

Binuclear Co(II)Co(II), Co(II)Co(III) and Co(III)Co(III) complexes of “short” salen homologues derived from the condensation of salicylaldehyde and methanedi-amine or phenylmethanediamines. Synthesis, structures and magnetism †

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Binuclear Co(II)Co(II), Co(II)Co(III) and Co(III)Co(III) complexes are reported of dianionic ligands, L²⁻, derived from the condensation of two mol of salicylaldehyde, or substituted salicylaldehydes, and one mol of methanedi-amine or phenyl substituted methanediamines. Direct evidence for the binuclear nature of the compounds is provided by X-ray structural and FAB mass spectroscopy data. Oxidation of the Co(II)Co(II) complexes, [Co₂L₂], with iodine, in the presence of pyridine, produces two types of compounds depending on the nature of L: mixed valence Co(II)Co(III) dimers of [Co₂L₂(py)₂](I₃) stoichiometry, in the case of the phenylmethane derivatives and fully oxidised Co(III)Co(III) dimers, [Co₂L₂(py)₄](I₃)₂, obtained from the complexes with methanedi-amine. The crystal structures of [Co₂(salben)₂(py)₂](I₃) and [Co₂(salmen)₂(py)₄](I₃)₂ (salben = *N,N'*-phenylmethanediyl-diphenato, salmen = *N,N'*-methanediyl-diphenato) have been determined. In both dimers the Co atoms are bridged by two bis-bidentate ligands. The coordination geometry of the Co(II) chromophore, CoN₂O₂, was found to be distorted tetrahedral, as preliminarily suggested by near infrared and room-temperature magnetic susceptibility data. The Co(III) environments, CoO₂N₄, involving two additional pyridine nitrogens, are regular octahedral. The magnetic behaviour of representative compounds has been determined and discussed.

Complexes of the salen type ligands (see Chart 1, *n* = 2) have been widely investigated in the past both because of their basic interest in the field of coordination chemistry, and as models of certain enzymes.¹ More recent work has focused on their catalytic aspects² and their potential use in materials science.³ Such complexes are usually mononuclear, with a nearly planar coordination geometry,⁴ although deviations from such a

geometry have been reported,⁵ especially in the case of salen analogues with diamines different from ethylenediamine.^{6–8}

The problem of understanding how variations in the nature of the diamine moiety can influence the chemical, structural and physical properties of such complexes has received considerable attention. Efforts in this direction have mainly been concerned with the effects of increasing the bulkiness,⁷ or the length⁸ of the diamine chain. Much less information is presently available for the coordination chemistry of “short” salen homologues, *i.e.* ligands derived from the condensation of two mol of salicylaldehyde and one mol of methanedi-amine^{9,10} (see Chart 1, *n* = 1, R = H), or phenylmethanediamine¹¹ (*n* = 1, R = phenyl or *p*-substituted phenyl groups). We have therefore undertaken a study on metal complexes of these ligands.^{12,13} Owing to their steric constraints, such ligands are likely to give rise to oligo- and poly-nuclear species with uncommon coordination geometries and, hopefully, novel chemical and physical properties. Indeed, we have recently shown that the Cu(II) salben (*n* = 1, R = Ph) complex is binuclear and that, in the crystal, interdimer O(phenolato)–Cu contacts produce rather unusual tetrameric units with two different geometries at the copper centres.¹³

We report here on the syntheses and properties of a series of related binuclear Co(II)Co(II), Co(II)Co(III) and Co(III)Co(III) complexes with the ligands depicted in Chart 1 (*n* = 1).

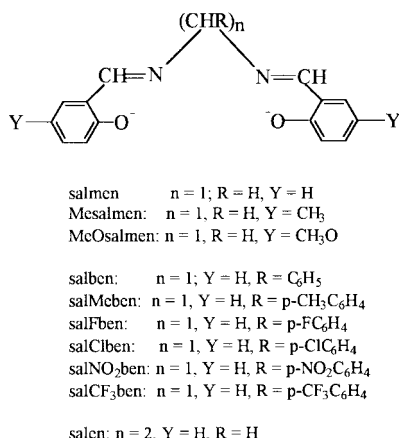


Chart 1

† Electronic supplementary information (ESI) available: Appendix, derivation of the expression for the average magnetic susceptibility of a Co(II)Co(II) dimer. See <http://www.rsc.org/suppdata/dt/b1/b105594c/>

Experimental

Analyses were from the microanalytical laboratory, the University of Milano. Diffuse reflectance spectra were recorded on a

Table 1 Elemental analyses,^a room temperature magnetic moments and FAB mass spectra^b of the compounds

