Synthesis, Structure, and Spectroscopic and Magnetic Properties of *catena*-μ-Aqua-diaquabis(2,6-dimethoxybenzoato)metal(II) Monohydrate Complexes of Manganese, Cobalt, Nickel, and Zinc.† *X*-Ray Crystal Structure of $[Co(dmba)_2(H_2O)_3]\cdot H_2O$ ‡

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Metal complexes of 2,6-dimethoxybenzoic acid (Hdmba), $[M(dmba)_2(H_2O)_3]\cdot H_2O$, for M = Mn^{II}, Co^{II}, Ni^{II}, or Zn^{II} have been prepared and studied by means of *X*-ray diffraction, electronic and i.r. spectroscopies as well as magnetic measurements. The crystal and molecular structure of the cobalt complex has been determined by single-crystal *X*-ray diffraction and refined by least-squares methods to *R* = 0.0347 on the basis of 1 337 independent significant counter data. Crystals are orthorhombic, space group $Pna2_1$, with unit-cell dimensions *a* = 7.934(3), *b* = 10.652(3), *c* = 26.423(7) Å, and *Z* = 4. The compound is polymeric, the metal atoms being linked to each other by bridging water molecules to form an infinite chain. The metal ion is six-co-ordinate, the equatorial ligands being two mutually *trans* water molecules and two unidentate carboxylate groups of the dmba anions. The metal–oxygen bonds in the bridge [2.165(4) and 2.172(4) Å] are longer than the other metal–oxygen distances [M–O(water) 2.091(7) and 2.033(8) Å; M–O(carboxy) 2.073(5) and 2.069(5) Å] giving rise to a tetragonally distorted octahedron at the metal ion. The intra-chain Co–Co distance along the *a* axis is 3.97 Å, whereas the shortest inter-chain distances along the *b* and *c* axes are 10.65 and 14.28 Å, respectively. The Mn, Ni, and Zn complexes are isomorphous with the cobalt compound. Magnetic susceptibility data, in the range 4.2—300 K, for the Co, Ni, and Mn complexes are reported and discussed in relation to the structural data.

As a part of a study of the complexes formed by interaction of metal ions with simple molecules mimicking humic acids, we have reported the crystal structures[1,2] and the thermal properties[3] of a number of complexes formed by 2,6-dihydroxybenzoic acid. In order to ascertain whether methyl substitution for the phenolic hydrogens could modify the co-ordination behaviour of such a ligand, we have prepared some metal complexes of 2,6-dimethoxybenzoic acid (Hdmba). Tetracarboxylate-bridged structures have been observed for the copper(II) complexes.[4] Compounds of formula $M(dmba)_2(H_2O)_4$ have been obtained for M = Mn, Ni, Co, or Zn. The structural, spectroscopic, and magnetic data of these complexes are reported in this paper.

Experimental

Materials.—2,6-Dimethoxybenzoic acid (Merck) was twice recrystallized from aqueous ethanol without further purification. The complexes were prepared by adding stoicheiometric amounts of metal salts (sulphate or acetate) to hot aqueous solutions of the ligand and adjusting the pH to 4—5. On standing, crystals separated after slow cooling. They were filtered off, washed with hot water, and air-dried. Analytical data for the metal complexes and the sodium salt (prepared by carefully neutralising 2,6-dimethoxybenzoic acid with sodium hydroxide and slowly evaporating the resulting solution) are given in Table 1.

Table 1. Analytical data (%)[a]

Compound	C	H	H_2O[b]
$[Co(dmba)_2(H_2O)_3]\cdot H_2O$	44.10 (43.80)	5.00 (5.30)	14.5 (14.60)
$[Ni(dmba)_2(H_2O)_3]\cdot H_2O$	43.65 (43.85)	5.10 (5.30)	14.5 (14.60)
$[Mn(dmba)_2(H_2O)_3]\cdot H_2O$	44.15 (44.20)	4.95 (5.35)	14.3 (14.75)
$[Zn(dmba)_2(H_2O)_3]\cdot H_2O$	43.15 (43.25)	4.70 (5.25)	14.3 (14.40)
$Na(dmba)\cdot 0.25H_2O$	52.10 (51.80)	4.35 (4.60)	2.0 (2.15)

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

Analytical and Spectroscopic Measurements.—The techniques and the intrumentation used in obtaining analytical, thermal, and spectroscopic data have been described previously.[5] Variable-temperature magnetic susceptibility data were determined by the Faraday method in the range 4.2—300 K.

