a crystallographic inversion center and is bonded to six oxygen atoms. Its octahedral coordination is severely distorted *versus* a square planar one. The four basal ligands are two water molecules (Cu–O, 1.966(3) Å) and two 2,6-DHB anions bound with one oxygen of the carboxylate group (Cu–O, 1.935(2) Å) while the axial positions are occupied by much more distant oxygens (Cu–O, 2.599(3) Å) of phenolic groups of adjacent 2,6-DHB anions. The shorter Cu–O interactions are similar to those found in the diaquabis(salicylato)copper(II) ($Cu-O_{(H_2O)}$ = 1.956 (mean), Cu–O = 1.929(6)–2.010(5) Å) [4]. The bond distances in the organic ligand are as expected, the relevant bond parameters being reported in Table IV.

All the hydrogen atoms bound to oxygens are involved in hydrogen bonds. Distances inherent in such interactions are reported in Table IV.

Hexaaquazinc(II) bis(2,6-dihydroxybenzoate) di-Hydrate (compound 2)

The zinc salt of the 2,6-DHB anion consists of one almost regular octahedron of $[Zn(H_2O)_6]^{2+}$, sur-

TABLE II. Positional and Thermal Parameters within $Cu(2,6\text{-}DHB)_2(H_2O)_2$.[a]

Atom	*X*	*Y*	*Z*	*B(1,1)*	*B(2,2)*	*B(3,3)*	*B(1,2)*	*B(1,3)*	*B(2,3)*
Cu	0.0000	0.0000	0.0000	0.0156(2)	0.00430(5)	0.00188(3)	0.0024(3)	0.0048(1)	0.0009(1)
O(1)	−0.2599(4)	−0.0111(3)	0.0963(2)	0.0176(8)	0.0053(2)	0.0023(1)	0.004(1)	0.0066(6)	0.0019(5)
O(2)	−0.1424(5)	−0.1732(3)	0.1958(2)	0.0234(11)	0.0048(3)	0.0034(2)	0.007(1)	0.0089(7)	0.0025(4)
O(3)	−0.6661(5)	0.1115(3)	0.1255(2)	0.0229(11)	0.0067(3)	0.0028(2)	0.008(1)	0.0068(7)	0.0026(4)
O(4)	−0.3170(5)	−0.1895(3)	0.3740(2)	0.0251(11)	0.0061(3)	0.0028(2)	0.006(1)	0.0081(7)	0.0028(4)
O(5)	0.1612(5)	−0.1592(3)	0.0427(2)	0.0254(11)	0.0042(3)	0.0021(2)	0.001(1)	0.0069(7)	0.0007(4)
C(1)	−0.2794(7)	−0.0801(4)	0.1757(3)	0.015(1)	0.0043(4)	0.0022(2)	−0.005(1)	0.0016(9)	0.0008(5)
C(2)	−0.4755(7)	−0.0413(3)	0.2452(3)	0.013(1)	0.0038(4)	0.0020(2)	−0.003(1)	0.0037(9)	0.0005(5)
C(3)	−0.4875(7)	−0.0994(4)	0.3404(3)	0.014(1)	0.0039(4)	0.0027(2)	−0.002(1)	0.0014(10)	0.0001(5)
C(4)	−0.6714(8)	−0.0666(4)	0.4052(3)	0.02(2)	0.0066(4)	0.0017(2)	−0.002(1)	0.0042(10)	0.0011(6)
C(5)	−0.8376(7)	0.0294(4)	0.3771(3)	0.021(1)	0.0075(6)	0.0028(2)	0.001(1)	0.0087(9)	−0.0019(6)
C(6)	−0.8315(7)	0.0894(4)	0.2852(3)	0.018(2)	0.0050(4)	0.0030(3)	0.004(1)	0.0030(10)	−0.0001(6)
C(7)	−0.6525(7)	0.0537(4)	0.2184(3)	0.016(1)	0.0046(4)	0.0019(2)	−0.004(1)	0.0019(9)	0.0002(5)
HC(4)	−0.683(6)	−0.108(3)	0.466(3)	2.0(8)					
HC(5)	−0.445(7)	0.444(4)	−0.081(3)	3.8(11)					
HC(6)	0.069(6)	0.156(3)	0.263(3)	1.9(8)					
HO(3)	−0.566(6)	0.097(3)	0.103(2)	0.7(7)					
HO(4)	−0.258(6)	0.297(3)	0.161(3)	1.6(8)					
HO(51)	0.091(8)	−0.184(4)	0.085(3)	4.4(11)					
HO(52)	0.164(7)	−0.207(4)	−0.005(3)	3.2(10)					

