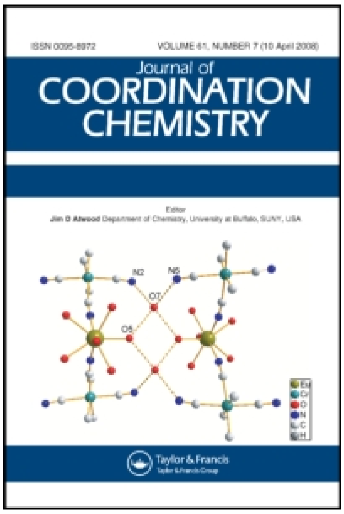

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

POlymeric Complexes of 3-Hydroxy-4-Methoxy- And 3-Methoxy-4-Hydroxybenzoic Acids. Crystal Structure of the Linear-Chain Complex of CO^II With 3-Hydroxy-4-Methoxybenzoic Acid

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To cite this Article Glowiak, Tadeusz , Kozlowski, Henryk , Erre, Liliana Strinna , Gulinati, Beatrice , Micera, Giovanni , Pozzi, Andrea and Bruni, Silvia(1992) 'POlymeric Complexes of 3-Hydroxy-4-Methoxy- And 3-Methoxy-4-Hydroxybenzoic Acids. Crystal Structure of the Linear-Chain Complex of CO^II With 3-Hydroxy-4-Methoxybenzoic Acid', Journal of Coordination Chemistry, 25: 1, 75 — 84

To link to this Article: DOI: 10.1080/00958979209407904

URL: http://dx.doi.org/10.1080/00958979209407904

J. Coord. Chem. 1992, Vol. 25, pp. 75–84
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POLYMERIC COMPLEXES OF 3-HYDROXY-4-METHOXY- AND 3-METHOXY-4-HYDROXYBENZOIC ACIDS. CRYSTAL STRUCTURE OF THE LINEAR-CHAIN COMPLEX OF CO^{II} WITH 3-HYDROXY-4-METHOXYBENZOIC ACID

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(Received January 16, 1991; in final form April 29, 1991)

Reaction of Cu^{II}, Co^{II}, and Ni^{II} with 3-hydroxy-4-methoxy- and 3-methoxy-4-hydroxybenzoic acids (hmba and mhba, respectively) yields hydrated complexes exhibiting stoicheiometries with 1:2 and 1:1 metal to ligand mol ratios. The 1:2 complexes, formed by Co^{II} with hmba and Cu^{II} with mhba, involve carboxylate groups and water molecules as donors. The structure of $[Co(hmba)_2(H_2O)_3]$ was determined by single-crystal X-ray analysis. It crystallizes in the monoclinic space group $I2/a$ with $a = 8.164(2)$, $b = 11.171(3)$, $c = 20.980(5)$ Å, $\beta = 91.42(3)°$, and $Z = 4$. The complex is a one-dimensional polymer with bridging water molecules ($Co–H_2O–Co = 128.04°$ and $Co \cdots Co = 4.082$ Å). The hexacoordination at each cobalt is completed by oxygens from two monodentate carboxylates and two water molecules. Stacking interactions between the parallel aromatic rings (3.5 Å) hold neighbouring chains together. Complexes with a 1:1 metal to ligand ratio ($M = Cu^{II}$, Co^{II} and Ni^{II}, L = hmba; $M = Co^{II}$ and Ni^{II}, L = mhba) also clearly involve phenolate groups in coordination to the metal. A structure for these compounds has been proposed on the basis of spectroscopic and thermogravimetric data.

