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Ligating properties of tridentate Schiff base ligands, 2-[[(2-pyridinylmethyl)imino]methyl] phenol (HSALIMP) and 2-[[[2-(2-pyridinyl)ethyl]imino]methyl]phenol (HSALIEP) with zinc(II), cadmium(II), nickel(II) and manganese(III) ions. X-ray crystal structures of the [Zn(SALIEP)(NO₃)]₂ dimer, [Mn(SALIEP)₂](ClO₄), and [Zn(AMP)₂(NO₃)₂]

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Abstract

A series of zinc(II), cadmium (II), nickel(II) and manganese (III) complexes with two potentially tridentate (NNO) Schiff base ligands, 2-[[(2-pyridinylmethyl)imino]methyl]phenol (HSALIMP) and 2-[[[2-(2-pyridinyl)ethyl]imino]methyl]phenol (HSALIEP) have been synthesized and structurally characterized through IR, ¹H, ¹³C, and 2-D NMR spectroscopy and in two cases by X-ray crystallography. The Schiff base ligands HSALIMP and HSALIEP are generated from 1 + 1 condensation of salicylaldehyde with 2-aminomethylpyridine and 2(2-aminoethyl)pyridine, respectively. HSALIMP behaves as a tridentate (NNO) or a bidentate (NN) ligand, depending upon the nature of the anion. On reaction with zinc(II) salts HSALIMP gives two types of complexes, (a) $[Zn(SALIMP)X]_2 \cdot yH_2O$ (X = NO₃, y = 0 (I); X = I, y = 3 (II) and (b) $[Zn(HSALIMP)Cl_2] \cdot H_2O$ (III). HSALIMP reacts with nickel(II) bromide to form a mononuclear complex [Ni(HSALIMP),Br₂] (VIII), in which one metal ion combines with two neutral HSALIMP ligands. However HSALIEP, a similar ligand with one additional carbon atom in the chain, acts as a tridentate ligand (NNO), with the phenolate oxygen deprotonated, irrespective of the nature of the anion, forming dimeric compounds of 1:1 metal:ligand stoichiometry with zinc(II) and cadmium(II) ions, $[Zn(SALIEP)X]_2 y H_2O(X = NO_3, y = 0 (IV); X = Cl, y = 2 (V);$ X = I, y = 1 (VI), [Cd(SALIEP) (NO₃)], C_2H_5OH (VII) and a monomeric complex of 1:2 metal: ligand stoichiometry with manganese(III) ion, [Mn(SALIEP)₂](ClO₄) (IX). The single crystal X-ray structures of the [Zn(SALIEP)(NO₃)]₂ (IV) dimer, $[Mn(SALIEP)_2](ClO_4)$ (IX), and $[Zn(AMP)_2(NO_3)_2]$ (X), a minor product obtained from the filtrate of I, have been determined. IV consists of centrosymmetric dimer in which deprotonated phenolates bridge the two five-coordinate metal atoms and link the two halves of the dimer. The structure of IX consists of a centrosymmetric molecule in which the manganese(III) ion is bound to two tridentate SALIEP ligands in a nearly regular octahedral arrangement. The structure of X consists of a centrosymmetric monomer in which the six coordinate octahedral zinc(II) ion is bonded equtorially to two bidentate 2-aminomethylpyridine ligands and axially to two monodentate nitrate groups. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

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In our earlier communications [1-3], we reported the synthesis and the ligating properties of the tridentate (N₂O) Schiff base ligands, 2-[[(2-pyridinylmethyl)-imino]methyl]phenol (HSALIMP) and 2-[[[2-(2-

pyridinyl)ethyl]imino]methyl]phenol (HSALIEP) with copper(II) and their saturated counterparts, 2-[[(2pyridinylmethyl)amino]methyl]phenol (HSALAMP) 2-[[[2-(2-pyridinyl) ethyl]amino]methyl]phenol and (HSALAEP) with copper(II), zinc(II) and cadmium(II) ions. The X-ray crystal structures of [Cu(SALIMP)- $(NO_3)],$ [Cu(HSALAMP)Cl₂]·C₂H₅OH [2], [Zn-(SALAEP)(NO₃)]₂ and [Cd(SALAEP)(NO₃)]₂ were also reported [1-3]. In these complexes, the Schiff bases behave either as tridentate (NNO) or bidentate (NN) ligands, depending upon the nature of the anions present and the reaction conditions.