[a] The form of the anisotropic thermal parameter is: $\exp[-(B(1,1)\cdot h^2 + B(2,2)\cdot k^2 + B(3,3)\cdot l^2 + B(1,2)\cdot h\cdot k + B(1,3)\cdot h\cdot l + B(2,3)\cdot k\cdot l)]$.

TABLE III. Positional and Thermal Parameters within $Zn(2,6\text{-}DHB)_2\cdot 8H_2O$.[a]

Atom	*X*	*Y*	*Z*	*B(1,1)*	*B(2,2)*	*B(3,3)*	*B(1,2)*	*B(1,3)*	*B(2,3)*
Zn	0.0000	0.0000	0.0000	0.01267(6)	0.00782(4)	0.00424(3)	0.00445(8)	0.00289(7)	0.00212(5)
O(1)	−0.0043(2)	0.2611(2)	−0.0197(1)	0.0171(3)	0.0100(2)	0.0068(1)	0.0071(4)	0.0053(3)	0.0051(3)
O(2)	0.1891(2)	−0.0151(1)	−0.1570(1)	0.0214(3)	0.0081(2)	0.0047(1)	0.0097(4)	0.0070(3)	0.0031(2)
O(3)	0.2751(2)	0.0715(2)	0.1342(1)	0.0163(3)	0.0123(2)	0.0057(1)	0.0018(4)	0.0001(3)	−0.0002(3)
O(4)	0.2569(2)	0.3899(2)	−0.2042(1)	0.0194(3)	0.0099(2)	0.0040(1)	0.0055(4)	0.0026(3)	0.0043(2)
O(5)	0.1809(2)	0.1671(2)	−0.3672(1)	0.0264(4)	0.0076(2)	0.0061(1)	0.0044(4)	0.0028(4)	0.0037(3)
O(6)	0.1731(2)	0.2134(2)	−0.6177(1)	0.0241(3)	0.0105(2)	0.0053(1)	0.0037(4)	0.0025(4)	−0.0001(3)
O(7)	0.3200(2)	0.6931(1)	−0.2641(1)	0.0227(3)	0.0080(2)	0.0051(1)	0.0073(4)	0.0034(3)	0.0025(2)
O(8)	0.4352(2)	0.7388(2)	0.0419(1)	0.0187(3)	0.0188(3)	0.0078(2)	0.0086(5)	−0.0002(4)	0.0074(3)
C(1)	0.2269(2)	0.3270(2)	−0.3304(2)	0.0120(3)	0.0089(2)	0.0051(2)	0.0064(5)	0.0038(4)	0.0039(3)
C(2)	0.2454(2)	0.4473(2)	−0.4355(2)	0.0103(3)	0.0083(2)	0.0043(2)	0.0060(4)	0.0025(4)	0.0029(3)
C(3)	0.2897(2)	0.6268(2)	−0.3982(2)	0.0108(3)	0.0093(2)	0.0047(2)	0.0066(5)	0.0032(4)	0.0027(3)

C(4)	0.3036(3)	0.7395(2)	−0.4957(2)	0.0152(4)	0.0087(2)	0.0076(2)	0.0072(5)	0.0055(5)	0.0056(4)
C(5)	0.2732(3)	0.6740(2)	−0.6321(2)	0.0151(4)	0.0139(3)	0.0065(2)	0.0103(5)	0.0056(5)	0.0102(4)
C(6)	0.2297(3)	0.4984(2)	−0.6734(2)	0.0153(4)	0.0150(3)	0.0043(2)	0.0091(6)	0.0028(4)	0.0050(4)
C(7)	0.2166(2)	0.3859(2)	−0.5751(2)	0.0116(3)	0.0099(3)	0.0051(2)	0.0057(5)	0.0025(4)	0.0018(4)