INTRODUCTION

As shown previously,[1–11] dihydroxybenzoic acids (dhb) and their analogues, which are useful models for natural phenolic ligands, bind metal ions very efficiently. In dilute aqueous solution the most effective coordination sites are provided by hydroxyl groups which are *ortho* (*e.g.* in 3,4- or 2,3-dhb).[5,7] However, the carboxyl group may also participate in metal ion binding, yielding, in some cases, polynuclear complexes. Solid state studies showed that at low pH, the carboxylic group could be

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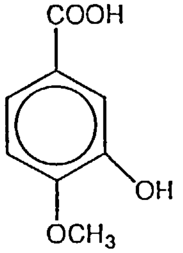
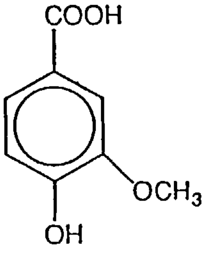
the main donor in the complexes formed by several diphenolic acids, *e.g.*, 2,4-, 2,5-, and 2,6-dhb or their derivatives.[8-11] Potentiometric and spectroscopic studies of dilute solutions confirmed the basic role of the carboxylate function, although they showed that the salicylate-type of coordination is predominant at pH 5.[6] Interaction of Cu^{II} with 2,3-dhb gives rise to remarkably different coordination equilibria,[7] since this ligand can exhibit both the salicylate and catecholate coordination types. Particularly, the simultaneous involvement of the three donors leads to the formation of oligonuclear species.



hmba



mhba

Since with 3,4-dhb the catecholate-type of coordination is favoured, we have now examined metal complexes with two of its derivatives, hmba and mhba, where one of the 3- or 4-hydroxyl groups is replaced by a methoxy group and thus excluded from primary interaction with the metal. This ligand modification may allow a more direct comparison of differences involving the carboxylate binding to the various metal ions. It should be noted that the ligands themselves are molecular components of polymeric soil organic matter.[12]

EXPERIMENTAL

Preparation of Complexes

The synthetic procedure was similar for all the complexes. Typically a solution or a suspension of 1.6 mmol of ligand in 50 to 100 cm^3 of water or ethanol was stirred while adding the stoicheiometric amount of metal salt (nitrate or acetate). Microcrystalline precipitates were formed immediately or with time. They were filtered, washed with diethyl ether and air-dried. Crystals of $[Co(hmba)_2(H_2O)_3]$ were obtained by slow concentration of a dilute solution of cobalt nitrate and the ligand in aqueous ethanol. Analytical data are given in Table I.

Physical Measurements

Elemental analyses were made with a Perkin Elmer 240B analyser. Thermogravimetric determination of H_2O was carried out on a Perkin Elmer TGS2 instrument at a scan rate of 5°C min^{-1}. X-band esr spectra (~9.15 GHz) were recorded on a Varian E9 spectrometer. Absorption spectra were obtained with a Beckman Acta M IV spectrophotometer by using the diffuse reflectance technique with $BaSO_4$ as reference. Ir spectra were recorded on a Bruker IFS 66 FT-IR spectrometer. Variable temperature magnetic susceptibility data were determined by the Faraday method. $Hg[Co(SCN)_4]$ was used as standard. Corrections for diamagnetism were applied by using Pascal's constants.

TABLE I
Analytical data (%)[a] for the complexes.

Complex	C	H	H_2O[b]
$Co(hmba)_2 \cdot 3H_2O$	42.50(42.97)	4.57(4.51)	12.0(12.07)
$Cu(mhba)_2 \cdot H_2O$	46.22(46.21)	3.93(3.88)	– (4.33)
$Cu(hmba) \cdot 1.5H_2O$	36.81(37.43)	3.44(3.53)	7.0(10.52)
$Co(hmba) \cdot 3H_2O$	34.76(34.43)	4.01(4.33)	13.0(19.35)
$Co(mhba) \cdot 2.5H_2O$	35.47(35.57)	3.87(4.10)	13.0(16.66)
$Ni(hmba) \cdot 3H_2O$	34.23(34.46)	4.30(4.34)	13.0(19.36)
$Ni(mhba) \cdot 4H_2O$	31.88(32.36)	4.75(4.75)	24.00(24.25)

[a] Calculated values in parentheses. [b] Thermogravimetric weight loss preceding decomposition of complex.