In continuation of our interest in the coordinating behaviour of ligands of this sort we wish to report the results of our investigations on the ligating properties of the tripodal [NNO] Schiff base ligands HSALIMP and HSALIEP with zinc(II), cadmium(II), nickel(II) and manganese(III) ions. The X-ray crystal structures of dimeric zinc(II) complex (IV), the monomeric manganese(III) complex (IX) of the ligand SALIEP, and the monomeric zinc(II) complex (X) of 2-amino methylpyridine are reported.

2. Experimental

2.1. Materials

The solvents were dried by standard procedures. 2-Aminomethyl pyridine and 2(2-aminoethyl)pyridine were used as supplied by Aldrich. All other chemicals used were analytical or reagent grade and used without further purification.

2.2. Synthesis of the ligands

2.2.1. 2-[[(2-pyridinylmethyl)imino]methyl]phenol (HSALIMP) and 2-[[[2-(2-pyridinyl)ethyl]imino] methyl]phenol (HSALIEP)

The Schiff base ligands HSALIMP and HSALIEP were obtained by reacting salicylaldehyde (3.1 g, 25 mmol) with 2-aminomethylpyridine (2.7 g, 25 mmol) and 2-(2-aminoethyl)pyridine (3.05 g, 25 mmol), respectively in absolute ethanol (50 ml) under reflux for about 30 min. They were used immediately to avoid noticeable degradation, which occurred on standing for extended periods. HSALIMP and HSALIEP were characterized through ¹H, ¹³C and 2D NMR spectroscopy (Tables 5 and 6).

2.3. Synthesis of the complexes

2.3.1. $[Zn(SALIMP)(NO_3)]_2$ (I)

HSALIMP (1.0 mmol), dissolved in warm dry ethanol (5 ml), was added dropwise to a solution of zinc nitrate (1.0 mmol) in dry ethanol (10 ml), with

stirring at 100°C. The colour of the reaction mixture immediately changed from dark yellow to off white. The resulting mixture was refluxed for 30 min and concentrated to about 10 ml under reduced pressure. An off white solid separated after keeping the concentrated mixture at r.t. for 12 h, was filtered off, washed with dry ethanol (3 × 5 ml) and dried under vacuum at 60°C for 12 h. Yield: 80%. *Anal.* Calc. for [Zn(-SALIMP)(NO₃)]₂ (I): C, 46.08; H, 3.25; N, 12.41; Zn, 19.35. Found: C, 45.82; H, 3.44; N, 12.08; Zn, 18.46%. λ_{max} (nm) (ε dm³ mol⁻¹ cm⁻¹): 374 (4110), 268 (6750).

2.3.2. $[Zn(SALIMP)I]_2 \cdot 3H_2O$ (II)

II was obtained, as an off white solid, in a similar manner to I by replacing $Zn(NO_3)_2$ with ZnI_2 and stirring the reaction mixture at ambient temperature for 2 h. Yield: 90%. *Anal.* Calc. for $[Zn(SALIMP)I]_2$ ·3H₂O (II): C, 36.24; H, 3.25; Zn, 15.21. Found: C, 35.94; H, 3.31; Zn, 14.57%. $\lambda_{max.}(nm)$ (ε dm³ mol⁻¹ cm⁻¹): 372 (7450), 269 (11150).