Compound	C	H	N	$\mu_{\text{eff}}/\mu_{\text{B}}$	m/z
1 [Co ₂ (salmen) ₂], C ₃₀ H ₂₄ Co ₂ N ₄ O ₄	58.0 (57.9)	4.0 (3.9)	9.1 (9.0)	4.52 ^c	623 ^d
2 [Co ₂ (Mesalmen) ₂], C ₃₄ H ₃₂ Co ₂ N ₄ O ₄	60.2 (60.2)	5.1 (5.1)	8.2 (8.2)	4.45 ^c	679 ^d
3 [Co ₂ (MeOsalmen) ₂], C ₃₄ H ₃₂ Co ₂ N ₄ O ₈	55.0 (55.0)	4.5 (4.3)	7.3 (7.5)	4.45 ^c	743 ^d
4 [Co ₂ (salben) ₂], C ₄₂ H ₃₂ Co ₂ N ₄ O ₄	65.0 (65.1)	4.2 (4.2)	7.0 (7.2)	4.15 ^c	775 ^d
5 [Co ₂ (salMeben) ₂], C ₄₄ H ₃₆ Co ₂ N ₄ O ₄	65.7 (65.8)	4.5 (4.5)	6.7 (6.0)	4.38 ^c	803 ^d
6 [Co ₂ (salClben) ₂], C ₄₂ H ₃₀ Cl ₂ Co ₂ N ₄ O ₄	59.9 (59.8)	3.5 (3.6)	6.5 (6.6)	4.46 ^c	843 ^d
7 [Co ₂ (salNO ₂ ben) ₂], C ₄₂ H ₃₀ Co ₂ N ₆ O ₈	57.8 (58.4)	3.5 (3.5)	9.4 (9.7)	4.25 ^c	865 ^d
8 [Co ₂ (salben) ₂ (py) ₂](I ₃), C ₅₂ H ₄₂ Co ₂ I ₃ N ₆ O ₄	47.9 (47.6)	3.3 (3.2)	6.0 (6.4)	4.28 ^e	932 ^f
9 [Co ₂ (salMeben) ₂ (py) ₂](I ₃)·H ₂ O, C ₅₄ H ₄₈ Co ₂ I ₃ N ₆ O ₅	47.7 (47.7)	3.5 (3.6)	6.1 (6.2)	4.70 ^e	960 ^f
10 [Co ₂ (salClben) ₂ (py) ₂](I ₃), C ₅₂ H ₄₀ Cl ₂ Co ₂ I ₃ N ₆ O ₄	45.2 (45.2)	2.7 (2.9)	5.9 (6.1)	4.68 ^e	1001 ^f
11 [Co ₂ (salNO ₂ ben) ₂ (py) ₂](I ₃), C ₅₂ H ₄₀ Co ₂ I ₃ N ₈ O ₈	44.7 (44.5)	2.9 (2.9)	7.8 (8.0)	4.29 ^e	1022 ^f
12 [Co ₂ (salmen) ₂ (py) ₄](I ₃) ₂ , C ₅₀ H ₄₄ Co ₂ I ₆ N ₈ O ₄	35.5 (35.3)	2.7 (2.6)	6.8 (6.6)	—	—
13 [Co ₂ (Mesalmen) ₂ (py) ₄](I ₃) ₂ , C ₅₄ H ₅₂ Co ₂ I ₆ N ₈ O ₄	36.9 (36.9)	3.1 (3.0)	6.2 (6.4)	—	—
14 [Co ₂ (MeOsalmen) ₂ (py) ₄](I ₃) ₂ , C ₅₄ H ₅₂ Co ₂ I ₆ N ₈ O ₈	36.0 (35.6)	2.8 (2.9)	5.9 (6.2)	—	—

^a Required values (%) in parentheses. ^b Positive ion from nitrobenzyl alcohol. ^c Per Co atom. ^d Corresponding to [Co₂L₂ + 1]⁺. ^e For the whole binuclear molecule. ^f Corresponding to [Co₂L₂(py)₂]⁺.

Jasco V-570 spectrophotometer while FAB mass spectra were obtained from 3-nitrobenzyl alcohol, on a VCA Analytical 7070 EQ with xenon as the FAB source, isotope cluster abundance was checked using local programs. Room temperature magnetic susceptibilities have been measured using a Magnetic Susceptibility Balance, Sherwood Scientific Ltd., Cambridge.¹⁴

All reagents were obtained from Fluka. The Schiff bases proligands were synthesised as described in the literature.^{10,11,13} H₂Mesalmen has not been described previously, it was prepared in 90% yield according to a procedures described in ref. 13; mp 137 °C; analysis: C, 72.4; H, 6.4; N, 9.6; C₁₇H₁₈N₂O₂ requires: C, 72.3; H, 6.4; N, 9.9%; ¹H NMR (CDCl₃ solution, δ in ppm from Me₄Si): 2.32 (6 H, CH₃), 5.46 (2 H, CH₂), 6.9–7.3 (6 H, phenyl protons), 8.49 (2 H, N=CH), 12.76 (2 H, OH).

Syntheses

All manipulations were carried out under a nitrogen atmosphere. The compounds synthesised, together with analytical and characterisation data are listed in Table 1.

Co(II)Co(II) complexes. These were all obtained, in 70–80% yields, by the procedure described in detail below for [Co₂(salben)₂] **4**. Equimolar amounts of cobalt acetate tetrahydrate (0.623 g, 2.5 mmol) and H₂salben (0.826 g) were dissolved, together with 2 cm³ of triethylamine, in 15 cm³ of ethanol. The solution was stirred at room temperature for 3 hours and the orange precipitate was filtered off, washed with ethanol and diisopropyl ether and dried *in vacuo*. Yield 70%, 0.656 g.

Co(II)Co(III) (type A) derivatives. [Co₂(salben)₂(py)₂](I₃) **8**. A suspension of **1** (0.198 g, 0.25 mmol) and I₂ (0.097 g, 0.38 mmol) in 15 cm³ of ethanol and 3 cm³ of pyridine was stirred at room temperature for 8 hours. The brown precipitate was filtered off, washed with ethanol and diisopropyl ether, and dried *in vacuo* yielding 0.296 g (90%) of a dark brown solid.

The other mixed valence derivatives **8–11** were obtained likewise, with 80–90% yields.