TABLE II
Positional and thermal ($Å^2$) parameters, with e.s.d.'s in parentheses, for the cobalt complex.

	x/a	*y/b*	*z/c*	$B^*_{eq}/B_{iso}(Å^2)$
Co	0	0	0	1.51(1)
O(1)	0.0660(2)	0.0814(2)	−0.0824(1)	2.8(1)
O(2)	−0.1589(2)	0.1803(2)	−0.1136(1)	2.8(1)
O(3)	−0.0411(2)	0.2726(2)	−0.3485(1)	4.1(1)
O(4)	0.2029(2)	0.1368(2)	−0.3771(1)	3.7(1)
O(5)	0.1135(2)	0.1347(2)	0.0495(1)	3.2(1)
O(6)	0.25	−0.0890(2)	0	2.0(1)
C(1)	−0.0231(2)	0.1342(2)	−0.1249(1)	2.1(1)
C(2)	0.0421(2)	0.1363(2)	−0.1909(1)	2.0(1)
C(3)	−0.0318(2)	0.2078(2)	−0.2382(1)	2.3(1)
C(4)	0.0236(3)	0.2043(2)	−0.2999(1)	2.4(1)
C(5)	0.1565(3)	0.1314(2)	−0.3150(1)	2.5(1)
C(6)	0.2314(3)	0.0623(2)	−0.2681(1)	2.9(1)
C(7)	0.1725(3)	0.0644(2)	−0.2062(1)	2.7(1)
C(8)	0.3384(4)	0.0656(4)	−0.3952(1)	5.5(1)
H(1)	−0.118(3)	0.262(2)	−0.228(1)	2.9(5)
H(2)	0.321(3)	0.010(2)	−0.279(1)	3.2(5)
H(3)	0.234(3)	0.010(2)	−0.173(1)	4.2(6)
H(4)	−0.138(3)	0.287(3)	−0.347(1)	5.5(7)
H(5)	0.305(4)	−0.030(3)	−0.391(1)	5.8(7)
H(6)	0.441(4)	0.087(3)	−0.372(1)	7.5(8)
H(7)	0.355(3)	0.083(3)	−0.433(1)	5.5(7)
H(8)	0.214(3)	0.125(2)	0.064(1)	4.9(6)
H(9)	0.080(2)	0.168(2)	0.074(1)	2.5(5)
H(10)	0.261(3)	−0.133(2)	−0.030(1)	4.2(6)

$^*B_{eq} = \frac{1}{3}\sum_{ij} B_{ij}a_i a_j (a_i \rightarrow a_j)$ for nonhydrogen atoms.

Crystal Structure Determination of [Co(hmba)$_2$(H$_2$O)$_3$]

Crystal data: $C_{16}H_{20}CoO_{11}$, $M = 447.26$, monoclinic, $a = 8.164(2)$, $b = 11.171(3)$, $c = 20.980(5)$ Å, $\beta = 91.42(3)°$, $U = 1{,}912.8(8)$ Å^3, λ(Mo-$K\alpha$) = 0.71069 Å, space group $I2/a$, $D_m = 1.54(1)$ g cm^{-3}, $Z = 4$, $D_c = 1.553(1)$ g cm^{-3}, $F(000) = 940$; crystal dimensions $0.15 \times 0.20 \times 0.45$ mm, μ(Mo-$K\alpha$) = 9.94 cm^{-1}, T = 294K.

Data collection

Measurements were performed on a Syntex P2$_1$ four-circle diffractometer using graphite-monochromated Mo-$K\alpha$ radiation and θ–2θ scan procedure up to $2\theta_{max} = 50°$. The h, k, and l parameters were varied as follows: (h) −9 to 9, (k) 0 to 13, and (l) −25 to 24. A total of 3,388 (1,694 independent) reflections was collected; $R_{merg} = 0.0167$. Some 1,390 reflections with $I > 3\,\sigma\,(I)$ were used in the structure solution and refinement. The data were corrected for Lorentz and polarization effects. Absorption corrections were not applied.

TABLE III
Bond distances (Å) and angles (°) with e.s.d.'s in parentheses, for the cobalt complex.

