DALTON
FULL PAPER

New pentanuclear mixed valence Co(II)–Co(III) complexes of "short" salen homologues †

Brunetto Chiari,[a] Antonio Cinti,[a] Ornella Crispu,[b] Francesco Demartin,*[c] Alessandro Pasini *[b] and Olivo Piovesana *[a]

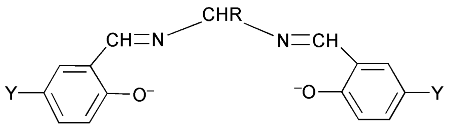
[a] *Dipartimento di Chimica, via Elce di Sotto 8, 06100 Perugia, Italy. E-mail: piovol@unipg.it*
[b] *Dipartimento di Chimica Inorganica Metallorganica e Analitica, and CNR ISTM, via Venezian 21, 20133 Milano, Italy. E-mail: alessandro.pasini@unimi.it*
[c] *Dipartimento di Chimica Strutturale e Stereochimica Inorganica, via Venezian 21, 20133 Milano, Italy. E-mail: francesco.demartin@unimi.it*

Received 27th June 2002, Accepted 15th October 2002
First published as an Advance Article on the web 14th November 2002

We describe herein a series of novel pentanuclear Co(II)–Co(III) mixed-valence cationic complexes of formula $[Co_5L_4(\mu_3\text{-}OH)_2]^+$ {L^{2-} = 2,2′-[1,1-methanediylbis(nitrilomethylidene)diphenate] or its arylmethane analogues}, obtained by controlled oxidation of $[Co_2L_2]$ precursors. The $[Co_5(\mu_3\text{-}OH)_2(salNO_2ben)_4]I\cdot2(CH_3)_2CO$ and $[Co_5(\mu_3\text{-}OH)_2(salClben)_4]I\cdot2DMF\cdot CH_2Cl_2$ compounds have been studied by X-ray methods and turn out to be isostructural. The structural data show that the cobalt atoms in the pentanuclear units are bridged by μ-O(phenolato) atoms and μ_3-OH groups and approximate three types of co-ordination geometries: tetrahedral, octahedral and trigonal-bipyramidal. The X-ray structure of one proligand, namely 2,2′-[1,1-(4-nitrophenylmethanediyl)-bis(nitrilomethylidene)diphenol] is also reported. The $\chi T(T)$ behaviour of the complex with this ligand has been studied in the 4–300 K range. The data clearly show that ferromagnetic as well as (much weaker) antiferromagnetic exchange interactions occur within the cluster. A simple exchange model has been developed which nicely reproduces the experimental data.

Magnetic molecular clusters of transition metal ions have been shown to display a wide variety of novel metal–metal interactions and corresponding physico-chemical properties that are of interest in research areas as different as materials science, catalysis, biochemistry and molecular electronics.[1–4] Consequently, the search for ligands which can give rise to molecular clusters of high nuclearity is a main theme of modern co-ordination chemistry.[5]

We have started to contribute to this search[6–8] by investigating the co-ordination properties of the quadridentate ligands L^{2-} of Scheme 1, namely 2,2′-[1,1-methanediylbis-(nitrilomethylidene)diphenate] and some of its arylmethane analogues.[9] We have termed these ligands "short" homologues of the well known salen, since the link between the two salicylaldehyde groups is a N–C–N, rather than a N–C–C–N chain. Such "short" ligands, because of the highly strained four membered $M–N_2–C$ chelate ring that would be present in mononuclear complexes, strongly favour the formation of structures in which the N–C–N groups bridge pairs of metal centres. Such M–N–C–N–M binucleating ability was first reported for a molybdenum(VI) complex of stoichiometry MoL_2 (R = H, Y = H).[10] More recently, we have synthesised a number of binuclear complexes of formula $[M_2L_2]$ with M = Co(II), Co(III), Ni(II), Cu(II) and Zn(II).[6–8]



salmen	R = H, Y = H
MeOsalmen	R = H, Y = CH_3O
Brsalmen	R = H, Y = Br
salben:	R = C_6H_5 Y = H,
salMeben	R = p-$CH_3C_6H_4$ Y = H,
salFben:	R = p-FC_6H_4 Y = H,
salClben	R = p-ClC_6H_4 Y = H,
$salNO_2ben$	R = p-$NO_2C_6H_4$ Y = H,
$salCF_3ben$	R = p-$CF_3C_6H_4$ Y = H,

Scheme 1

Here we demonstrate the ability of the ligands L to form molecular clusters of higher nuclearity. In particular we describe the synthesis, X-ray structures and magnetic properties of mixed valence pentanuclear Co(II)–Co(III) cationic complexes of formula $[Co_5L_4(OH)_2]^+$. The X-ray structure of the H_2salNO_2ben proligand has also been determined.

Experimental

Elemental analyses (Table 1) were from the Microanalytical Laboratory, the University of Milano. FAB mass spectra were obtained from 3-nitrobenzyl alcohol on a VCA Analytical 7070 EQ with xenon as the FAB source, isotope cluster abundances were checked using local programs.