Attempts to synthesise [Co₂(salmen)₂(py)₂](I₃). A slurry of [Co₂(salmen)₂] **1** (0.408 g, 0.65 mmol) in 15 cm³ of ethanol containing 3 cm³ of pyridine was treated with 0.240 g (0.945 mmol) of I₂, stirred at room temperature for 6 hours and filtered. The solid (0.650 g) was extracted five times with CH₂Cl₂ (10 cm³ × 5) leaving analytically pure **1** (0.120 g). Addition of diisopropyl ether to the combined filtrates, concentrated to 10 cm³, gave a precipitate which was again extracted with CH₂Cl₂ leaving more **1** and a solution from which analytically pure **12** was obtained upon treatment with diisopropyl ether.

Co(III)Co(III) (type B) derivatives. [Co₂(MeOsalmen)₂(py)₄](I₃)₂ **14**. This compound was prepared stirring 0.371 g

(0.5 mmol) of **3**, and 0.381 g (1.5 mmol) of I₂ in 15 cm³ of ethanol containing 3 cm³ of pyridine. After 6 hours at room temperature the precipitate was filtered off, washed with ethanol and dried. Yield 90%, 0.819 g. The other Co(III)Co(III) dimers **12–14** were obtained by the same procedure, yields 80–90%.

Attempts to synthesise [Co₂(salben)₂(py)₄](I₃)₂. [Co₂(salben)₂] (0.262 g, 0.338 mmol) and I₂ (0.438 g, 1.72 mmol) were treated in 15 cm³ of ethanol containing 6 cm³ of pyridine. The slurry was stirred at room temperature for 36 hours and filtered, giving 0.403 g of analytically pure [Co₂(salben)₂(py)₂](I₃) (92%).

X-Ray data collection and structure determination

Crystals suitable for X-ray diffraction studies were obtained by slow diffusion of a diisopropyl ether into a CH₂Cl₂ solution of [Co₂(salben)₂(py)₂](I₃) and of ethanol into a pyridine solution of [Co₂(salmen)₂(py)₄](I₃)₂. For both compounds, a crystal sample was mounted on a glass fibre in a random orientation and collected at room temperature on a Siemens SMART CCD area-detector diffractometer. Graphite monochromatised Mo-K α radiation ($\lambda = 0.71073$ Å) was used with the generator working at 50 kV and 35 mA. 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 $0 < \theta < 25^\circ$. Intensity data were collected in the full sphere (ω scan method); 2100 frames (20 s per frame, $\Delta\omega = 0.3^\circ$) and the first 100 frames recollected to have a monitoring of the crystal decay, which was not observed. An absorption correction was applied using the SADABS routine.¹⁵ Both structures were solved by direct methods (SIR 97)¹⁶ and refined with full-matrix least squares. Anisotropic displacement parameters were assigned to all non-hydrogen atoms. The hydrogen atoms were included in the structure model riding on their C atoms. A summary of crystal data and structure refinement parameters is given in Table 2.

CCDC reference numbers 168844 and 168845.

See <http://www.rsc.org/suppdata/dt/b1/b105594c/> for crystallographic data in CIF or other electronic format.

Magnetic measurements

Variable-temperature susceptibility measurements, in the range 4–300 K, were performed as previously described.¹³ Susceptibilities were corrected for the diamagnetism of the ligand systems, estimated as (in cm³ K mol⁻¹ units) -5.91×10^{-4} for [Co₂(salben)₂(py)₂](I₃), -6.11×10^{-4} for [Co₂(salNO₂ben)₂(py)₂](I₃), -4.18×10^{-4} for [Co₂(salClben)₂], -2.70×10^{-4} for [Co₂(salmen)₂] and -3.66×10^{-4} for [Co₂(salben)₂]. Temperature independent paramagnetism was assumed to be negligible.

Table 2 Summary of X-ray single crystal data and structure refinement parameters for [Co₂(salmen)₂(py)₄](I₃)₂ and [Co₂(salben)₂(py)₂](I₃)

Compound	[Co ₂ (salmen) ₂ (py) ₄](I ₃) ₂	[Co ₂ (salben) ₂ (py) ₂](I ₃)
Formula	C ₅₀ H ₄₄ Co ₂ I ₆ N ₈ O ₄	C ₅₂ H ₄₂ Co ₂ I ₃ N ₆ O ₄
<i>M</i>	1700.24	1313.52
Crystal system	Monoclinic	Monoclinic
Space group	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> /Å	13.502(1)	15.914(1)
<i>b</i> /Å	22.661(2)	19.167(1)
<i>c</i> /Å	18.792(2)	17.252(1)
β /°	101.10(1)	106.05(1)
<i>U</i> /Å ³	5642(1)	5057(1)
<i>Z</i>	4	4
<i>T</i> /K	293(2)	293(2)
<i>D_c</i> /g cm ⁻³	2.002	1.725
<i>F</i> (000)	3216	2564
Crystal size/mm	0.15 × 0.12 × 0.25	0.15 × 0.18 × 0.30
μ /cm ⁻¹	39.20	25.38
Transmission factors	0.653–1.000	0.776–1.000
$2\theta_{\max}$ /°	64	59
Reflections collected, unique	8853	6534
Observed reflections [<i>I</i> > 2σ(<i>I</i>)]	5977	3557
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] ^a	<i>R</i> 1 = 0.035	<i>R</i> 1 = 0.040
<i>R</i> indices (all data)	<i>R</i> 1 = 0.056, <i>wR</i> 2 = 0.089	<i>R</i> 1 = 0.084, <i>wR</i> 2 = 0.101

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|, wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}.$$

Results and discussion

Co(II)Co(II) complexes 1–7

These complexes were obtained by reaction of cobalt(II) acetate with the proligands in the presence of triethylamine. Characterisation data are reported in Table 1.