Atom	*X*	*Y*	*Z*	*B, A2*	*Atom*	*X*	*Y*	*Z*	*B, A2*
HO(11)	−0.108(3)	0.282(3)	−0.030(2)	3.3(5)	HO(7)	0.308(3)	0.615(3)	−0.217(2)	3.2(4)
HO(12)	0.062(4)	0.292(3)	−0.089(3)	6.1(7)	HC(4)	0.335(3)	0.856(3)	−0.469(2)	3.2(4)
HO(21)	0.207(3)	−0.107(3)	−0.185(2)	3.3(4)	HC(5)	0.282(3)	0.757(2)	−0.700(2)	2.9(4)
HO(22)	0.180(3)	0.033(3)	−0.218(2)	3.3(5)	HC(6)	0.212(3)	0.449(3)	−0.766(2)	3.8(5)
HO(31)	0.260(3)	0.107(3)	0.206(2)	4.0(5)	HO(81)	0.494(4)	0.691(3)	0.071(2)	4.8(6)
HO(32)	0.359(4)	0.134(3)	0.104(3)	5.2(6)	HO(82)	0.462(7)	0.828(6)	0.088(5)	6.0(16)
HO(6)	0.163(4)	0.165(3)	−0.547(3)	4.9(6)					

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[a] The form of the anisotropic thermal parameter is: $\exp[-B(1,1)\cdot h^2 + B(2,2)\cdot k^2 + B(3,3)\cdot l^2 + B(1,2)\cdot hk + B(1,3)\cdot hl + B(2,3)\cdot kl)]$.

TABLE IV. Interatomic Distances and Angles within $Cu(2,6\text{-}DHB)_2(H_2O)_2$.[a]

Distances (Å)					
Cu–O(1)	1.935(2)	C(1)–C(2)	1.487(5)	O(3)–HO(3)	0.64(3)
Cu–O(5)	1.966(3)	C(2)–C(3)	1.403(4)	O(4)–HO(4)	0.65(3)
Cu–O(3)″	2.599(3)	C(2)–C(7)	1.403(4)	O(5)–HO(51)	0.74(4)
C(1)–O(1)	1.288(4)	C(3)–C(4)	1.381(5)	O(5)–HO(52)	0.80(4)
C(1)–O(2)	1.245(4)	C(4)–C(5)	1.380(5)	C(4)–HC(4)	0.92(3)
C(7)–O(3)	1.365(4)	C(5)–C(6)	1.370(5)	C(5)–HC(5)	0.86(4)
C(3)–O(4)	1.365(4)	C(6)–C(7)	1.388(4)	C(6)–HC(6)	0.92(3)
Angles (deg)					
O(1)–Cu–O(5)	94.0(1)	O(1)–C(1)–O(2)	123.4(3)	O(4)–C(3)–C(4)	116.9(3)
O(1)–Cu–O(5)′	86.0(1)	O(1)–C(1)–C(2)	116.0(3)	C(3)–C(4)–C(5)	118.8(4)
O(1)–Cu–O(3)″	95.0(1)	O(2)–C(1)–C(2)	120.6(3)	C(4)–C(5)–C(6)	121.9(4)
O(1)–Cu–O(3)‴	85.0(1)	C(1)–C(2)–C(3)	120.3(3)	C(5)–C(6)–C(7)	119.4(4)
O(3)″–Cu–O(5)	87.9(1)	C(1)–C(2)–C(7)	121.6(3)	C(6)–C(7)–C(2)	120.6(3)
O(3)″–Cu–O(5)′	92.3(1)	C(3)–C(2)–C(7)	118.1(3)	C(6)–C(7)–O(3)	116.7(3)
		C(2)–C(3)–O(4)	121.9(3)	C(2)–C(7)–O(3)	122.7(3)
		C(2)–C(3)–C(4)	121.3(3)		
Hydrogen Bonding					
O·····H–O	O·····O	O·····H			
O(1)···HO(3)–O(3)	2.557(4)	1.99(3)			
O(2)···HO(4)–O(4)	2.584(4)	2.01(4)			
O(2)···HO(51)–O(5)	2.666(4)	1.98(4)			
O(4)···HO(52)–O(5)	2.755(4)	1.95(4)			