Reagent grade chemicals were used throughout. The Schiff base proligands were prepared as described previously.[7–9,11] $H_2salFben$, H_2salCF_3ben and $H_2Brsalmen$ have been synthesised by the same procedures.[3,4] Yields, melting points, elemental analyses (with required values in parentheses) and relevant ^{1}NMR data for these compounds are: $H_2salFben$: 90%; 133 °C; C, 77.5 (77.4); H, 5.0 (5.0); N, 8.0 (8.0%); δ (ppm *versus* Me_4Si, $CDCl_3$ solutions, all reported peaks are singlets with correct integrations): 12.85 (OH), 8.57 (s, N=CH), 5.98 (s,

---

† Electronic supplementary information (ESI) available: Table S1 (selected interatomic distances and angles for H_2salNO_2ben, $[Co_5(\mu_3\text{-}OH)_2(salNO_2ben)_4]I\cdot CH_3CO$ and $[Co_5(\mu_3\text{-}OH)_2(salClben)_4]I\cdot2DMF\cdot CH_2Cl_2$) and the expression for the magnetic susceptibility. See http://www.rsc.org/suppdata/dt/b2/b206221f/

DOI: 10.1039/b206221f

Table 1 FAB mass spectra[a] and elemental analyses[b] of the compounds.

Compound	FAB	C	H	N
$[Co_5(OH)_2(salben)_4]I·4H_2O$	1641	54.5 (54.8)	4.0 (4.1)	6.0 (6.1)
$[Co_5(OH)_2(salMeben)_4]I·0.5C_6H_{14}O$	1698	58.3 (58.3)	4.2 (4.3)	6.1 (6.1)
$[Co_5(OH)_2(salNO_2ben)_4]I·3H_2O$	1822	50.1 (50.4)	3.6 (3.4)	8.2 (8.4)
$[Co_5(OH)_2(salNO_2ben)_4]I_{2.25}$[c]	1822	44.6 (44.9)	3.0 (2.8)	7.2 (7.4)
$[Co_5(OH)_2(salClben)_4]I·3H_2O$	1781	51.8 (51.5)	3.9 (3.7)	6.1 (6.1)
$[Co_5(OH)_2(salClben)_4]I_5$[d]	1781	41.5 (41.8)	2.8 (2.6)	4.5 (4.6)
$[Co_5(OH)_2(salFben)_4]I·1/2C_6H_{14}O$	1713	55.4 (55.2)	3.7 (3.7)	6.0 (5.9)
$[Co_5(OH)_2(salCF_3ben)_4]I_3$	1914	46.3 (46.0)	2.9 (2.7)	4.8 (4.9)
$[Co_5(OH)_2(salmen)_4]I·C_6H_{14}O$	1338	50.5 (50.6)	4.0 (4.1)	7.4 (7.2)
$[Co_5(OH)_2(MeOsalmen)_4]I·3H_2O$	1580	46.3 (46.4)	4.2 (4.1)	6.4 (6.4)
$[Co_5(OH)_2(Brsalmen)_4]I·H_2O$	1968	40.0 (40.1)	2.7 (2.5)	6.1 (6.2)

[a] Positive ions from nitrobenzyl alcohol. [b] Required values (%) in parentheses. [c] This sample gave $[Co_5(OH)_2(salNO_2ben)_4]I$ upon crystallization from $CHCl_3$/isopropyl ether. [d] This sample gave $[Co_5(OH)_2(salClben)_4]I$ upon crystallization from $CHCl_3$/isopropyl ether.

CHR). H_2salCF_3ben: 80%; 145 °C; C, 66.4 (66.3); H, 4.4 (4.3); N, 7.1 (7.0%); δ: 12.74 (OH), 8.62 (N=CH), 6.04 (CHR). $H_2Brsalmen$: 93%; 153 °C; C, 43.9 (44.1), H, 3.0 (2.9); N, 6.6 (6.8%); δ: 12.87 (OH), 8.46 (N=CH), 5.49 (CH_2).

The starting $[Co_2L_2]$ and $[Co_2L_2(py)_2]I_3$ complexes were obtained as described in ref. 8.

Preparation of the pentanuclear complexes

$[Co_5(\mu_3\text{-}OH)_2(salben)_4]I·4H_2O$. A suspension of 0.341 g (0.39 mmol) of $[Co_2(salben)_2]$ in 15 ml of chloroform, saturated with water, was treated with 0.022 g of I_2 (0.087 mmol). The slurry was stirred at room temperature for three days. The mustard-brown precipitate was collected by filtration, washed with $CHCl_3$ and dried *in vacuo*. Yield 80%, 0.230 g.

$[Co_5(\mu_3\text{-}OH)_2(salNO_2ben)_4]I·3H_2O$. 0.168 g of $[Co_2(salNO_2ben)_2]$ (0.19 mmol) and 0.0124 g of I_2(0.049 mmol) were added to 15 ml of CH_2Cl_2 saturated with water. Stirring the slurry for 48 hours at room temperature gave 0.115 g (75%) of a yellow-brown precipitate. Crystals suitable for X-ray diffraction studies were obtained by slow diffusion of hexane into a concentrated acetone solution. Under these conditions the compound crystallized with two molecules of acetone.

The other compounds were obtained in similar ways.

Hydrolysis of $[Co_2(salClben)_2.py_2]I_3$. The complex (0.211 g) was dissolved in 25 mL of DMF and the solution was layered with diisopropyl ether. The brown powder obtained after one week was redissolved in CH_2Cl_2. Upon diffusion of diisopropyl ether brown crystals of $[Co_5(\mu_3\text{-}OH)_2(salClben)_4]I·2DMF·CH_2Cl_2$, suitable for X-ray diffraction studies, were collected after ten days.

Elemental analyses, and FAB mass data of the compounds are reported in Table 1.