Although no X-ray structure determination of Co(II)Co(II) compounds could be made owing to the difficulty of growing crystals suitable for diffraction studies, convincing evidence for the binuclear nature of these compounds is provided by their FAB mass spectra, which show clusters of peaks at *m/z* values corresponding to [Co₂L₂ + 1]⁺ (100% abundance), by the magnetic exchange effects revealed by the variable-temperature magnetic susceptibility measurements, and, although in a less direct way, by the results of the oxidation experiments and the bridging coordination features of the ligands revealed by the structures of two oxidised derivatives (*vide infra*).

The coordination geometry in the Co(II) dimers is most likely distorted tetrahedral, as suggested by the observed room-temperature μ_{eff} values per Co atom (4.2–4.5 μ_B), in the range reported for several tetrahedral Schiff bases Co(II) complexes.^{17–19} The near infrared reflectance spectra, see Fig. 1, agree with such a view in showing two bands around 1150–1220 and 910–960 nm, absent in the Co(III) derivatives described below, similar to the d–d transitions reported for tetrahedral Co(II) Schiff bases complexes.^{18,19}

Oxidation with iodine: Co(II)Co(III) 8–11 and Co(III)Co(III) 12–14

Preliminary experiments, performed in CHCl₃ and with low I₂/Co ratios (0.2–0.5), gave ill characterised compounds.^{12,20} The achievement of the products here described was obtained by increasing the ratio and by performing the reactions in the presence of pyridine. The apparent role of this extra ligand in the Co(II)→Co(III) oxidation process is to stabilise the latter ion by satisfying its preference for six-coordination. The fact that [Co(salen)] is oxidised by iodine to [Co(salen)I]²¹ of uncertain structure⁶ which, in the presence of pyridine, gives rise to the hexa-coordinate⁶ [Co(salen)I(py)], is in agreement with such a view.

As for the role of the I₂/Co molar ratio, this has been found to be linked to the nature of the ligand L. In fact salben derivatives 4–7 gave only the mixed valence [Co₂L₂(py)₂](I₃) (type A) compounds 8–11, even in the presence of an excess of iodine and for long reaction times. On the contrary with the salmen 1–3 derivatives only the wholly oxidised Co(III) [Co₂L₂(py)₄](I₃)₂

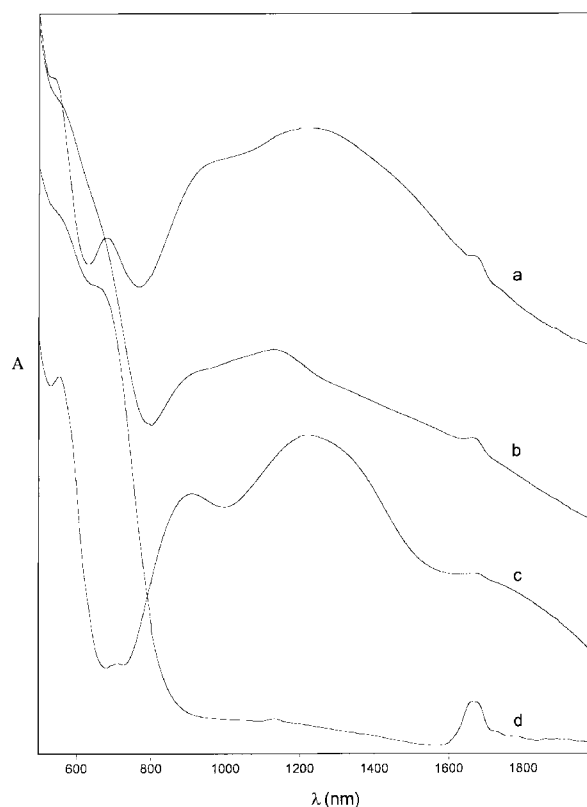


Fig. 1 Reflectance spectra of [Co₂(salben)₂](a), [Co₂(salben)₂(py)₂](I₃) (b), [Co₂(salmen)₂] (c) and [Co₂(salmen)₂(py)₄](I₃)₂ (d).

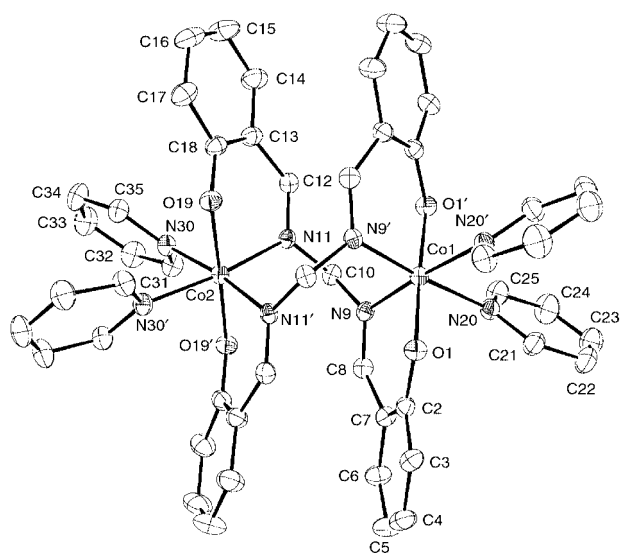
(type B) species 12–14 were obtained. Oxidation reactions of 1–3, carried out with I₂/Co = 0.75, gave a mixture of type B compounds and unreacted [Co₂L₂], which could be separated by fractional crystallisation.