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† Taken as Part 9 of the series 'Interaction of Metal Ions with Humic-like Models.' Part 8 is ref. 5.

‡ *catena*-μ-Aqua-diaquabis(2,6-dimethoxybenzoato-*O*)cobalt(II) hydrate (1/1).

Supplementary data available (No. SUP 56693, 4 pp.): magnetic susceptibility data. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Table 2. Atomic positional parameters with estimated standard deviations for $[Co(dmba)_2(H_2O)_3]\cdot H_2O$

Atom	*x*	*y*	*z*
Co	−0.065 65(8)	−0.249 4(1)	−0.250
O(1A)	−0.156 5(5)	−0.382 4(4)	−0.199 6(2)
O(2A)	0.088 0(5)	−0.457 2(4)	−0.171 5(2)
C(1A)	−0.067 3(8)	−0.456 7(5)	−0.173 1(2)
C(2A)	−0.165 6(7)	−0.552 3(5)	−0.142 4(2)
C(3A)	−0.191 6(9)	−0.672 2(6)	−0.161 0(2)
C(4A)	−0.277 4(9)	−0.759 7(7)	−0.133 6(3)
C(5A)	−0.338(1)	−0.729 9(7)	−0.087 0(3)
C(6A)	−0.315(1)	−0.612 1(8)	−0.066 5(3)
C(7A)	−0.225 5(9)	−0.523 9(6)	−0.094 6(3)
O(3A)	−0.124 6(7)	−0.691 1(4)	−0.208 2(2)
C(8A)	−0.140(1)	−0.815 8(8)	−0.228 6(3)
O(4A)	−0.193 8(8)	−0.403 3(5)	−0.078 4(2)
C(9A)	−0.251(2)	−0.372(1)	−0.031 1(4)
O(1B)	0.021 3(5)	−0.123 8(4)	−0.303 7(2)
O(2B)	−0.222 8(5)	−0.051 7(4)	−0.332 8(2)
C(1B)	−0.068 8(8)	−0.068 1(5)	−0.336 7(2)
C(2B)	0.018 0(8)	−0.029 8(6)	−0.384 3(2)
C(3B)	0.058 8(9)	0.094 7(6)	−0.392 5(3)
C(4B)	0.145(1)	0.130 1(7)	−0.436 2(3)
C(5B)	0.188(1)	0.040 3(8)	−0.471 2(3)
C(6B)	0.150(1)	−0.084 4(8)	−0.464 1(3)
C(7B)	0.063 8(9)	−0.118 2(7)	−0.419 4(3)
O(3B)	0.012 5(7)	0.176 7(4)	−0.355 3(2)
C(8B)	0.060(1)	0.303 8(7)	−0.359 1(4)
O(4B)	0.016 7(6)	−0.238 2(4)	−0.408 3(2)
C(9B)	0.081(1)	−0.337 0(8)	−0.438 7(3)
O(1)	0.183 5(5)	−0.332 3(3)	−0.250 7(2)
O(2)	−0.138 1(5)	−0.365 2(4)	−0.310 1(2)
O(3)	0.009 1(6)	−0.132 2(4)	−0.193 6(2)
O(4)	0.329 8(9)	−0.368 0(8)	−0.104 9(2)
H(11)	0.173(8)	−0.387(5)	−0.224(2)
H(12)	0.201(8)	−0.381(6)	−0.275(2)
H(21)	−0.251(8)	−0.368(6)	−0.313(2)
H(22)	−0.104(7)	−0.345(6)	−0.333(2)
H(31)	0.088(8)	−0.132(5)	−0.192(2)
H(32)	−0.048(8)	−0.133(5)	−0.167(2)