X-Ray crystal structure determination

Details of the procedures concerning data collection and refinement of the structures are reported in Table 2. Crystals were mounted on a glass fiber in a random orientation and collected at room temperature on a Siemens SMART CCD area-detector diffractometer. Graphite monochromatized Mo–Kα radiation (λ = 0.71073 Å) was used with the generator working at 50 kV and 35 mA. Preliminary cell parameters and orientation matrix were obtained from least-squares refinement on reflections measured in three different sets of 20 frames each, in the range $0 < \theta < 25°$. Intensity data were collected in the full sphere (ω scan method); 2100 frames (20 s per frame, $\Delta\omega = 0.3°$) and the first 100 frames recollected in order to monitor any crystal decay. An absorption correction was applied using the SADABS routine.[12] The structures were solved by direct methods using SHELXS 86[13] and full-matrix least-squares refinements on F^2 were performed using SHELXL 97.[14] All non-H atoms were refined anisotropically and H atoms were seen in difference Fourier maps; for compounds $[Co_5(\mu_3\text{-}OH)_2(salClben)_4]I·2DMF·CH_2Cl_2$ and $[Co_5(\mu_3\text{-}OH)_2(salNO_2ben)_4]I·2(CH_3)_2CO$, those of the bridging OH groups were refined, whereas the others were placed and thereafter allowed to ride on their parent atoms; the hydrogen atoms of the solvent molecules were not introduced in the model. All the hydrogen atoms of H_2salNO_2ben were refined.

CCDC reference numbers 188686–188688.

See http://www.rsc.org/suppdata/dt/b2/b206221f/ for crystallographic data in CIF or other electronic format.

Magnetic measurements

Variable-temperature susceptibility measurements on $[Co_5(\mu_3\text{-}OH)_2(salNO_2ben)_4]I·2(CH_3)_2CO$, in the range 4–300 K, were performed as previously described.[7] Susceptibilities were corrected for diamagnetism of the ligands estimated as -960.46×10^{-6} cm^3 K mol^{-1}. Temperature independent paramagnetism was assumed to be negligible.

Results and discussion

We obtained the first example of pentanuclear $[Co_5L_4(OH)_2]^+$ complexes by repeated crystallizations from DMF and CH_2Cl_2 (see Experimental section) of the mixed valence Co(II)–Co(III) complex $[Co_2(salClben)_2.py_2]I_3$, which is the product of the oxidation of $[Co_2(salClben)_2]$ with excess I_2 in the presence of pyridine.[8] We then isolated $[Co_5(OH)_2(salNO_2ben)_4]I$ by oxidation of $[Co_2(salNO_2ben)_2]$, in the absence of pyridine with I_2 in CH_2Cl_2. Both compounds were obtained by chance and their formation was clearly due to non-strictly anhydrous conditions. However, since preliminary X-ray measurements showed them to be isostructural, we reasoned that the pentanuclear structural motif should be a favoured one for cobalt complexes with L ligands. A reproducible synthesis was eventually achieved by long digestion of the parent $[Co_2L_2]$ complexes with 0.2 mol of I_2 per binuclear moiety, at room temperature, in wet $CHCl_3$ or CH_2Cl_2, according to eqn. (1):

$$5\,[Co_2L_2] + I_2 + 2\,H_2O \longrightarrow 2\,[Co_5L_4(OH)_2]I + 2\,H_2L \quad (1)$$

The proligands H_2L were indeed recovered from the solutions. The compounds crystallize with variable amounts of solvent molecules. Prepared compounds and elemental analyses are reported in Table 1, together with FAB mass spectral data which clearly show their pentanuclear nature which is retained in solutions of nitrobenzyl alcohol.

Higher amounts of I_2 can also be used, provided the reaction is carried out in the absence of donor ligands, which stabilise the $[Co_2L_2(py)_2]^+$ or $[Co_2L_2(py)_4]^{2+}$ as reported in a previous paper.[8] In a few instances we have obtained materials which analyse for $[Co_5L_4(OH)_2]I_x$ with x = 2–6, however iodine was

Table 2 Crystallographic data

Compound	$[Co_5(OH)_2(salNO_2ben)_4]I\cdot 2(CH_3)_2CO$	$[Co_5(OH)_2(salClben)_4]I\cdot 2DMF\cdot CH_2Cl_2$	H_2salNO_2ben
Formula	$C_{90}H_{74}Co_5IN_{12}O_{20}$	$C_{91}H_{78}Cl_6Co_5IN_{10}O_{12}$	$C_{21}H_{17}N_3O_4$
M	2065.2	2137.98	375.38
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$P2_1/n$	$Pna2_1$
a/Å	15.771(1)	15.495(2)	9.211(2)
b/Å	25.007(2)	25.344(4)	15.578(3)
c/Å	23.185(2)	23.663(3)	13.018(3)
β/°	99.88(1)	101.64(1)	
V/Å^3	9008(1)	9101(2)	1867.8(6)
Z	4	4	4
F(000)	4184	4320	784
D_{calc}/g cm^{-3}	1.523	1.560	1.335
μ(Mo Kα)/cm^{-1}	13.21	14.74	0.94
Independent reflections	12972	23202	2112
Observed reflections [$I>2\sigma(I)$]	9829	13363	1522
Final R and R_w indices[a]	0.042, 0.122	0.049, 0.121	0.036, 0.087
Largest diff. peak and hole/e Å^{-3}	1.47, −0.49	1.09, −0.76	0.14, −0.12

[a] $R = [\Sigma(F_o - k|F_c|) / \Sigma F_o]$. $R_w = [\Sigma w(F_o - k|F_c|)^2 / \Sigma w F_o^2]^{1/2}$.

lost upon standing or by crystallization and their FAB mass spectra showed the pattern of the $[Co_5L_4(OH)_2]^+$ cation. We were unable to obtain crystals suitable for the X-ray investigation of these materials, but we believe that they contain either some polyiodide, as the anion, or some molecular iodine, probably clathrated. Examples of these materials are also reported in Table 1.