Type A dimers are paramagnetic with three unpaired electrons (Table 1) and show the d–d bands typical of tetrahedral Co(II), although with an intensity lower than those of the parent compounds (Fig. 1). These bands are absent in the Co(III)–Co(III) derivatives which are diamagnetic. The nature of both types of oxidised derivatives was elucidated by the X-ray structures of [Co₂(salben)₂(py)₂](I₃) 8 and [Co₂(salmen)₂(py)₄](I₃)₂ 12. We shall describe the latter first because its features will help assigning the oxidation states of the Co atoms of 8.

Table 3 Selected interatomic distances (Å) and angles (°) for **12**^a

I(1)–I(2)	2.9072(4)	C(2)–C(7)	1.413(4)
I(2)–I(3)	2.9563(4)	O(19)–C(18)	1.323(4)
Co(1)–O(1)	1.898(2)	C(7)–C(8)	1.437(4)
Co(1)–N(20)	1.998(3)	C(18)–C(13)	1.407(4)
Co(1)–N(9)	1.949(2)	C(8)–N(9)	1.297(4)
Co(2)–O(19)	1.894(2)	N(9)–C(10)	1.465(3)
Co(2)–N(11)	1.962(2)	C(13)–C(12)	1.448(4)
Co(2)–N(30)	1.977(2)	N(11)–C(12)	1.291(4)
O(1)–C(2)	1.325(4)	N(11)–C(10)	1.473(3)
I(1)–I(2)–I(3)	178.98(1)	Co(2)–O(19)–C(18)	123.5(2)
O(1)–Co(1)–N(20)	90.9(1)	C(2)–C(7)–C(8)	121.1(3)
O(1)–Co(1)–N(9)	91.5(1)	Co(1)–N(20)–C(21)	120.0(2)
N(20)–Co(1)–N(9)	89.2(1)	Co(1)–N(20)–C(25)	121.2(2)
N(20)–Co(1)–N(20')	86.0(1)	C(21)–N(20)–C(25)	118.5(3)
N(9)–Co(1)–N(9')	95.7(1)	O(19)–C(18)–C(13)	123.1(3)
O(1)–Co(1)–O(1')	177.6(1)	C(7)–C(8)–N(9)	126.1(3)
N(20)–Co(1)–N(9')	175.0(1)	Co(1)–N(9)–C(8)	122.5(2)
O(1)–Co(1)–N(9')	90.1(1)	Co(1)–N(9)–C(10)	122.1(2)
O(19)–Co(2)–N(11)	89.6(1)	C(8)–N(9)–C(10)	115.1(2)
O(19)–Co(2)–N(30)	92.2(1)	C(18)–C(13)–C(12)	120.8(3)
N(11)–Co(2)–N(30)	88.7(1)	Co(2)–N(11)–C(12)	122.1(2)
O(19)–Co(2)–O(19')	178.8(1)	Co(2)–N(11)–C(10)	122.1(2)
N(11)–Co(2)–N(30')	173.5(1)	C(12)–N(11)–C(10)	115.1(2)
N(11)–Co(2)–N(11')	96.9(1)	Co(2)–N(30)–C(35)	121.1(2)
N(30)–Co(2)–N(30')	85.9(1)	Co(2)–N(30)–C(31)	120.9(2)
O(19)–Co(2)–N(30')	86.9(1)	C(35)–N(30)–C(31)	117.4(3)
Co(1)–O(1)–C(2)	125.8(2)	C(13)–C(12)–N(11)	125.6(3)
O(1)–C(2)–C(7)	123.6(2)	N(9)–C(10)–N(11)	110.4(2)

^a Primed atoms related to unprimed ones by the symmetry transformation $-x, y, 1/2 - z$.

**Fig. 2** ORTEP view of the cation of **12**.

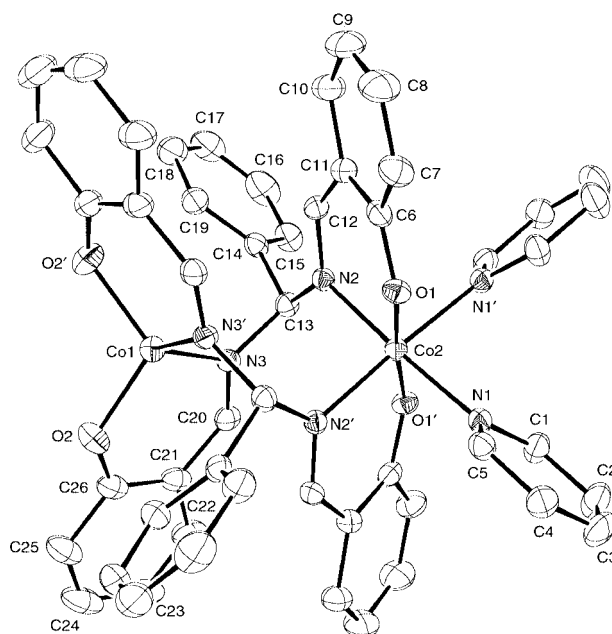
X-Ray crystal structure of 12. The unit-cell contains binuclear $[\text{Co}_2(\text{salmen})_2(\text{py})_4]^{2+}$ cations, with the metal atoms located along a crystallographic C_2 axis and I_3^- anions in general position. An ORTEP²² view of the cation is shown in Fig. 2, selected bond lengths and angles are reported in Table 3. Each cobalt atom is octahedrally coordinated to two O-phenolato and two imine nitrogen atoms of two bridging salmen ligands and by two pyridine nitrogens. The bridging salmen ligands are twisted about the two-fold axis and form an eight-membered bimetallacycle. The intradimer $\text{Co} \cdots \text{Co}$ separation is 4.397(2) Å. The I_3^- anion is unsymmetrical, with an average I–I distance of 2.932 Å, slightly larger than that found in $[\text{Co}_2(\text{salben})_2(\text{py})_2](\text{I}_3)$ [2.9166(4) Å].