2.3.3. $[Zn(HSALIMP)Cl_2] \cdot H_2O$ (III)

III was obtained similarly by replacing ZnI₂ with ZnCl₂. Yield: 87%. *Anal.* Calc. for [Zn(HSALIMP)Cl₂]· H₂O (III): C, 42.60; H, 3.85; N, 7.64; Zn, 17.83. Found: C, 42.85; H, 3.39; N, 7.90; Zn, 17.66%. λ_{max} (nm) (ε dm³ mol⁻¹ cm⁻¹): 375 (4650), 318 (2650), 266 (10400).

2.3.4. $[Zn(SALIEP)(NO_3)]_2$ (IV)

A solution of HSALIEP (1.0 mmol) in dry ethanol (15 ml) was added dropwise with constant stirring to a solution of zinc(II) nitrate (1.0 mmol) in the same solvent (15 ml) at ambient temperature. A pale yellow solid separated immediately. The resulting mixture was stirred at ambient temperature for 2 h and the solid was filtered off, washed with ethanol (2 × 5 ml) and dried under vacuum at 60°C for 12 h. Yield: 80%. *Anal.* Calc. for [Zn(SALIEP)(NO₃)]₂ (IV): C, 47.54; H, 3.96; N, 11.88; Zn, 18.50. Found: C, 47.77; H, 3.76; N, 12.04; Zn, 18.62%. $\lambda_{max.}$ (nm) (ε dm³ mol⁻¹ cm⁻¹): 367 (7935), 268 (11020).

2.3.5. $[Zn(SALIEP)Cl]_2 \cdot 2H_2O(V)$

V was prepared by the same procedure as used for the synthesis of IV by replacing zinc nitrate with zinc chloride. Yield: 86%. *Anal.* Calc. for [Zn(-SALIEP)Cl]₂·2H₂O (V): C, 48.84; H, 4.36; Zn, 19.04. Found: C, 49.33; H, 4.39; Zn, 19.59%. $\lambda_{max.}$ (nm) (ε dm³ mol⁻¹ cm⁻¹): 368 (7205), 268 (10920).

2.3.6. $[Zn(SALIEP)I]_2 \cdot H_2O$ (VI)

VI was obtained similarly by replacing zinc nitrate with zinc iodide. Yield: 85%. *Anal.* Calc. for [Zn(-SALIEP)I]₂·H₂O (VI): C, 39.40; H, 3.28; N, 6.57; Zn, 15.34. Found: C, 39.29; H, 3.46; N, 6.67; Zn, 15.11%. $\lambda_{max.}$ (nm) (ε dm³ mol⁻¹ cm⁻¹): 368 (5300), 305 (2835), 267 (9690).

2.3.7. $[Cd(SALIEP)(NO_3)]_2 \cdot C_2H_5OH$ (VII)

A solution of HSALIEP (1.0 mmol) in dry ethanol (20 ml) was added dropwise with constant stirring to a solution of cadmium nitrate (1.0 mmol) in the same solvent (10 ml) at ambient temperature. The resulting mixture was stirred at ambient temperature for 24 h. Triethylamine (2 mmol) was added and the solution was concentrated to 5 ml under reduced pressure. The resulting solution produced a pale yellow solid after standing at r.t. for 24 h, which was filtered off, washed with dry ethanol (2×2 ml) and dried under vacuum at 60°C for 8 h. Yield: 75%. *Anal.* Calc. for [Cd-(SALIEP)(NO₃)]₂·C₂H₅OH (VII): C, 42.52; H, 3.82; Cd, 26.59. Found: C, 43.08; H, 3.75; Cd, 26.78%. λ_{max} (nm) (ε dm³ mol⁻¹ cm⁻¹): 375 (4475), 314 (1125), 269 (8975).

2.3.8. [Ni(HSALIMP)₂Br₂] (VIII)

HSALIMP (2.0 mmol), dissolved in dry ethanol (20 ml), was added dropwise to a solution of nickel bromide (1.0 mmol) in the same solvent (10 ml), with stirring at r.t. After stirring the resulting mixture for approximately 20 min, a purple coloured solid started separating and it was stirred further for 2 h. The purple solid was filtered off, washed with dry ethanol (3 × 5 ml) and dried under vacuum at 60°C for 8 h. Yield: 66%. *Anal.* Calc. for [Ni(SALIMP)₂Br₂] (VIII): C, 48.55; H, 3.73; Ni, 9.13. Found: C, 48.11; H, 3.95; Ni, 9.41%. $\lambda_{max.}$ (nm) (ε dm³ mol⁻¹ cm⁻¹): 876 (18), 817 (16), 394 (10975), 269 (21500). μ_{eff} (300 K) = 3.11 BM and μ_{eff} (93 K) = 3.06 BM.