All compounds have room temperature μ_{eff} values of about 9 μ_B, which, as discussed later, are in agreement with the structures described below.

Structure of H_2salNO_2ben

In Schiff bases derived from salicylaldehyde the enolimine tautomer is usually favoured over the ketamine form.[15–17] This is also the case of the cobalt and copper complexes of L (Scheme 1), as found by X-ray structure determinations of some of these complexes,[7,8] but we were curious to know whether the enolimine tautomer was present also in the unco-ordinated proligands. For this purpose, we have determined the X-ray structure of H_2salNO_2ben which gave crystals suitable for diffraction studies upon slow evaporation of an ethanol solution of the compound. A perspective view of the molecule is shown in Fig. 1, while selected bond distances and angles are reported in Table S1 (see ESI †), these values are normal for a structure containing a Schiff base derived from salicylaldehyde and a diamine.[15,16] The molecule adopts a conformation which is determined by the presence of intramolecular O–H ··· N hydrogen bonds, involving the phenolic functions and the iminic nitrogens of the same portion of the molecule [O(1) ··· N(9) 2.618(3) Å; O(25) ··· N(17) 2.624(4) Å; O(1)–H(1) ··· N(9) 147(3)° and O(25)–H(25) ··· N(17), 147(5)°]. The NO_2 group is essentially in the plane of the phenyl ring to which it is attached.

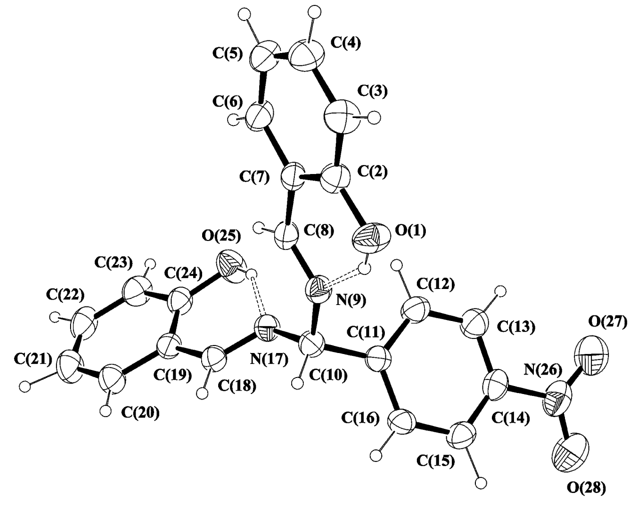


Fig. 1 ORTEP[31] view of the H_2salNO_2ben proligand.

Structures of the pentanuclear complexes $[Co_5(\mu_3\text{-}OH)_2(salNO_2ben)_4]I\cdot 2(CH_3)_2CO$ and $[Co_5(\mu_3\text{-}OH)_2(salClben)_4]I\cdot 2DMF\cdot CH_2Cl_2$

The data in Table 2 clearly show that the two compounds are isostructural. Minor differences in the unit cell parameters arise essentially from the different kinds of solvent molecules trapped in the crystal lattice.

Selected bond distances and angles are reported in Table S1 (see ESI †). An ORTEP view of $[Co_5(\mu_3\text{-}OH)_2(sal\ NO_2ben)_4]^+$ is shown in Fig. 2. The five cobalt atoms are held together by four bridging $salNO_2ben$ ligands (denoted a, b, c and d) and two μ_3-bridging OH groups. The latter are also involved in hydrogen bonding interactions with the two oxygen atoms of the acetone molecules [O(1) ··· O(204) 2.698(7) Å; O(2) ··· O(104) 2.795(5) Å]. Each $salNO_2ben$ ligand acts as bis-bidentate and binds two metal ions through couples of O-phenolato and imine nitrogen atoms. Four phenolic oxygen atoms [O(1b), O(1d), O(25a) and O(25c)] bridge two metal ions each, giving rise to a cluster which comprises four Co ions

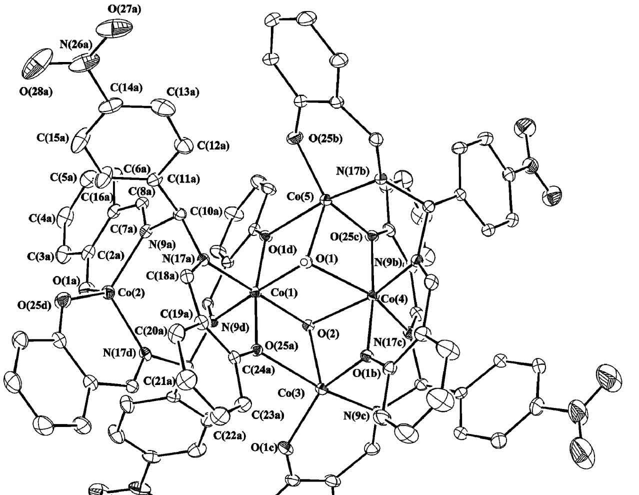


Fig. 2 ORTEP[31] view of the$[Co_5(\mu_3\text{-}OH)_2(salNO_2ben)_4]^+$ cation.