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[a] The primed (′), double-primed (″) and triple-primed (‴) refer to the following equivalent positions: (′) (−x, −y, −z); (″) (1 + x, y, z); (‴) (−1 − x, −y, −z).

TABLE V. Interatomic Distances and Angles within $Zn(2,6\text{-}DHB)_2 \cdot 8H_2O$.

Distances (Å)					
Zn–O(1)	2.107(1)	C(1)–C(2)	1.481(2)	O(1)–HO(11)	0.73(2)
Zn–O(2)	2.050(1)	C(2)–C(3)	1.407(2)	O(1)–HO(12)	0.87(3)
Zn–O(3)	2.138(1)	C(2)–C(7)	1.404(2)	O(2)–HO(21)	0.78(2)
C(1)–O(4)	1.283(2)	C(3)–C(4)	1.381(2)	O(2)–HO(22)	0.75(2)
C(1)–O(5)	1.260(2)	C(4)–C(5)	1.382(2)	O(3)–HO(31)	0.75(2)
C(7)–O(6)	1.363(2)	C(5)–C(6)	1.384(3)	O(3)–HO(32)	0.77(3)
C(3)–O(7)	1.362(2)	C(6)–C(7)	1.386(2)	O(6)–HO(6)	0.83(2)
				O(7)–HO(7)	0.81(2)
				O(8)–HO(81)	0.66(3)
				O(8)–HO(82)	0.78(5)
				C(4)–HC(4)	0.92(2)
				C(5)–HC(5)	0.98(2)
				C(6)–HC(6)	0.94(2)
Angles (deg)					
O(1)–Zn–O(2)	90.95(5)	O(4)–C(1)–O(5)	122.0(1)	O(7)–C(3)–C(4)	118.6(1)
O(1)–Zn–O(2)′	89.05(5)	O(4)–C(1)–C(2)	118.6(1)	C(3)–C(4)–C(5)	119.1(1)
O(1)–Zn–O(3)	90.66(5)	O(5)–C(1)–C(2)	119.4(1)	C(4)–C(5)–C(6)	121.6(1)
O(1)–Zn–O(3)′	89.34(5)	C(1)–C(2)–C(3)	121.0(1)	C(5)–C(6)–C(7)	118.9(2)
O(2)–Zn–O(3)	87.08(6)	C(1)–C(2)–C(7)	121.1(1)	C(6)–C(7)–C(2)	121.1(1)
O(2)–Zn–O(3)′	92.92(6)	C(3)–C(2)–C(7)	117.9(1)	C(6)–C(7)–O(6)	118.2(1)
		C(2)–C(3)–O(7)	120.2(1)	C(2)–C(7)–O(6)	120.7(1)
		C(2)–C(3)–C(4)	121.2(1)		
Hydrogen Bonding					
O·····H–O		O·····O		O·····H	
O(4)···HO(12)–O(1)		2.734(2)		1.89(3)	
O(4)···HO(7)–O(7)		2.511(2)		1.78(2)	
O(4)···HO(81)–O(8)		2.907(2)		2.27(3)	
O(5)···HO(22)–O(2)		2.661(2)		1.91(2)	
O(5)···HO(6)–O(6)		2.542(2)		1.77(3)	
O(6)···HO(31)–O(3)		2.753(2)		2.01(3)	
O(7)···HO(21)–O(2)		2.737(2)		1.97(2)	
O(8)···HO(11)–O(1)		2.835(2)		2.13(2)	
O(8)···HO(32)–O(3)		2.980(2)		2.23(3)	

rounded by 2,6-DHB anions and clathrate water molecules as shown in Fig. 2. The $[Zn(H_2O)_6]^{2+}$ moiety has Zn–O interactions ranging from 2.050(1) to 2.138(1) Å, with a mean value of 2.098 Å, very similar to those found in other hexaaquazinc(II) salts [8, 9].