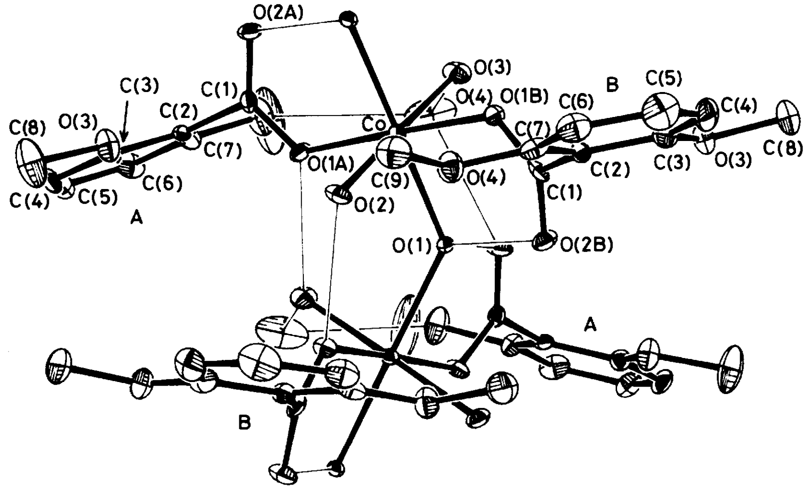

Figure 1. View of the stacking of canted octahedral moieties along the *a* axis for $[Co(dmba)_2(H_2O)_3]\cdot H_2O$

Hg[Co(SCN)$_4$] was used as a susceptibility standard. All data were corrected for diamagnetism using Pascal's constants.

X-Ray Structure Determination of $[Co(dmba)_2(H_2O)_3]\cdot H_2O$. —*Crystal data.* $C_{18}H_{26}CoO_{12}$, M = 493.33, orthorhombic, space group *Pna*2$_1$ (no. 33), a = 7.934(3), b = 10.652(3), c = 26.423(7) Å, U = 2 233 Å^3, D_c = 1.47 g cm^{-3}, Z = 4, $F(000)$ = 1 028, $\lambda(\text{Mo-}K_\alpha)$ = 0.710 73 Å, $\mu(\text{Mo-}K_\alpha)$ = 8.22 cm^{-1}.

Intensity data: collection and reduction. A pink single crystal of the cobalt derivative of dimensions 0.08 × 0.10 × 0.35 mm was selected for *X*-ray analysis and mounted along the needle direction (the *c* axis). Accurate crystal cell parameters were measured and data collection made on a Nonius CAD-4 diffractometer using graphite-monochromatized Mo-K_α radiation.

A total of 2 279 independent reflections were collected in the range $6 \leqslant 2\theta \leqslant 50°$ for the octant $+h$, $+k$, $+l$. The intensity data were collected by the ω-scan method using a scan range of $(1.0 + 0.35 \tan\theta)°$, with a 25% extension at each end for background determination. The scan rate was varied from 1 to 10° min^{-1} on the basis of a fast prescan of each reflection and only those where $\sigma(I)/I \leqslant 1.0$ were judged possible observed reflections and were collected more slowly. Three strong representative reflections were periodically measured to check on the stability of the system and no significant decay was found.

The Lorentz and polarization corrections were applied to the measured data, together with 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, and 0.97. A total of 1 337 independent reflections with $I > \sigma(I)$ were used in structure solution and refinement.

Structure solution and refinement. The structure was solved by conventional Patterson and Fourier methods assuming the non-centrosymmetric space group *Pna*2$_1$ (no. 33) which has been confirmed by successful refinement.