[Co(1), Co(3), Co(4) and Co(5)] as well as the two μ_3-OH groups. A fifth Co atom [Co(2)] is bound to such a cluster by means of the a and d ligands.

The five cobalt atoms show three different co-ordination geometries: one is tetrahedral [Co(2)], two display trigonal bipyramidal geometry [Co(3) and Co(5)] and two are octahedral [Co(1) and Co(4)]. Distortions from the ideal geometries are severe and make the actual site symmetry of each cobalt ion not higher than C_{2v}. It is not unusual to find cobalt atoms with two different co-ordination geometries in the same complex,[18,19] but the present cation is a remarkable example where three types of co-ordination are observed in the same compound.

The two octahedral cobalt atoms, in spite of having the same ligand environment, display significantly different bond lengths: the average Co(1)–O and Co(1)–N distances, 1.905 Å and 1.956 Å, respectively, are shorter than the corresponding Co(4)–O and Co(4)–N distances of 2.119 Å and 2.117 Å. This can be related to a different oxidation state of the two metal ions. Moreover the Co(1)–O and Co(1)–N distances are comparable to the Co–O and Co–N distances found for Co(III) in the related $[Co_2(salmen)_2(py)_4]^{2+}$ and $[Co_2(salben)_2(py)_2]^+$ cations.[8] Although the relationship between ligand to cobalt distances and cobalt oxidation states is not always straightforward,[20] it appears safe to assign Co(1) as the Co(III) ion.

Interestingly, the moiety comprising Co(1) and Co(2) and the two $salNO_2ben$ ligands (a) and (d) is very similar to the one observed in the $[Co_2(salben)_2(py)_2]^+$ cation,[8] which also contains a tetrahedral Co(II) and an octahedral Co(III) atom. The main difference between the two moieties is that hexa-co-ordination of Co(III) is completed by two OH groups in the former compound and two pyridine molecules in the latter.

A shorter metal–metal weak interaction of Co(4) with Co(3) [2.910(1) Å] and Co(5) [2.915(1) Å] is also observed with respect to the corresponding interactions realized by Co(1) [3.203(1) Å and 3.187(1) Å, respectively].

As in the structure of the H_2salNO_2ben proligand, all the NO_2 moieties are essentially in the plane of the phenyl ring to which they are attached.

The geometrical parameters of the $[Co_5(\mu_3\text{-}OH)_2(salClben)_4]^+$ cation are reported in Table S1 (see ESI) and are comparable with the corresponding parameters of the $salNO_2ben$ analogue. In the salClben derivative two $(CH_3)_2NCHO$ molecules are hydrogen-bonded to the μ_3-bridging OH groups [O(1) ··· O(1)s 2.634(4) Å; O(2) ··· O(6)s 2.690(4) Å]. No short intermolecular interactions below the sum of the van der Waals radii occurs between the CH_2Cl_2 molecule or the I^- anion and their neighbours.

Magnetism

Variable temperature magnetic susceptibility data for the representative compound $[Co_5(\mu_3\text{-}OH)_2(salNO_2ben)_4]I\cdot 2(CH_3)_2CO$ are shown in Fig. 3, in the χT *versus* T form. At room temperature χT has a value of 10.2 cm^3 K mol^{-1}, consistent with the presence in the pentanuclear unit of a spin-paired octahedral Co(III) ion (with $S = 0$), identified from the structural data as Co(1), and four uncoupled, spin free Co(II) ions with $S = 3/2$ and an average g value of 2.33. The tetranuclear Co(II) core, which approximately conforms to C_{2v} symmetry, is depicted in Fig. 4a, where the cobalt atoms are labelled according to Fig. 2.

A rigorous magnetic susceptibility calculation for a Co(II) cluster of high nuclearity is in general difficult to perform since, owing to the complex magnetic structure of the cobaltous ion,[21–23] the Hamiltonian for the problem must include isotropic as well as anisotropic exchange contributions, single ion terms describing the effects of zero-field splitting, spin–orbit coupling *etc.*[21,22,24–27] Unfortunately, exact diagonalization of a Hamiltonian of this type is extremely difficult,[21,22] mainly because of the exceedingly large size of the matrix involved, *e.g.* 16^n × 16^n for a cluster of n octahedral Co(II) ions. Although several mathematical approaches to such a diagonalization problem have been offered,[24–26] they are difficult to apply in the present case because the low core symmetry and the different types of local Co(II) geometry make the problem over-parameterized and therefore of limited significance in data fitting.

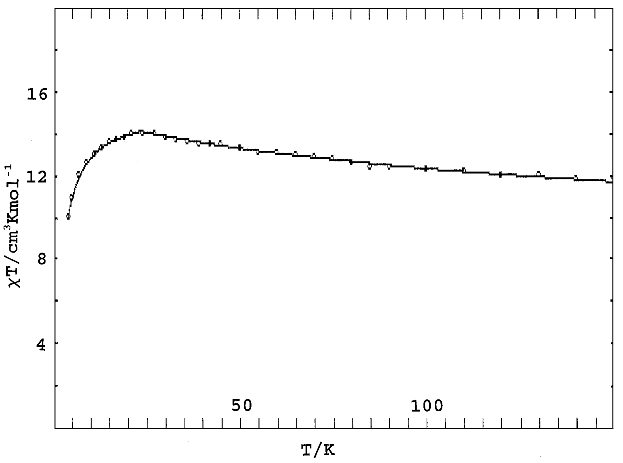


Fig. 3 Magnetic susceptibility data for $[Co_5(\mu_3\text{-}OH)_2(salNO_2ben)_4]I\cdot 2(CH_3)_2CO$. The solid line through the data was generated by the model described in the text.