Unlike the case of the $Cu(2,6\text{-}DHB)_2(H_2O)_2$ molecule, the 2,6-DHB anion is not directly coordinated to the metal atom. The bond distances and angles within the uncoordinate anion, reported in Table V, are very similar to those found for the coordinate anion in the copper species, the difference being restricted to the carboxylate group which has more similar C–O bond lengths when not coordinated. The packing is stabilized by a large number of hydrogen bonds and the shorter O····O interactions are reported in Table V.

Hexaaquametal(II) bis(2,6-dihydroxybenzoate) dihydrate (metal = Mn, Fe, Co, Ni, Cu)

X-ray data of these compounds showed them all to be isostructural with $Zn(2,6\text{-}DHB)_2 \cdot 8H_2O$.

Thermal Analysis

TG analyses of $M(2,6\text{-}DHB)_2 \cdot 8H_2O$ showed that loss of six water molecules occurred at rather low temperatures (50–100 °C), whereas the remaining two molecules were removed in one- or two-step processes in the 100–160 °C temperature range. Exceptions are the Ni- and Fe-complexes which apparently release all the water molecules in a one-step process (50–110 °C), but the shape of the DTG trace reveals that the loss could be better interpreted as the superposition of distinct overlapped stages. $Cu(2,6\text{-}DHB)_2(H_2O)_2$ undergoes dehydration in

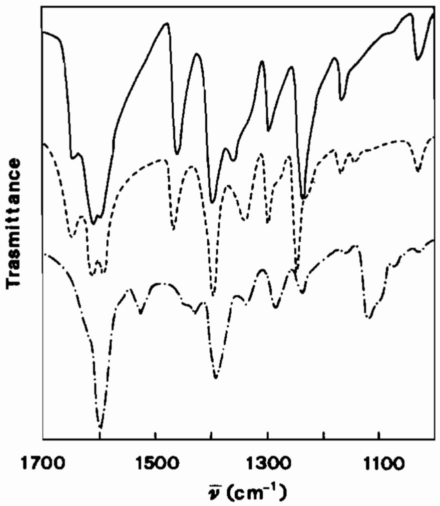

Fig. 3. Infrared spectra of Na(2,6-DHB)$\cdot$1.5H_2O (——), Mn(2,6-DHB)$_2$$\cdot$8$H_2O$ (-----) and Mn(2,6-DHB*)$_2$$\cdot$8$D_2O$ (–·–).

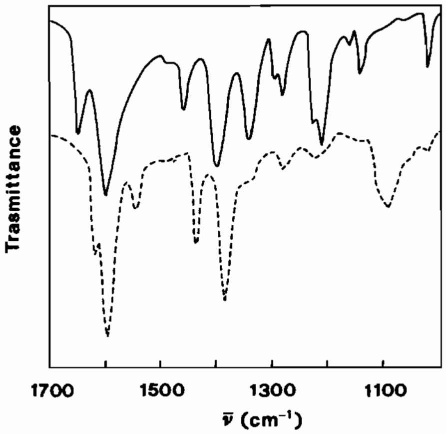

Fig. 4. Infrared spectra of Cu(2,6-DHB)$_2$(H_2O)$_2$ (——) and Cu(2,6-DHB*)$_2$(D_2O)$_2$ (-----).