Co-Co^i	4.082	O(4)-C(8)	1.422(4)
Co-O(1)	2.038(1)	C(1)-C(2)	1.495(3)
Co-O(5)	2.038(2)	C(2)-C(3)	1.400(3)
Co-O(6)	2.270(1)	C(3)-C(4)	1.382(3)
O(1)-C(1)	1.280(2)	C(4)-C(5)	1.400(3)
O(2)-C(1)	1.250(2)	C(5)-C(6)	1.382(3)
O(3)-C(4)	1.369(3)	C(6)-C(7)	1.395(3)
O(4)-C(5)	1.366(2)	C(7)-C(2)	1.378(3)
O(1)-Co-O(5)	88.64(6)	C(1)-C(2)-C(3)	120.6(2)
O(1)-Co-O(6)	86.50(5)	C(1)-C(2)-C(7)	120.1(2)
O(5)-Co-O(6)	85.76(5)	C(3)-C(2)-C(7)	119.3(2)
Co-O(6)-Co^i	128.04(5)	C(2)-C(3)-C(4)	120.2(2)
Co-O(1)-C(1)	129.7(1)	C(3)-C(4)-C(5)	120.1(2)
O(1)-C(1)-O(2)	123.3(2)	C(4)-C(5)-C(6)	119.7(2)
O(1)-C(1)-C(2)	116.3(2)	C(5)-C(6)-C(7)	119.8(2)
O(2)-C(1)-C(2)	120.5(2)	C(6)-C(7)-C(2)	120.9(2)
O(3)-C(4)-C(3)	123.6(2)	C(4)-O(3)-H(4)	116(2)
O(3)-C(4)-C(5)	116.3(2)	C(1)-O(2)...H(4)^{ii}	141(1)
C(5)-O(4)-C(8)	117.8(2)	C(1)-O(2)...H(10)^{iii}	112(1)
O(4)-C(5)-C(4)	115.1(2)	H(8)-O(5)-H(9)	101(2)
O(4)-C(5)-C(6)	125.2(2)	H(10)-O(6)-H(10)^i	104(2)

hydrogen bonds		*distances*		*angles*
D-H...A	D-H	H...A	D...A	D-H...A
O(3)-H(4)...O(2)^{ii}	0.81(3)	1.87(3)	2.610(2)	152(3)
O(5)-H(8)...O(1)^i	0.87(3)	1.89(3)	2.755(2)	169(2)
O(5)-H(9)...O(3)^{iv}	0.70(2)	2.04(2)	2.716(2)	166(2)
O(6)-H(10)...O(2)^v	0.80(2)	1.97(2)	2.713(2)	155(2)

symmetry codes: (i) $\frac{1}{2} - x, y, -z$; (ii) $-\frac{1}{2} - x, \frac{1}{2} - y, -\frac{1}{2} - z$; (iii) $-\frac{1}{2} + x, -y, z$; (iv) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (v) $\frac{1}{2} + x, -y, z$.

Structure solution and refinement

The structure was solved by Patterson and Fourier methods and refined by anisotropic block-diagonal least-squares methods (H atoms isotropic).[13] The final refinement values were $R = 0.024$, $R_w = 0.029$, and $S = 3.319$. The function minimized was $\Sigma w(F_o - F_c)^2$ with $w = 1/\sigma^2(F)$. Positional parameters are listed in Table II, and interatomic distances and angles in Table III. Full lists of anisotropic temperature factors and observed and calculated structure factors are available from the Editor.

RESULTS AND DISCUSSION

Molecular Structure of [Co(hmba)$_2$(H$_2$O)$_3$]

The cobalt complex of 3-hydroxy-4-methoxybenzoic acid exists as a one-dimensional polymer in which water molecules bridge [Co(hmba)$_2$] units (Figure 1). Two ligand molecules coordinate as monodentates to the metal ion *via* carboxylate oxygen atoms. Two water molecules complete the coordination about the cobalt ion. The structure shown in Figure 1 is similar to that of the analogous cobalt complex of 2,6-dimethoxybenzoic acid (dmba)[11] and finds as other analogues the Co^{II}, Fe^{II} and Ni^{II} hippurates.[14,15] Water-bridged polymeric structures have been also found in ternary Cu^{II} complexes of acetate or *N*-protected amino acids with nitrogenous bases.[16,17] In the present complex the Co–H$_2$O–Co bridge is bent with an angle of 128.04° and the metal–metal distance is 4.082 Å. The corresponding values for the dmba complex are 132.3° and 3.97 Å, respectively. In the dimethoxybenzoate complex the distance between Co^{II} and the oxygen atom of the bridging water molecule is distinctly shorter (2.165–2.172 Å) than in the hmba polymer (2.270 Å). On the other hand, the mean Co–O(equatorial) distance (2.038 Å) is shorter than in the dmba derivative (2.070 Å).