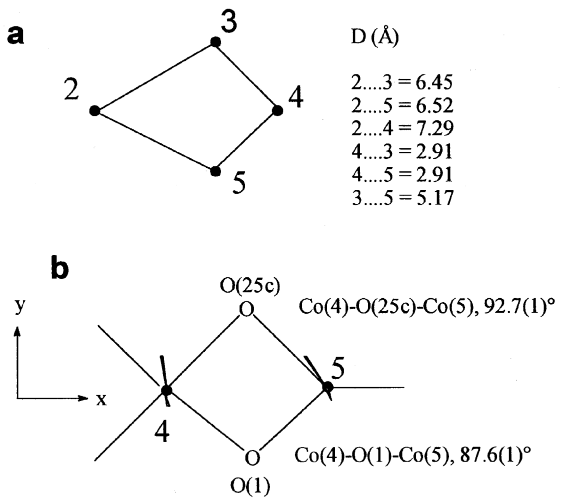


Fig. 4 (a) Schematic view of the magnetic tetranuclear Co(II) core in the pentanuclear units of the compounds. (b) View of the interacting Co(4)–Co(5) binuclear moiety in the pentanuclear units.

Under the circumstances, we have tentatively developed an intuitive, simple model suggested by a consideration of the observed $\chi T(T)$ dependence and previously obtained results[8] for $[Co_2(salNO_2ben)_2(py)_2](I_3)$, which contains a magnetically isolated Co(II) ion with the same geometry and chemical environment as those of Co(2). These results show that the fourfold degeneracy of the tetrahedral $^4A_2$ single ion ground state is split into two Kramers doublets, |±3/2> and |±1/2>, separated by an energy of $|2D|$ = 22 cm^{-1} (D = zero-field splitting parameter).

Upon decreasing the temperature from ≈ 300 K, the cluster χT value gradually increases revealing the presence of dominant ferromagnetic interactions (in the range 60–300 K the χ^{-1} *vs.* T plot shows a positive θ value of 8.7 K), goes through a flat broad maximum, centred around 25 K, corresponding to a value (≈ 14 cm^3 K mol^{-1}) which closely corresponds to that expected for a system comprised of two virtually uncoupled spins of $S = 9/2$ and $S' = 3/2$ (14.2 cm^3 K mol^{-1}, for $g = 2$) and then rapidly decreases.

Noting that, with $|2D| = 22$ cm^{-1}, a virtually uncoupled Co(2) ion is expected to approximately act as an $S = 3/2$ spin-only ion in the 300–25 K range, owing to a comparable thermal population of the $|\pm 3/2>$ and $|\pm 1/2>$ levels, the simplest interpretation for the $\chi T(T)$ behaviour of the cluster is that dominant exchange interactions within the triangular 4–5–3-subsystem (that contains the shortest exchange paths) give rise to a ferromagnetic subsystem ground state of $S = 9/2$ which becomes preferentially populated near 25 K. At lower temperatures, once the spins of 3, 4 and 5 become strongly aligned, the subsystem behaves like a single spin with "fictitious" quantum number 9/2 and the χT behaviour of the cluster is then controlled by the coupling (predictably small because of the long superexchange pathway) between the $S = 9/2$ and the $S = 3/2$ subsystems, zero-field splitting of the subsystems or, more likely, a combination of the two. Exchange coupling between the subsystems is likely to have negligible effects in the high temperature regime, *i.e.* when the three spins of the subsystem are not effectively aligned.

These hypotheses and considerations suggest that the data above ≈25 K may be reasonably described by means of the H_{tr} Hamiltonian (representing the system as comprised of the trinuclear unit and a virtually independent Co(2) ion) shown in eqn. (2).

$$H_{\mathrm{tr}} = H_1 + H_2 \qquad (2)$$

Where

$$H_1 = -2J(S_3{\cdot}S_4 + S_4{\cdot}S_5 + S_3{\cdot}S_5) + 2(J - J')(S_3{\cdot}S_5) \qquad (3)$$

and

$$H_2 = \beta g_{\mathrm{u}} B_{\mathrm{u}} S_{\mathrm{u}} + D(S_z - 5/4) \qquad (4)$$

In H_{tr}, the H_1 term represents the interactions within the 4–5–3 subsystem and H_2 is the usual Hamiltonian for an axially distorted tetrahedral Co(II) ion.[21,23] In H_1 and H_2, J is the coupling constant for the 3–4 and the symmetry related 4–5 pairs, J' represents the coupling between the 3 and 5 centres, D is the zero-field splitting parameter and the index u denotes the direction of the applied B magnetic field.

The expressions for the magnetic susceptibility are derived in the ESI.†

In the fitting calculations, the $<g>$ and $|D|$ parameters of H_2 were held constant at 2.32 and 11 cm^{-1}, respectively, *i.e.*, the previously found values[8] for $[Co_2(salNO_2ben)_2(py)_2]I_3$. The best $\chi T(T)$ theoretical curve was obtained with $J = 40.0$ cm^{-1}, $J' = -15.0$ cm^{-1} and, as shown in Fig. 3, nicely reproduces the experimental data.