The two possible structure enantiomers were refined, taking into account the anomalous scattering effects, and the presented final solution exhibits slightly lower values for the agreement indices. All the non-hydrogen atoms were treated anisotropically, the hydrogen atoms of the co-ordinated water molecules were refined with a fixed isotropic thermal parameter, the hydrogen atoms of the clathrate water molecule were omitted while those bonded to the carbon atoms were located in their ideal positions (C–H 0.95 Å) after each cycle of refinement.

Table 3. Interatomic distances (Å) and angles (°) in $[Co(dmba)_2(H_2O)_3]{\cdot}H_2O$*

Co–O(1A)	2.073(5)	C(1A)–C(2A)	1.52(1)	O(3A)–C(8A)	1.44(1)	C(4B)–C(5B)	1.37(1)
Co–O(1B)	2.069(5)	C(2A)–C(3A)	1.38(1)	C(7A)–O(4A)	1.38(1)	C(5B)–C(6B)	1.37(1)
Co–O(2)	2.091(7)	C(3A)–C(4A)	1.36(1)	O(4A)–C(9A)	1.37(1)	C(6B)–C(7B)	1.41(1)
Co–O(3)	2.033(8)	C(4A)–C(5A)	1.36(1)	C(1B)–O(1B)	1.27(1)	C(2B)–C(7B)	1.37(1)
Co–O(1)	2.165(4)	C(5A)–C(6A)	1.38(1)	C(1B)–O(2B)	1.24(1)	C(3B)–O(3B)	1.36(1)
Co–O(1′)	2.172(4)	C(6A)–C(7A)	1.39(1)	C(1B)–C(2B)	1.49(1)	O(3B)–C(8B)	1.41(1)
Co ··· Co′	3.97	C(2A)–C(7A)	1.38(1)	C(2B)–C(3B)	1.38(1)	C(7B)–O(4B)	1.36(1)
C(1A)–O(1A)	1.27(1)	C(3A)–O(3A)	1.37(1)	C(3B)–C(4B)	1.40(1)	O(4B)–C(9B)	1.42(1)
C(1A)–O(2A)	1.23(1)						

O(1A)–Co–O(1)	92.6(2)	O(2)–Co–O(3)	177.7(3)	C(3A)–C(4A)–C(5A)	119.9(8)	C(3B)–C(2B)–C(7B)	119.5(7)
O(1A)–Co–O(1′)	87.8(2)	O(1)–Co–O(1′)	178.9(3)	C(4A)–C(5A)–C(6A)	121.4(8)	C(2B)–C(3B)–C(4B)	120.2(8)
O(1A)–Co–O(2)	89.4(2)	Co–O(1)–Co′	132.3(1)	C(5A)–C(6A)–C(7A)	118.3(8)	C(2B)–C(3B)–O(3B)	116.1(7)
O(1A)–Co–O(3)	92.9(3)	O(1A)–C(1A)–O(2A)	125.2(7)	C(6A)–C(7A)–O(4A)	124.0(8)	C(4B)–C(3B)–O(3B)	123.7(8)
O(1B)–Co–O(1)	87.3(2)	C(2A)–C(1A)–O(1A)	115.2(6)	C(6A)–C(7A)–C(2A)	120.9(7)	C(3B)–C(4B)–C(5B)	119.3(8)
O(1B)–Co–O(1′)	92.3(2)	C(2A)–C(1A)–O(2A)	119.6(7)	C(2A)–C(7A)–O(4A)	115.1(6)	C(4B)–C(5B)–C(6B)	121.9(8)
O(1B)–Co–O(2)	87.3(2)	C(1A)–C(2A)–C(3A)	120.4(6)	C(3A)–O(3A)–C(8A)	116.3(6)	C(5B)–C(6B)–C(7B)	117.8(8)
O(1B)–Co–O(3)	90.5(2)	C(1A)–C(2A)–C(7A)	121.2(6)	C(7A)–O(4A)–C(9A)	116.8(8)	C(6B)–C(7B)–O(4B)	123.5(8)
O(1)–Co–O(2)	90.2(2)	C(3A)–C(2A)–C(7A)	118.4(6)	O(1B)–C(1B)–O(2B)	124.2(7)	C(6B)–C(7B)–C(2B)	121.2(8)
O(2)–Co–O(1′)	88.7(2)	C(2A)–C(3A)–C(4A)	121.1(6)	C(2B)–C(1B)–O(1B)	116.5(7)	C(2B)–C(7B)–O(4B)	115.3(7)
O(1′)–Co–O(3)	91.6(2)	C(2A)–C(3A)–O(3A)	113.6(6)	C(2B)–C(1B)–O(2B)	119.1(7)	C(3B)–O(3B)–C(8B)	119.5(8)
O(3)–Co–O(1)	89.5(2)	C(4A)–C(3A)–O(3A)	125.3(6)	C(1B)–C(2B)–C(3B)	120.1(7)	C(7B)–O(4B)–C(9B)	118.4(7)
O(1A)–Co–O(1B)	176.6(2)			C(1B)–C(2B)–C(7B)	120.3(6)		