X-Ray crystal structure of 8. The unit-cell contains binuclear $[\text{Co}_2(\text{salben})_2(\text{py})_2]^{+}$ cations with the metal centres along crystallographic C_2 axes and I_3^- anions located on crystallographic

Table 4 Selected interatomic distances (Å) and angles (°) for **8**^a

I(1)–I(2)	2.9166(4)	N(3)–C(20)	1.295(4)
Co(1)–N(3)	1.986(3)	N(2)–C(13)	1.503(4)
Co(1)–O(2)	1.894(2)	N(2)–C(12)	1.296(3)
Co(2)–O(1)	1.882(2)	C(13)–C(14)	1.518(4)
Co(2)–N(1)	1.995(2)	C(20)–C(21)	1.440(4)
Co(2)–N(2)	1.961(2)	C(21)–C(26)	1.415(5)
O(1)–C(6)	1.312(3)	C(26)–O(2)	1.310(4)
N(1)–C(5)	1.326(4)	C(12)–C(11)	1.419(5)
N(1)–C(1)	1.351(4)	C(11)–C(6)	1.412(4)
N(3)–C(13)	1.484(3)		
N(3)–Co(1)–O(2)	96.0(1)	Co(1)–N(3)–C(20)	121.1(2)
N(3)–Co(1)–N(3')	111.8(1)	C(13)–N(3)–C(20)	116.1(2)
O(2)–Co(1)–O(2')	112.0(1)	Co(2)–N(2)–C(13)	119.7(2)
O(2)–Co(1)–N(3')	121.5(1)	Co(2)–N(2)–C(12)	120.2(2)
O(1)–Co(2)–N(1)	88.8(1)	C(13)–N(2)–C(12)	119.3(2)
O(1)–Co(2)–N(2)	94.1(1)	N(3)–C(13)–N(2)	107.2(2)
N(1)–Co(2)–N(2)	87.8(1)	N(3)–C(13)–C(14)	110.7(2)
N(1)–Co(2)–N(1')	88.2(1)	N(2)–C(13)–C(14)	116.9(2)
N(2)–Co(2)–N(2')	96.1(1)	N(1)–C(5)–C(4)	122.7(3)
O(1)–Co(2)–O(1')	175.0(1)	N(3)–C(20)–C(21)	127.6(3)
O(1)–Co(2)–N(2')	89.3(1)	C(20)–C(21)–C(26)	124.4(3)
N(1)–Co(2)–O(1')	87.7(1)	C(21)–C(26)–O(2)	123.8(3)
Co(2)–Co(1)–C(6)	125.1(2)	N(2)–C(12)–C(11)	127.4(3)
Co(2)–N(1)–C(5)	122.7(2)	C(12)–C(11)–C(6)	122.9(3)
Co(2)–N(1)–C(1)	119.4(2)	O(1)–C(6)–C(11)	123.7(3)
C(5)–N(1)–C(1)	117.9(3)	O(1)–C(6)–C(7)	117.9(3)
Co(1)–N(3)–C(13)	122.8(2)	Co(1)–O(2)–C(26)	126.7(2)

^a Primed atoms related to unprimed ones by the symmetry transformation $-x, y, 1/2 - z$.

**Fig. 3** ORTEP view of the cation of **8**.

inversion centres. A view of the cation is shown in Fig. 3, with selected bond distances and angles reported in Table 4. The two cobalt atoms in each cation are bridged by two salben ligands and show different ligand environments. Co(1) is coordinated by two O (phenolato) and two imine nitrogen atoms and displays a distorted tetrahedral geometry: the O(2)–Co(1)–O(2') and N(3)–Co(1)–N(3') angles of $\sim 112^\circ$ differ little from the ideal tetrahedral angle but the O(2)–Co(1)–N(3) and the O(2)–Co(1)–N(3') angles of 96.0(1) and 121.5(1)°, respectively, reflect a relevant distortion from the ideal tetrahedral geometry.