The χT decrease below ≈25 K is more difficult to understand since, as already noted, several factors can contribute to it. Surprisingly, the low temperature data can be successfully fitted with use of the simplest Hamitonian which can be written for the system, *i.e.*, $H_{\mathrm{tet}} = -2J_{\mathrm{AB}}(S_{\mathrm{A}}{\cdot}S_{\mathrm{B}})$, where $S_{\mathrm{A}} = 9/2$ and $S_{\mathrm{B}} = 3/2$ (see ESI† for the magnetic susceptibility expression). The best fit, shown in Fig. 3, gives $J_{\mathrm{AB}} = -0.3$ cm^{-1}. One possible explanation of such a feature is that the lowest energy zero-field splitting levels of the Co(3,4,5) and Co(2) subsystems are $|\pm 9/2>$ and $|\pm 3/2>$, respectively, these being preferentially populated at low temperature. Due to the poor ability of powder χ data to reveal the sign of D parameters and the difficulty of calculating $|D(9/2)|$, additional experimental evidence is needed to confirm this model.

The obtained results invite a few comments.

(i) The calculations neglect any orbital magnetism effect. Although such an approximation to magnetic exchange (which is appropriate only in situations where the local ground states are well isolated singlets[22]) can be in some way justified by the low symmetry of the magnetic centres, at best C_{2v} (the ground state of an ion with this symmetry cannot be orbitally degenerate because all the irreducible representations of the C_{2v} group are one-dimensional), it remains tentative since the role of the excited terms is difficult to assess.

(ii) In spite of the drastic approximations used, the best fit coupling constants are in agreement with our preliminary arguments and, more relevant, with the structural features of the compound. The magnitude of the J values follow the lengths of the exchange pathways and, in particular, the dominant 4 ··· 3 and 4 ··· 5 ferromagnetic interactions strongly conform to the geometry of the bridging units. This is schematically shown in Fig. 4b, where it is clearly apparent that the largest contribution to the exchange comes from the interaction between the *xy* magnetic orbitals which point along the metal–bridge direction and can be strongly delocalised towards the bridges. According to current exchange orbital models,[28] this dominant contribution leads to antiparallel spin alignment for bridging angles larger than 90°, the most commonly observed situation, and to parallel spin alignment for bridging angles close to 90°, which is the case here.

Conclusions

The pentanuclear structural motif here described appears to be remarkably favoured for cobalt complexes with the ligands of Scheme 1, as it has been achieved with all such ligands by direct oxidation of the parent dinuclear Co(II) complexes $[Co_2L_2]$. The fact that this pentanuclear moiety has been obtained also by long digestion of the mixed valence Co(II)–Co(III) $[Co_2(salClben)_2(py)_2]^+$ in wet solvents, is also in agreement with such a stability. Moreover FAB mass spectra, taken from nitrobenzyl alcohol solutions, gave peaks corresponding to such a motif, showing that it is present also in solution. Several factors can contribute to such a stability, among which we suggest the following:

(i) The lability of the Co(II) ion. Since we start from Co_2L_2 and we end up with Co_5L_4 stoichiometry, one ligand L must be lost.

(ii) The stable structure of the binuclear mixed valence $[Co_2L_2]^+$ species,[8] which is one of the building blocks of the pentanuclear structure [here Co(2) and Co(1)].

(iii) The tendency of Co(III) to hexa-co-ordination. In the presence of pyridine this is achieved by this ligand, but in its absence and in wet reaction media, two water molecules fill the vacant co-ordination positions. Such molecules are probably deprotonated by the ligand anion dissociated from a Co(II). As suggested by the fact that H_2L is recovered from the reaction mixtures.

(iv) The μ bridging ability of the phenolato oxygen atoms, a well known feature of this group.[20,29,30]

(v) The μ_3 bridging ability of the OH groups. This is an important point: once the binuclear mixed valence moiety [(Co(2) and Co(1)] is formed, oligomerization cannot proceed if the Co(III) ion is co-ordinated to a ligand with no bridging ability, such as pyridine.

(vi) Finally it must be stressed that only rather long incubation times of the reaction mixtures gave high yields of these pentanuclear compounds, suggesting that both kinetic and thermodynamic factors contribute to the formation of the pentanuclear cluster.

Thus the "short" salen homologues described behave not only as bis-binucleating, as previously reported,[7,8] but they are able to form polynuclear structures.

Acknowledgements

We thank the Ministero dell'Università e della Ricerca Scientifica e Tecnologica for financial support.

References

1 (*a*) O. Kahn, in *Magneto-Structural Correlations in Exchange Coupled Systems*, ed. R. D. Willet, D. Gatteschi and O. Kahn, NATO ASI Series C, vol 140, Riedel, Dordrecht, Holland, 1985, p. 37; (*b*) E. I. Solomon and D. E. Wilson, in *Magneto-Structural Correlations in Exchange Coupled Systems*, ed. R. D. Willet, D. Gatteschi and O. Kahn, NATO ASI Series C, vol 140, Riedel, Dordrecht, Holland 1985, p. 463; (*c*) O. Kahn, *Struct. Bonding (Berlin)*, 1987, **68**, 89; (*d*) R. N. Muller, in *Molecular Magnetism: from Molecular Assemblies to Devices*, ed. E. Coronado, P. Dalhaes, D. Gatteschi and J. S. Miller, NATO ASI Series E, vol. 321, Kluwer, Dordrecht, Holland, 1996, p. 553; (*e*) A. Bencini and D. Gatteschi, in *EPR of Exchange Coupled Systems*, Springer Verlag, Berlin, 1990, p. 210.