Hydrogen bonding

O ··· H–O	O ··· O	O ··· H	H–O	Angle
O(1A) ··· H(31)–O(3)	2.66	2.04	0.63	170
O(2A) ··· H(11)–O(1)	2.59	1.70	0.93	159
O(1B) ··· H(21)–O(2)	2.71	1.83	0.90	168
O(2B) ··· H(12)–O(1)	2.60	1.79	0.84	163
O(4) ··· H(32)–O(3)	2.74	1.90	0.84	177
O(2A) ··· O(4)	2.77			
O(4A) ··· O(4)	2.98			

* The primes refer to atoms at the following related positions: $\frac{1}{2} + x, -\frac{1}{2} - y, z$ (Co); $-\frac{1}{2} + x, -\frac{1}{2} - y, z$ [O(1)].

Computations were performed on a PDP 11/34 computer using the Enraf-Nonius structure determination package (SDP).[6] The final values of the conventional agreement indices *R* and *R′* were 0.0347 and 0.0327 respectively, while the goodness of fit was 1.10 using a weighting 'fudge factor' of 0.03. The final difference-Fourier map was flat, the first peak (0.3 e Å^{-3}) being near the clathrate water molecule. Final atomic positional parameters are reported in Table 2.

Results

Molecular Structure of $[Co(dmba)_2(H_2O)_3]{\cdot}H_2O$.—A partial view of the packing of the title compound is reported in Figure 1. Selected bond lengths and angles are given in Table 3. The metal ion is six-co-ordinated by oxygen atoms. Due to the presence of one bridging water molecule per metal atom, the solid-state structure of the compound consists of infinite chains of tetragonally elongated octahedra [Co–O(axial) 2.17, Co–O(equatorial) 2.07 Å (mean values)] sharing the axial oxygen atoms. The four equatorial ligands comprise two mutually *trans* water molecules [Co–O(2),O(3) 2.06 Å (mean)] and two dmba anions bonded through one oxygen of the carboxylate group [Co–O(1A),O(1B) 2.07 Å (mean)]. The metal–oxygen bonds correspond well to those found in the compound $[Co(hipp)_2(H_2O)_3]{\cdot}2H_2O$ (hipp = hippurate),[7] having a similar structure. Also, the bond distances within the dimethoxybenzoate ligand are considered to be normal. The presence of the bulky methyl groups, compared with 2,6-dihydroxybenzoate,[2] causes the approximate orthogonality between the phenyl rings and the CO_2 carboxylate moieties (mean value of the two dihedral angles, 80°). The CO_2 groups are also nearly orthogonal to the equatorial plane of the metal co-ordination (mean value of the two dihedral angles, 105°) because of the presence of intramolecular hydrogen bonding between the axial bridging water molecule and the non-co-ordinating oxygens of the carboxylate groups [O(2A) and O(2B)].

The Co–O(1)–Co′ 'intra-chain' angle is of 132.3(1)° and consequently the equatorial planes of the octahedra are not perpendicular to the direction of propagation of the chains (the crystallographic *a* axis), the normal to the least-squares equatorial plane making an angle of 26.3° with the *a* axis.