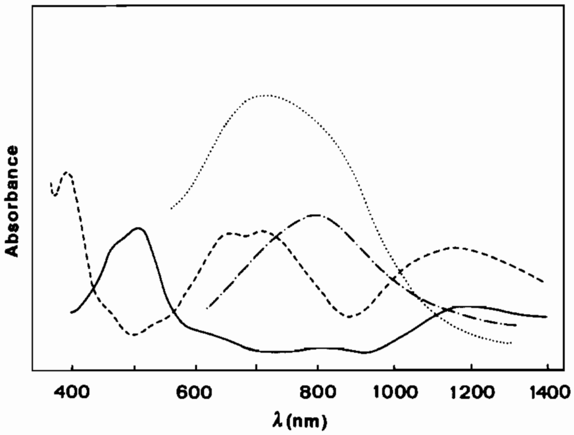

Fig. 5. Diffuse reflectance spectra of Co(2,6-DHB)$_2$$\cdot$8$H_2O$ (——), Ni(2,6-DHB)$_2$$\cdot$8$H_2O$ (-----), Cu(2,6-DHB)$_2$$\cdot$8$H_2O$ (–·–) and Cu(2,6-DHB)$_2$(H_2O)$_2$ (......).

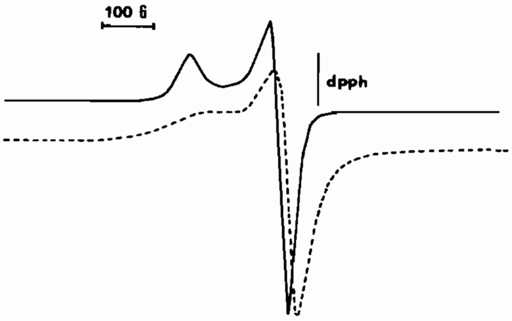

Fig. 6. X-band ESR spectra of polycrystalline samples of Cu(2,6-DHB)$_2$$\cdot$8$H_2O$ (——) and Cu(2,6-DHB)$_2$(H_2O)$_2$ (-----) at room temperature.

a single step (150–180 °C) at temperatures higher than for the M(2,6-DHB)$_2$$\cdot$8$H_2O$ complexes.

Further details on the thermal properties, such as the order of thermal stability found for both the hexaaquametal(II) and the anhydrous M(2,6-DHB)$_2$ complexes together with the coordinative variations taking place after dehydration are reported in a subsequent paper of this series [10].

Infrared Spectra

The M(2,6-DHB)$_2$$\cdot$8$H_2O$ complexes and Na(2,6-DHB) 1.5H_2O exhibit similar IR features which distinguish them from Cu(2,6-DHB)$_2$(H_2O)$_2$, but the differences are too small to be diagnostic for different coordination modes of the ligand (see Figs. 3 and 4). Of particular interest could be the examination of the 1700–1000 cm^{-1} range, where bands associated with stretching modes of carboxylate groups (ν_{as}(CO)$_2$ and ν_s(CO_2)) and the phenolic in-plane bending vibration (δ(OH)) are expected. Whereas ν_{as}(CO_2) and ν_s(CO_2) are easily recognized after examination of deuterated samples, some difficulties arise with the identification of δ(OH). According to literature data [11–13], these modes should give a predominant contribution to bands expected at about 1200 cm^{-1}. Absorptions ascribed to δ(OH) are detected at 1250 cm^{-1} for M(2,6-DHB)$_2$$\cdot$8$H_2O$ and at 1210 cm^{-1} for Cu(2,6-DHB)$_2$(H_2O)$_2$. After deuteration these bands are shifted to 1120 and 1095 cm^{-1}, respectively. As regards ν(CO_2) absorptions it must be noted that, contrary to expectation [14], almost identical values (ν_{as}(CO_2) = 1593–1598 cm^{-1}, ν_s(CO_2) = 1395–1398 cm^{-1}) are observed for all the complexes studied.