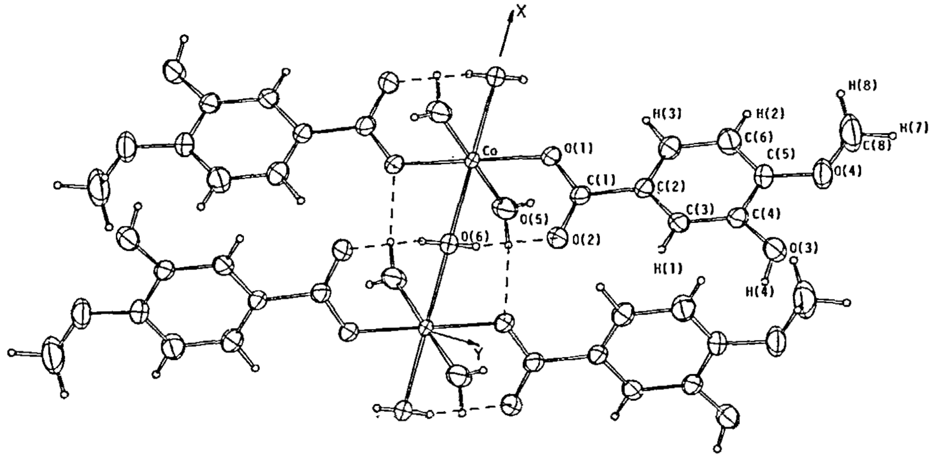


FIGURE 1 Perspective view of [Co(hmba)$_2$(H$_2$O)$_3$].

An interesting structural feature of the polymeric H$_2$O-bridged [Co(hmba)$_2$] species is evident on examination of the two neighbouring chains. The two phenolic ligands related by a centre of symmetry at 1/4, 1/4, and −1/4, are stacked, as shown in

Figure 2. The aromatic rings are exactly parallel to each other, with a distance of 3.5 Å between the planes and the atoms C-4 and C-6 lie exactly between two carbons of the lower ring. Since all the ligands interact in this mode, the stacking is most likely a very important factor for the stabilization of the polymeric structure.

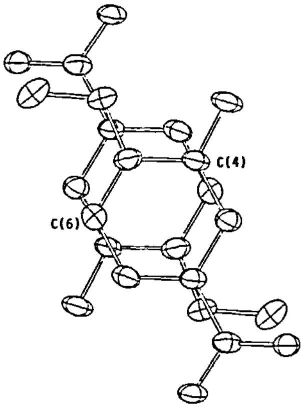


FIGURE 2 Stacking interaction between aromatic rings in [$Co(hmba)_2(H_2O)_3$].

Spectroscopic and Magnetic Data

The electronic spectrum of [$Co(hmba)_2(H_2O)_3$] is consistent with hexacoordination at the metal ion because of the two principal absorption bands around 8750 cm^{-1} (v_1) and 19000 cm^{-1} (v_3), and a shoulder at 16000 cm^{-1} (v_2). Ir spectra show, besides stretches due to coordinated carboxylate groups (1539 and 1386 cm^{-1}), bands attributed to phenolic groups (3360 cm^{-1}); water molecules are responsible for broad absorptions at 3250 cm^{-1}. Magnetic susceptibility data as a function of temperature are shown in Figure 3. Using the equation for isotropic Heisemberg coupling in one dimension,[14] the experimental measurements above 15K were fitted by $S = 3/2$, $g = 2.7$ and $J = -1.9\,cm^{-1}$, indicating antiferromagnetic interactions between metal centres.