The intra-chain Co ··· Co distance is 3.97 Å. The shorter inter-chain Co ··· Co distance of 10.65 Å is due to the translation of one cell edge along the *b* direction, while the second shorter inter-chain Co ··· Co distance is 14.28 Å. In the complex $[Co(hipp)_2(H_2O)_3]{\cdot}2H_2O$ the shorter inter-chain distance is 6.903 Å and the chains are connected through hydrogen bonding. In the present case the hydrogen bonds involve only atoms belonging to the same chain.

$[M(dmba)_2(H_2O)_3]{\cdot}H_2O$ (M = Mn, Ni, *or* Zn).—*X*-Ray diffraction analysis has shown these complexes to be isomorphous with the cobalt compound.

Infrared Spectra.—The $[M(dmba)_2(H_2O)_3]{\cdot}H_2O$ complexes and $Na(dmba){\cdot}0.25H_2O$ exhibit quite similar i.r. spectra. The bands associated with the carboxylate stretching vibrations, $\nu_{asym.}(CO_2)$ and $\nu_{sym.}(CO_2)$, are found at 1 558 and 1 405 cm^{-1}, respectively, for all the metal complexes and at 1 619 and 1 417 cm^{-1} for the sodium salt. The relatively small $\nu_{asym.}(CO_2)$ −

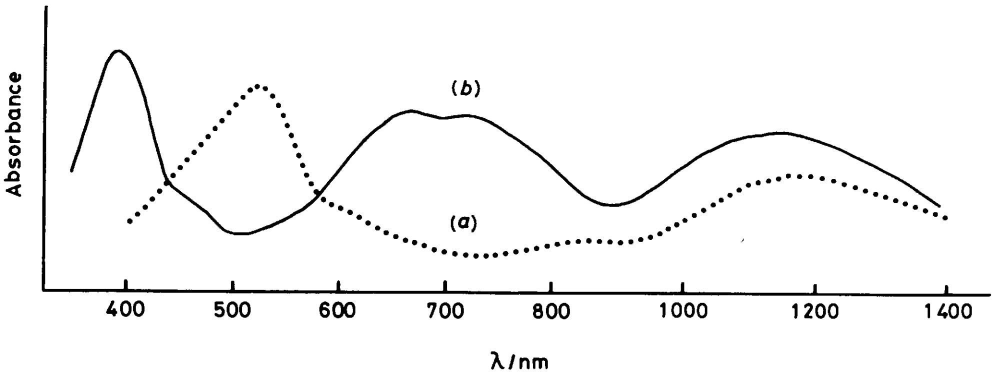

Figure 2. Diffuse reflectance electronic spectra of $[M(dmba)_2(H_2O)_3]{\cdot}H_2O$: (*a*) M = Co, (*b*) M = Ni

Table 4. Assignment of *d–d* bands for $[M(dmba)_2(H_2O)_3]{\cdot}H_2O$

Compound	λ/nm	Assignment
M = Co^{II}	1 180	${}^4T_{1g} \rightarrow {}^4T_{2g}$
	590	${}^4T_{1g} \rightarrow {}^4A_{2g}$
	525	${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$
M = Ni^{II}	1 148	${}^3A_{2g} \rightarrow {}^3T_{2g}$
	720	${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$
	660	${}^3A_{2g} \rightarrow {}^1E_g$
	450	${}^3A_{2g} \rightarrow {}^1T_{1g}$
	390	${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$

$\nu_{sym.}(CO_2)$ separation in the spectra of the complexes is unexpected for a unidentate co-ordination of carboxylate. Such a trend is reasonably explained by the involvement of the non-co-ordinated carboxylate oxygen in intramolecular hydrogen bonding, analogously to the case of 2,6-dihydroxybenzoate complexes.[1]

Electronic Spectra.—The electronic spectra of the Ni^{II} and Co^{II} complexes (Figure 2) in the range of the *d–d* transitions are characteristic of essentially octahedral symmetry with crystal field parameters very similar to each other and to those of regular octahedral chromophores.[8] The assignment of the *d–d* bands is reported in Table 4. The electronic spectrum of the Mn^{II} complex shows, as expected,[8] very weak spin-forbidden *d–d* bands.