2 T. Kuroda-Sowa, M. Lamm, A. L. Rheingold, C. Frommen, W. M. Reiff, M. Nakano, A. L. Maniero, L.-C. Brunel, G. Christou and D. N. Hendrickson, *Inorg. Chem.*, 2001, **40**, 6469.

3 G. Christou, *Acc. Chem. Res.*, 1989, **22**, 328.

4 K. L. Taft, G. C. Papaefthymiou and S. J. Lippard, *Inorg. Chem.*, 1994, **33**, 1510.

5 (*a*) R. E. Winpenny, *Adv. Inorg. Chem.*, 2001, **52**, 1; (*b*) R. E. Winpenny, *J. Chem. Soc., Dalton Trans.*, 2002, 1.

6 A. Pasini, R. P. Ferrari, S. Lanfranconi, A. Pozzi, E. Laurenti and M. Moroni, *Inorg. Chim. Acta*, 1997, **226**, 1.

7 A. Pasini, F. Demartin, O. Piovesana, B. Chiari, A. Cinti and O. Crispu, *J. Chem. Soc., Dalton Trans.*, 2000, 3467.

8 B. Chiari, A. Cinti, O. Crispu, F. Demartin, A. Pasini and O. Piovesana, *J. Chem. Soc., Dalton Trans.*, 2001, 3611.

9 T. Takajo, S. Kambe and W. Ando, *Synthesis*, 1984, 256.

10 X. Xu, X. Wang, H. Liu and X. You, *J. Chem. Soc., Dalton Trans.*, 1993, 1332.

11 N. Choudary, D. L. Hughes, U. Kleinkes, L. F. Larkworthy, G. J. Leigh, M. Maiwald, C. J. Marmion, J. R. Sanders, G. W. Smith and C. Sudbrake, *Polyhedron*, 1977, **16**, 1517.

12 G. M. Sheldrick, SADABS, University of Göttingen, Germany, 1996.

13 G. M. Sheldrick, SHELXS 86, *Acta Crystallogr., Sect A*, 1990, **46**, 467.

14 G. M. Sheldrick, SHELXL 97, University of Göttingen, 1997.

15 M. Kabak, A. Elmali, Y. Elerman and T. N. Durlu, *J. Mol. Struct.*, 2000, **553**, 187.

16 C.-H. Ming, H.-L. Kwong, W.-C. Chu, K.-F. Cheng, W.-S. Lee, H.-S. Yu, C.-T. Yeung and K.-K Cheung, *Eur. J. Inorg Chem.*, 2002, 1456.

17 A. Koll, M. Rospenk, E. Jagodzinska and T. D. Dziembowska, *J. Mol. Struct.*, 2000, **555**, 193.

18 (*a*) E. K. Brechin, S. G. Harris, S. Pearson and R., E. P. Winpenny, *J. Chem. Soc., Dalton Trans.*, 1997, 1665; (*b*) E. K. Brechin, S. G. Harris, S. Pearson and R., E. P. Winpenny, *Chem. Commun.*, 1996, 1439.

19 K. Dimitrou, J.S. Sun, K. Folting and G. Christou, *Inorg. Chem.*, 1995, **34**, 4160.

20 M. Calligaris, G. Nardin and L. Randaccio, *Coord. Chem. Rev.*, 1972, **7**, 385.

21 O. Kahn, *Molecular Magnetism*, VCH, New York, 1993, p. 38.

22 M. E. Lines, *J. Chem. Phys.*, 1971, **55**, 2977.

23 R. L. Carlin, in *Magnetochemistry*, Springer-Verlag, Berlin 1986, p. 65.

24 J. J. Borras-Almenar, J. M. Clemente-Juan, E. Coronado, A. V. Palii and B. S. Tsukerblat, *J. Phys. Chem. A*, 1998, **102**, 200.

25 H. Zhao, R. Clerac, J.-S. Sun, X. Ouyang, J. M. Clemente-Juan, C. J. Bomez-Garcia, E. Coronado and K. R. Dunbar, *J. Solid State Chem.*, 2001, **159**, 281.

26 J. J. Borras-Almenar, J. M. Clemente-Juan, E. Coronado and B. S. Tsukerblat, *Inorg. Chem.*, 1999, **38**, 6081.

27 (*a*) T. Moriya, in *Magnetism*, ed. G. T. Rado and H. Suhl, Academic Press, New York, 1963, vol. 1, p. 85; (*b*) J. Kanamori, in *Magnetism*, ed. G. T. Rado and H. Suhl, Academic Press, New York, 1963, vol. 1, p. 127; (*c*) T. Moriya, *Phys. Rev. B*, 1960, **120**, 91.

28 O. Kahn, *Molecular Magnetism*, VCH, New York, 1993, p. 190 and references therein.

29 (*a*) M. Aly, *Rev. Inorg. Chem.*, 1996, **16**, 316; (*b*) S. Yamada, *Coord. Chem. Rev.*, 1999, **190–192**, 537.

30 D. A. Atwood, *Coord. Chem. Rev.*, 1997, **165**, 267.

31 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.