2.3.9. [Mn(SALIEP)₂](ClO₄) (IX)

HSALIEP (2.0 mmol), dissolved in dry ethanol (20 ml), was added dropwise to a solution of manganese(III) acetate (1.0 mmol) in the same solvent (10 ml), with stirring at room temperature. After stirring the resulting mixture at r.t. for approximately 16 h, sodium perchlorate (4.0 mm) dissolved in methanol (5 ml) was added. A deep red solution formed which was left at r.t. for slow evaporation and after a few hours a reddish brown crystalline solid separated. It was filtered off, washed with ethanol (3 × 5 ml) and methanol (2 × 1 ml) and dried under vacuum at r.t. for 8 h. Yield: 66%. *Anal.* Calc. for [Mn(SALIEP)₂](ClO₄) (**IX**): C, 55.40; H, 4.65; N, 9.22; Mn, 9.05. Found: C, 55.52; H, 4.33; N, 9.27; Mn, 8.95%.

Crystals suitable for X-ray studies were obtained by the slow evaporation of a solution of the complex in a mixture of methanol:ethanol (1:1).

2.3.10. $[Zn(AMP)_2(NO3)_2](X)$

X was obtained as a minor product from the filtrate of I. 2-Aminomethylpyridine found in this complex could have been produced by the hydrolysis of the Schiff base ligand HSALIMP.

2.4. Physical measurements

NMR spectra were recorded with a Varian XL-300 and JEOL XL-300 spectrometer (SiMe₄ internal standard) in DMSO (d₆), and electronic spectra were recorded in DMF solution with a Varian DMS 100 UV–Vis spectrometer in the range 200–900 nm. Infrared spectra were recorded as KBr discs in the range 200–4000 cm⁻¹ using a Pye Unicam SP-300 IR instrument. Microanalyses were carried out by Microanalytical Service, University of Otago, Dunedin, New Zealand and zinc, cadmium, manganese, and nickel were determined volumetrically using EDTA titrations. Magnetic measurements were carried out by the Gouy method from room temperature to liquid nitrogen temperature. The apparatus was supplied by Newport Instruments. The tube was calibrated with [Ni(en)₃]S₂O₃.

2.5. Crystallographic data collection and refinement of the structures

2.5.1. [Zn(SALIEP)(NO₃)]₂ (IV)

The crystals of IV are colourless and irregular in shape. The diffraction intensities of an approximately $0.25 \times 0.25 \times 0.35$ mm crystal were collected with graphite monochromatized Mo Ka radiation using a Rigaku AFC6S diffractometer at $26 \pm 1^{\circ}$ C and the ω -2 θ scan technique to a 2 θ_{max} value of 50.1°. A total of 2862 reflections were measured, of which 2681 $(R_{int} = 0.035)$ were unique and 1826 were considered significant with $I_{\text{net}} > 2.0\sigma(I_{\text{net}})$. Azimuthal scans of several reflections indicated no need for an absorption correction. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient = 0.19462E-06). The cell parameters were obtained from the least-squares refinement of setting angles of 24 carefully centered reflections with 2θ in the range 40.12–44.95°.