Magnetic Measurements.—Plots of magnetic susceptibility down to 4 K for the Co, Ni, and Mn complexes are shown in Figure 3. The magnetic behaviour of the Co and Ni complexes shows striking resemblance to that observed previously for the analogous metal(II) hippurates.[7] For example, the Ni compound deviates from the Curie-Weiss law below 60 K and exhibits a broad antiferromagnetic transition. Based on the structural data, a magnetic interaction of the antiferromagnetic type, mediated by the bridging water molecules, is expected along the crystallographic *a* axis. Inter-chain interactions due to dipolar coupling along the other crystallographic directions, being proportional to r^{-3} (r = metal–metal distance), are not expected to contribute significantly above 4 K. Thus the magnetic behaviour may be interpreted as reflecting ordering in only one direction (the *a* axis) and a primary intra-chain interaction arising through a superexchange mechanism. Using the appropriate equation[7] for the magnetic susceptibility of isotropic ions in linear chains, a value for the exchange integral of $J = -12$ cm^{-1} ($g = 2.23$) is found for Ni. Analogously, the Mn complex exhibits a broad maximum in the susceptibility near 15 K, as expected for an antiferromagnetic linear chain system, as in $Cs[MnCl_3]{\cdot}2H_2O$.[9] The experimental data fit the above equation at the high-temperature range with $J = -3$ cm^{-1} ($g = 2.00$), but deviations from theory become increasingly pronounced with decreasing temperature. The magnetic susceptibility of $[Co(dmba)_2(H_2O)_3]{\cdot}H_2O$ is similar to that of $[Co(hipp)_2(H_2O)_3]{\cdot}2H_2O$[7] where deviations from simple antiferromagnetic behaviour were attributed to the 'Dzyaloshinsky-Moriya antisymmetric spin-exchange interaction'.[10,11] The differences in the magnetic behaviour of dmba complexes of Mn, Co, and Ni, which are isostructural, may be related to differences in the metal ions.

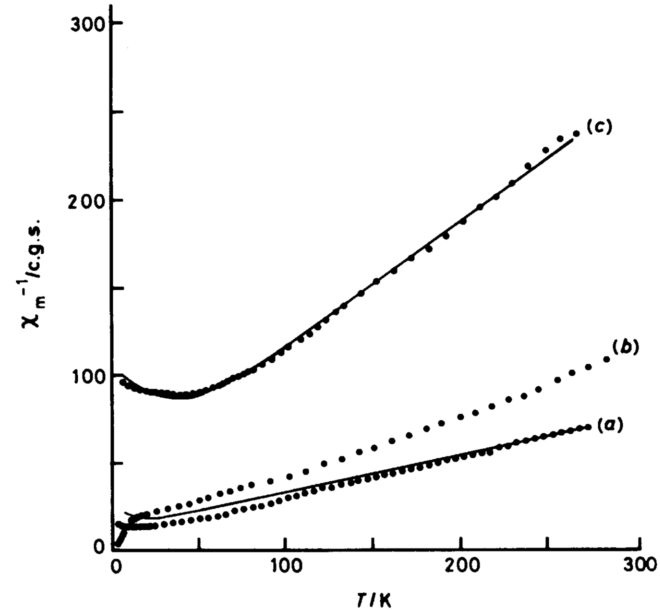

Figure 3. Inverse of the measured (●) and calculated (———) magnetic susceptibility *versus* temperature for $[M(dmba)_2(H_2O)_3]{\cdot}H_2O$: (*a*) M = Mn, (*b*) M = Co, (*c*) M = Ni; χ_m (c.g.s.) = $4\pi \times 10^{-6}$ m^3 mol^{-1}

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