Cobalt(II) Complexes

Co^{II} forms equimolar complexes with 3-methoxy-4-hydroxybenzoic and 3-hydroxy-4-methoxybenzoic acids. Although we were not able to obtain crystals suitable for X-ray analysis, some information about the structure of these compounds could be drawn from spectroscopic data and thermogravimetric measurements. The deep colour of solid samples of both equimolar complexes is distinctly different to that of [$Co(hmba)_2(H_2O)_3$] and suggests major differences in metal coordination sites in both types of cobalt(II) species. As indicated by the *d-d* region of the absorption spectra, $Co(mhba){\cdot}2.5H_2O$ exhibits features distinctive of both octahedral (*e.g.*, bands centred around 20000 cm^{-1}) as well as tetrahedral or distorted tetrahedral (a band around 15750 and a broad tail below 7000 cm^{-1}) chromophores. The $Co(hmba){\cdot}3H_2O$ complex also exhibits similar features. The stoicheiometry of the equimolar complexes requires that the phenolic groups are deprotonated and involved in metal ion coordination because only direct binding to a metal promotes hydroxyl group deprotonation.[5-11] The presence of bound phenolate groups in the 1:1 species is substantiated by examination of ir and nir spectra. In the nir, free mhba and hmba exhibit intense absorption bands, distinctive of phenolic groups, at 4673 and 4684 cm^{-1}, respectively. These absorptions are assigned to $\nu(OH) + \delta(OH)$ combinations, as supported by deuteriation. In fact, the frequencies correspond well with those expected by combining the corresponding ir bands $3480 + 1205 = 4685$ and $3410 + 1305 = 4715$ cm^{-1}, for the mhba and hmba ligands, respectively. Deprotonation and metal ion binding leads to the disappearance of the combined vibrations. On the contrary, complexes with a 1:2 M:L ratio still exhibit the combination bands (*e.g.*, 4630 cm^{-1} for $[Co(hmba)_2(H_2O)_3]$).

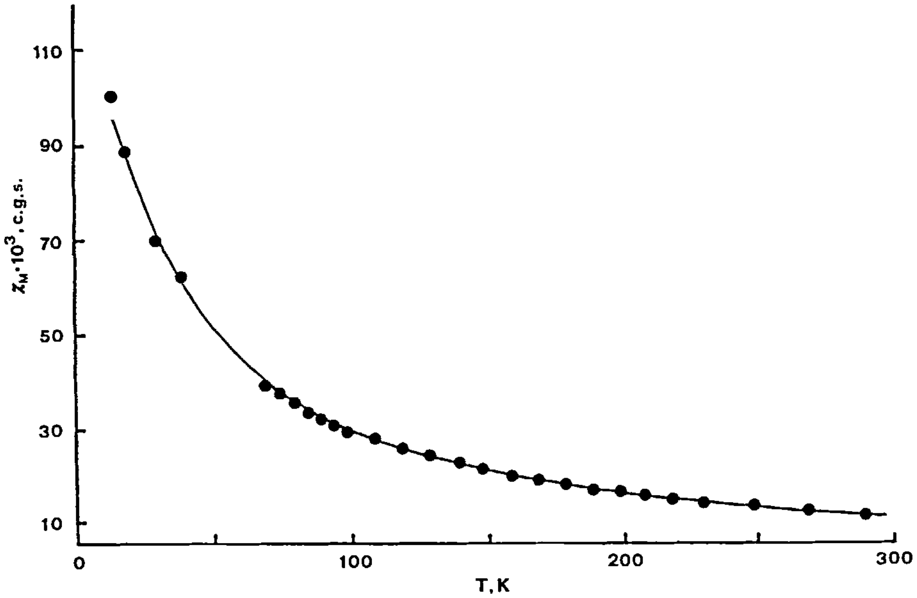


FIGURE 3 Measured (●) and calculated (—) magnetic susceptibility *versus* temperature for $[Co(hmba)_2(H_2O)_3]$.