The Co(2) atom, which is linked to two additional pyridine molecules, exhibits an almost regular octahedral geometry, very similar to that observed for the Co(III) atoms in **12**. Such a feature, upon consideration of the diamagnetism of the Co(III)Co(III) dimers and the $S = 3/2$ paramagnetism of the

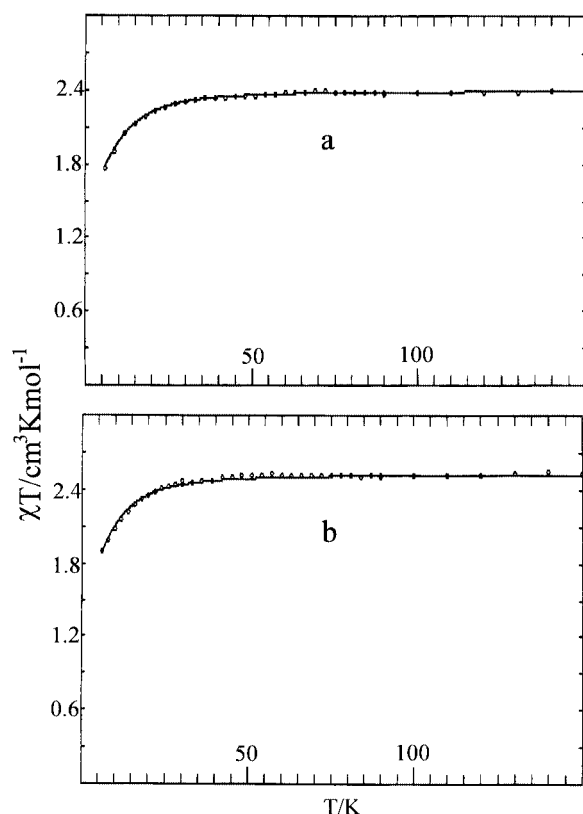


Fig. 4 Magnetic susceptibility data and best theoretical curve for **8** (a) and **11** (b).

Co(II)Co(III) derivatives, leaves little doubt that the Co atom in the 3+ oxidation state is Co(2).

The Co(1)–N(imine) and Co(1)–O distances are slightly larger than the corresponding distances for Co(2). The bridging Schiff bases are twisted about the two-fold axis and form an eight-membered bimetallic cycle similar to that found in the binuclear moiety of [Cu₂(salben)₂].¹³ Both the Co...Co intradimer separation, 4.176(2) Å, and the N–C–N bridging angle, 107.2(2)° differ significantly from the corresponding values, 4.397(2) Å and 110.4(2)°, respectively, observed for the above described Co(III)Co(III) dimer.

Magnetic studies

Tetrahedral Co(II) has an orbital singlet ⁴A₂ ground state which, in the presence of axial distortions, is split into two Kramers doublets: |±3/2⟩ and |±1/2⟩. Such a zero field splitting (zfs) is the most important source of paramagnetic anisotropy, that is of susceptibilities that differ as the measuring magnetic field is rotated with respect to the principal (||, ⊥) axis of the system. The total spin Hamiltonian taking into account the effect of the applied magnetic field (*H_u*) may be written as eqn. (1):

$$H = \beta g_u H_u S_u + D(S_z^2 - 5/4) \quad (1)$$

where *D* is a scalar term (the zfs parameter), the index *u* denotes the direction of the applied magnetic field and other symbols have their usual meaning. Hamiltonian (1), when operating on the *S* = 3/2 basis set, and taking *g_x* = *g_y* = *g_z*, provides eqn. (2)²³ for the average magnetic susceptibility, *χ*, approximated as *χ* = (*χ_z* + 2*χ_x*)/3:

$$\chi = \{Ng^2\beta^2/(kT)\} [(1 + 9e^{2x})/3 + \{4 + (3/x)(1 - e^{2x})\}/2] \{4(1 + e^{-2x})\}^{-1} \quad (2)$$

where *x* = *D*/k*T*.

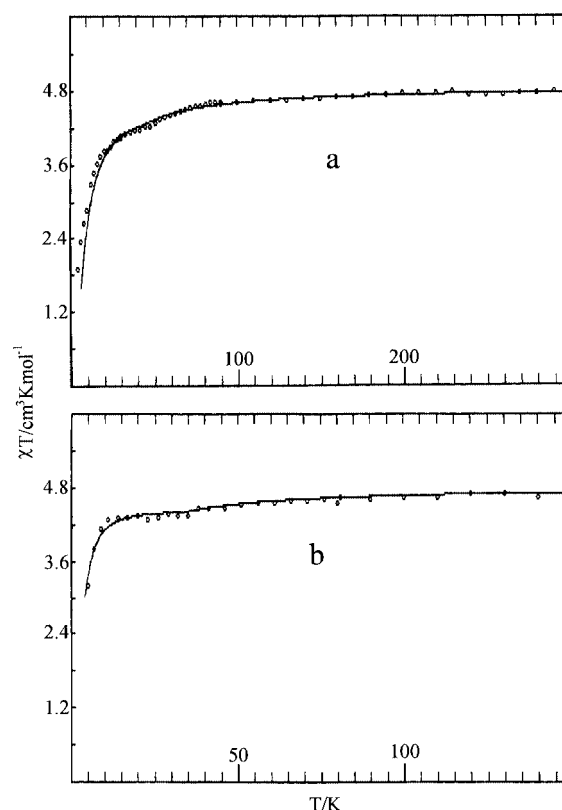


Fig. 5 Magnetic susceptibility data and best theoretical curve for **1** (a) and **6** (b).

Eqn. (2) was used to fit the magnetic susceptibility data for [Co₂(salben)₂(py)₂](I₃) **8** and [Co₂(salNO₂ben)₂(py)₂](I₃) **11**, in which the only magnetic centre is the pseudo-tetrahedral Co(II) ion. The data and best theoretical curves are shown in Fig. 4.