Such observation is of course related to the structural features. In fact, the uncoordinated oxygen atom of the carboxylate group in Cu(2,6-DHB)$_2$-

TABLE VI. ESR and Absorption Data for Cu(II)-salicylate and -2,6-dihydroxybenzoate Complexes.[a]

Compound	Geometry	Eq. ligands	Axial ligands, distance (Å)	λ_{max} (nm)	$g_{\parallel}$	$g_{\perp}$	Ref.
$Cu(sal)_2(H_2O)_2 \cdot 2H_2O$	planar	$2COO^-$, $2H_2O$		660	2.314	2.074	3, this work
$Cu(2,6\text{-}DHB)_2(H_2O)_2$	dist. oct.	$2COO^-$, $2H_2O$	2 OH, 2.599	715	2.335	2.082	this work
$Cu(sal)_2(H_2O)_2$	sq. pyr.	$2COO^-$, $2H_2O$	1 OH, 2.266	750	2.371	2.086	4, this work
$Cu(2,6\text{-}DHB)_2 \cdot 8H_2O$	oct.	$4H_2O$	$2H_2O$	790	2.391	2.096	this work

[a] sal = salicylate.

$(H_2O)_2$ is involved in the intramolecular hydrogen bond, which produces quite similar C–O distances. Consequently, the stretching vibrations of bidentate, monodentate and uncoordinated carboxylate groups show similar values.

Electronic and ESR Spectra

The *d–d* electronic spectra of the $M(2,6\text{-}DHB)_2 \cdot 8H_2O$ (see Fig. 5) are fairly similar to those reported in the literature for the hexaaquacations either in aqueous solution or in the solid state, *e.g.* in refs. [15–16]. Therefore, they do not need further examination, being typical of an almost regular octahedral coordination of water molecules at each metal ion. In contrast, the electronic spectrum of $Cu(2,6\text{-}DHB)_2(H_2O)_2$ shows an absorption maximum whose position is clearly indicative of tetragonally distorted hexacoordination [17]. Accordingly, the powder ESR spectra agree with an increase in tetragonal distortion on passing from $Cu(2,6\text{-}DHB)_2 \cdot 8H_2O$ to $Cu(2,6\text{-}DHB)_2(H_2O)_2$ (see Fig. 6). Furthermore, inspection of the data summarized in Table VI shows that, within the series of copper(II) salicylate and 2,6-dihydroxybenzoate complexes a direct correlation of the ESR and absorption data with the coordination geometry is apparent. According to theory [18], the weaker the axial bonding, the lower the g values and the higher the absorption energy.

Discussion and Conclusions

This study provides new structural information on a well-known and supposedly understood class of complexes, such as salicylates. In fact, we report the first examples of outer-sphere arrangements, in the solid state, involving a salicylate-like ligand.

The easy isolation of hexaaquametal(II) dihydroxybenzoate species is probably due to the favourable formation of an extended network of hydrogen bonds which allows the ion to retain the inner aquo-shell also in the solid state. Such behavior represents striking evidence of the weak coordinating properties of the 2,6-DHB ligand, which could act as potential donor of two types of oxygen (carboxylic and phenolic) atoms. However, phenolic groups, unless deprotonated, have little tendency to coordinate metal ions. Deprotonation allows coordination of the phenolate group (and the formation of chelate structures), but requires suitable pH values, although some ions, such as Cu(II), are able to promote deprotonation and subsequent coordination [19].

The carboxylate group also has poor coordinating ability in solution. In fact, NMR evidence for outer-sphere binding of the sulphosalicylate anion to metals such as Mn^{2+} has already been reported [20, 21], whereas carboxylate coordination takes place in the solid Mn(II)–salicylate complex [6].

Our results show that, when conditions are suitable, electrostatic attraction, accompanied by hydrogen bonding, prevails against direct metal–carboxylate bonds, permitting salicylate-like molecules to be involved in outer-sphere arrangements in the absence of a solution-like environment. On the other hand, the coordination behaviour of salicylic-like ligands is strongly dependent on the nature of the ions. The great tendency of Cu^{2+} to coordinate both carboxylate and phenolate groups is well known. Accordingly, from acid solutions, in addition to $Cu(2,6\text{-}DHB)_2 \cdot 8H_2O$, the diaquabis(2,6-dihydroxybenzoato) complex is also obtained. This gives further support to our previous observation [22] that in acidic solutions of Cu^{2+} and DHB a predominant form of copper(II) is never present and inner- and outer-sphere species coexist.

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Supplementary Material Available

Tables of structure amplitudes are available.

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