In the 1:1 species steric factors do not permit the simultaneous coordination of both donors to one metal. Therefore the ligand molecule can act as a bridge *via* carboxylate and phenolate groups to form octahedral and tetrahedral coordination spheres, respectively. The octahedral case should have basic donor sets similar to that observed in the X-ray structure of $[Co(hmba)_2(H_2O)_3]$, *i.e.*, the metal ion is bound to carboxylate groups and water molecules. The tetrahedral site *could* involve two phenolate oxygens and two water molecules.

Additional support for this type of structure is given by thermogravimetry. Upon dehydration, $[Co(hmba)_2(H_2O)_3]$ loses three water molecules in a single stage (110–165°C) to attain a tetrahedral coordination structure (as substantiated by the absorption spectrum), probably involving bidentate coordination by carboxylate groups. Accordingly, a significant decrease in $\Delta(\nu_{as} - \nu_s)$ is detected for the carboxylate stretches (1535 and 1395 cm^{-1}). The anhydrous tetrahedral structure remains stable to the decomposition point. On the contrary, $Co(mhba) \cdot 2.5H_2O$ and

Co(hmba)·$3H_2O$ lose water molecules in distinct stages. In the first step, 1.5 and 2 water molecules are removed from the complexes, respectively, over a rather narrow temperature range (30–115°C). The second step is not so sharp and overlaps with the range for the decomposition of the complexes (*ca* 300°C). Indeed, after the first loss of water, the complexes attain tetrahedral geometry at all metal sites (bands around 17400 cm^{-1}, broad absorption centred around 7500 cm^{-1}, distinct shoulders at 8300 and 6500 cm^{-1}). This indicates that partial dehydration transforms the hexacoordinated (involving carboxylates) complex into the tetrahedral chromophore. The tetrahedral site contains water molecules which cannot be removed unless decomposition occurs.

Copper(II) Complexes

Cu^{II} with mhba forms a complex having the $Cu(mhba)_2 \cdot H_2O$ stoicheiometry. Esr spectra (Figure 4) clearly indicate the presence of an acetate-like dimeric species. The triplet state spectrum can be analyzed using $g_{\parallel} = 2.37$, $g_{\perp} = 2.08$ and $D = 0.35\ cm^{-1}$. Similar values were found for analogous dimeric complexes of dmba.[9] In the latter case the dimeric nature of the species was also confirmed by X-ray structural studies. No distinctive features in the "monomeric" region of the esr spectra could be observed for the $Cu(mhba)_2 \cdot H_2O$ complex.

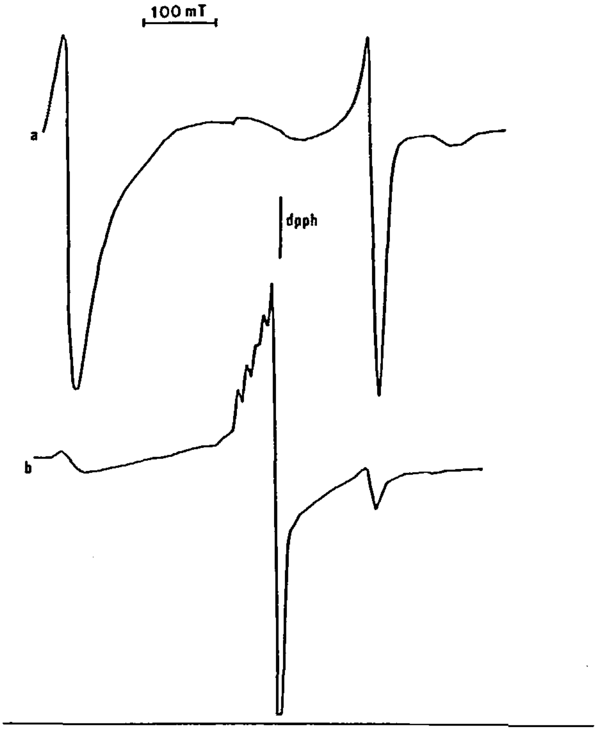


FIGURE 4 X-band powder esr spectra of (a) $Cu(mhba)_2.H_2O$ and (b) Cu(hmba)·$1.5H_2O$.