The best fit *g* and |*D*| values are 2.26 and 11.5 cm^{−1}, respectively for the former compound and 2.32 and 11.0 cm^{−1} for the latter. These values are in the ranges (2.2–2.4 for *g*²³ and 1 to ~15 cm^{−1} for |*D*|²⁴ so far observed for single Co(II) ions in distorted tetrahedral environments.

The magnetic susceptibility data for [Co₂(salmen)₂] **1** and [Co₂(salClben)₂] **6** are shown in Fig. 5. The room-temperature values of *χT* indicate that the dimers contain two *S* = 3/2 spins and the small negative *θ* (the Weiss constant) values obtained from the *χ* vs. 1/*T* plots in the high-temperature regime, strongly suggest the presence of antiferromagnetic interactions.

The spin Hamiltonian chosen for the analysis of the magnetic susceptibility data is given by eqn. (3):

$$H = H_0 - \beta g_u S_u H_u \quad (3)$$

where *S_u* = (*S₁* + *S₂*)_{*u*}, *u* = *x*, *y* or *z* and:

$$H_0 = -2J(S_1 \cdot S_2) - D_1 S_{1z}^2 - D_2 S_{2z}^2 \quad (4)$$

Hamiltonian (3) ignores the anisotropic exchange term *S₁*·*D₁₂*·*S₂* that is usually small, dominated by the local anisotropy *D₁* and *D₂*. We have solved Hamiltonian (3) by application of the van Vleck formalism, using the *S₁* = *S₂* = 3/2 basis set, with *D₁* = *D₂* = *D* and *g_x* = *g_y* = *g_z* = *g*. In addition, quantisation along the *z* direction and axial symmetry (*S_x* = *S_y*) were assumed. The expression for the average magnetic susceptibility is derived in the Appendix (see electronic supplementary information†) in a form suitable for computer simulation.

The best fit theoretical curves, in the *χT* vs. *T* form are shown in Fig. 5. Best fit parameters are *g* = 2.25 and *J* = −1.7 cm^{−1} and *D* = 3.0 cm^{−1} for **1** and *g* = 2.22, *J* = −0.7 and *D* = 1.9 cm^{−1} for **6**.

The low J values observed for the two compounds are in agreement with previously discussed inability of the present bridging ligands to support sizeable magnetic exchange of either sign.¹³

As to the D parameters, the seeming inconsistency between the values obtained for the exchange coupled Co(II) dimers **1** and **6** ($2\text{--}3\text{ cm}^{-1}$) and those ($\sim 11\text{ cm}^{-1}$) observed for the uncoupled Co(II) ions in **8** and **11**, is not too surprising. Indeed, the problem of relating zero-field splittings to single ion (D_0) and anisotropic exchange contributions in exchange coupled systems (D_{CoCo}), is a difficult one, both from an experimental and a theoretical point of view. At present, reliable information on this matter is available²⁴ only for systems in which the $-2J(S_1 \cdot S_2)$ magnetic exchange term dominates any other term in the spin Hamiltonian. If so states with different values of the total spin quantum number, S are so well separated in energy that, in principle, the zero field splitting of each S multiplet, D_S , can be measured using EPR techniques (but not magnetic susceptibility measurements) and, under fortunate circumstances, can be quantitatively related to anisotropic contributions.^{24,25} Clearly, relationships between D_S and D_{CoCo} and D_{Co} parameters lose any significance when, as in the case of our compounds, the J and zfs terms in the spin Hamiltonian are of comparable magnitude. In such a situation, states with different S can mix since S is no longer a good quantum number.

Conclusions

The binuclear nature of the fourteen new Co complexes, together with the previously obtained results for the related Cu(II) compounds,¹³ provide convincing evidence that "short" salen homologues strongly favour the formation of bridging structures. The apparent reluctance of these ligands to form mononuclear complexes, similar to those usually observed with salen (which only rarely forms binuclear structures²⁶), is most likely related to the considerable strain that would be present in four-membered chelate M–N–C–N rings. The present cage-like structures involve several interesting features. First the rather unusual coordination geometry of Co(II): tetrahedral with a relevant distortion arising from the obliged bite angle of the salicylaldimine moiety and the conformation of the cage. Second the weakness of the Co(II)–Co(II) exchange interactions that, by analogy with the related Cu(II) case,¹³ most likely arises from an unfavourable conformation of the eight-membered bimetallic cycle M–N–C–N–M–N–C–N. A third interesting point is the different behaviour towards oxidation of the salmen and salben derivatives. Such difference could arise from a different conformational freedom of the two types of bimetallic cycles and the fact that the first step of oxidation reaction must be the formation of a Co(II)Co(III) compound with one octahedral Co centre. This may bring about some changes of the conformation of the bimetallic cycle and, consequently, of the geometry of the other metal centre which may become suitable (salmen case) or unsuitable (salben) for its oxidation (such behaviour has been denoted "mechanical coupling"²⁷). Clearly in the absence of X-ray structures of the Co(II)Co(II) precursors and of a type A compound of salmen, this remains only a hypothesis. Packing effects may also be important in stabilising the different types of oxidised products.

Interestingly, the isolation of the mixed valence type A compounds offers the opportunity of comparing magnetic data for magnetically dilute and exchange coupled Co(II) ions in similar local environments. Such an analysis, in particular, illustrates the difficulty in determining reliable zero field splittings in weakly exchange coupled systems.

Finally, as stated above, the finding that different oxidation products can be isolated using low I_2/Co ratios, opens the possibility of obtaining a number of other compounds, including polynuclear derivatives.²⁰ This novel and rich chemistry is currently under thorough investigation.

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