Very different behaviour was found for hmba. Elemental analysis indicated unambiguously the formation of the equimolar compound Cu(hmba)·$1.5H_2O$. This complex exhibits a more complicated powder esr spectrum (Figure 4) consisting of the usual triplet signals (with parameters similar to those above) and a very intense pattern in the "monomeric" region ($g_{\parallel} = 2.34$, $A_{\parallel} = 140\,cm^{-1}$). The stoicheiometry of the complex requires two negative charges, *i.e.*, deprotonated carboxylic and hydroxyl groups, in Cu^{II} coordination. Some evidence for the involvement of the phenolate donor is provided by the reflectance absorption spectra which show, besides the "dimeric transition" around $26300\,cm^{-1}$,[18] a distinct shoulder at about $24400\,cm^{-1}$. The latter is assigned to a phenolate oxygen to Cu^{II} charge transfer.[5-7] The triplet region of the spectrum shows that two metal ions are bridged by the carboxylates of four ligands to yield an acetate type coordination. Nir spectroscopy supports these conclusions through a combination band for the phenolic groups at $4673\,cm^{-1}$ for $Cu(mhba)_2 \cdot H_2O$; a similar band is not shown by Cu(hmba)·$1.5H_2O$. In any case, in the latter complex, steric factors prevent the carboxylate and deprotonated 3-hydroxyl groups from being coordinated simultaneously to the same metal ion. Thus two other metal ions must be involved in coordination to the phenolic oxygen atoms of the dinuclear unit. Molecular models support the possibility of Cu^{II} binding to two adjacent $3\text{–}O^-$ donors. This coordination mode may lead to some distortion in the tetragonal environment of the metal ion towards tetrahedral geometry, due to a slight hindrance introduced by neighbouring aromatic rings. There is, however, a further possibility for the involvement of the phenolate oxygens in metal ion binding. Four Cu^{II} ions can act as bridges between two "acetate" dimers, each coordinating phenolate oxygen atoms of pairs of adjacent ligands. The number of water molecules in the complex is just that expected to complete the five- and four-coordination of the copper atoms bound to carboxylate and phenolate groups, respectively. It is significant to observe that, based on molecular models, the structures involving both phenolate and carboxylate groups bound to metals are less favoured with the ligand having the 4-hydroxyl group available for coordination. Hence the observation of only acetate-type binding in the Cu^{II}-mhba system (see above) is fully consistent with the structure of the ligand.

Nickel(II) complexes

With Ni^{II}, only complexes having the 1:1 metal to ligand ratio have been isolated, namely Ni(hmba)·$3H_2O$ and Ni(mhba)·$4H_2O$. These complexes also involve both binding sites, as confirmed by nir spectra. The geometry is octahedral, as substantiated by electronic spectra, which show bands around 8500 (ν_1), 13800 (ν_2) and $26000\,cm^{-1}$ (ν_3). Ir spectra show stretches due to metal-bound water molecules (broad bands at 3390 (hmba) and 3320 (mhba) cm^{-1}) and to carboxylates (hmba: 1560 and $1394\,cm^{-1}$; mhba: 1510 and $1373\,cm^{-1}$). Although the latter values cannot be assumed as being diagnostic of the mode of coordination because of likely hydrogen bonding to water molecules, they cannot exclude bidentate coordination of carboxylates. As for the cobalt complexes, dehydration occurs in consecutive stages and is not complete prior to decomposition. However, hexacoordination of the metal ion persists after partial loss of water. Dehydration produces a significant decrease in the $\Delta(\nu_{as} - \nu_s)$ value, which is now strongly suggestive of bidentate carboxylate coordination (*e.g.*, for the mhba complex the bands are shifted to 1504 and $1390\,cm^{-1}$). Electronic spectra fail to discriminate between carboxylate and phenolate sites so that in this case mixed carboxylate–phenolate coordination is possible.

ACKNOWLEDGEMENTS

This work was supported by the Polish Academy of Sciences (Project CPBP 01.12) and the Italian National Council of Research.

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