The structure was solved by direct methods [4,5]. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 1826 observed reflections $(I > 2.00\sigma(I))$ and 200 variable parameters and converged with unweighted and weighted agreement factors of $R = \Sigma ||F_o| - |F_c||/$ $\Sigma |F_{o}| = 0.034$ and $R_{w} = [(\Sigma w(|F_{o}| - |F_{c}|)^{2} / \Sigma w F_{o}^{2})]^{1/2} =$ 0.026. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.27 and -0.29 e Å⁻³, respectively. Neutral-atom scattering factors [6] and anomalous-dispersion terms [7,8] were taken from the usual sources. All calculations were performed with the TEXSAN [9] crystallographic software package using a VAX 3100 work station. A summary of the crystal and other data is given in Table 1 and selected bond distances and angles are given in Table 2. Atomic coordinates, anisotropic thermal parameters, a full listing of bond distances and angles, and a listing of structure factors are deposited (see Section 5).

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A summary of crystallographic data for [Zn(SALIEP)(NO₃)]₂ (IV), [Mn(SALIEP)₂](ClO₄) (IX) and [Zn(AMP)₂(NO₃)₂] (X)

Compound	IV	IX	X	
Chemical formula	C ₂₈ H ₂₆ N ₆ Zn ₂ O ₈	C ₂₈ H ₂₆ N ₄ O ₆ ClMn	$C_{12}H_{16}N_6O_6Zn$	
Formula weight	705.31	604.93	405.67	
Crystal system	monoclinic	triclinic	monoclinic	
Space group	$P2_1/c$	$P\overline{1}$	$P2_1/c$	
a (Å)	9.300(5)	11.406(5)	8.834(2)	
b (Å)	18.012(3)	13.081(4)	8.864(4)	
c (Å)	8.699(5)	11.312(5)	10.188(2)	
α (°)	_	101.37(3)	_	
β (°)	91.46(4)	110.10(4)	101.36(2)	
γ (°)	_	111.33(2)	_	
$V(Å^3)$	1457(2)	1373(1)	782.1(4)	
Ζ	2	2	2	
$2\theta_{\max}$ (°)	50.1	50.1	50.1	
$T(\mathbf{K})$	299	299	299	
λ (Å) (Mo K α)	0.71069	0.71069	0.71069	
D_{calc} (g cm ⁻³)	1.608	1.464	1.722	
μ (cm ⁻¹)	17.45	6.07	16.50	
R ^a	0.034	0.059	0.026	
R _w ^b	0.026	0.066	0.025	
Max. shift/ δ	0.00	0.00	0.00	
F(000)	720	624	416	
GOF	1.63	2.76	2.03	
Crystal size (mm)	$0.25 \times 0.25 \times 0.35$	$0.35 \times 0.20 \times 0.20$	$0.35 \times 0.25 \times 0.20$	

^a
$$R = \Sigma(|F_{o}| - |F_{c}|) / \Sigma |F_{o}|.$$

^b
$$R_{\rm w} = [(\Sigma w(|F_{\rm o}| - |F_{\rm c}|)^2 / \Sigma w F_{\rm o}^2)]^{1/2}.$$

2.5.2. $[Mn(SALIEP)_2](ClO_4)$ (IX), $[Zn(AMP)_2](NO_3)_2$ (X)

Data collection and structure solutions for IX and X were carried out in a similar manner. Summaries of crystal and other data are given in Table 1. Selected

bond distances and angles are given in Tables 3 and 4, respectively. Atomic coordinates, anisotropic thermal parameters, a full listing of bond distances and angles, and a listing of structure factors are deposited (see Section 5).

Table 2

Bond distances (Å) and angles (°) relevant to the zinc coordination sphere in [Zn(SALIEP)(NO₃)]₂ (IV)

		ADC ^a			ADC ^a
Zn(1)-O(1)	1.994(2)	1	Zn(1)–O(1)	2.103(2)	3
Zn(1) - O(2)	2.051(3)	1	Zn(1)-N(1)	2.087(3)	1
Zn(1)-N(2)	2.096(3)	1	Zn(1)-Zn(1)*	3.184(1)	3
O(1) - Zn(1) - O(1)	78.01(9)	O(1)-Zn(1)-O(2)	129.8(1)		
O(1)-Zn(1)-N(1)	91.6(1)	O(1)-Zn(1)-N(2)	116.8(1)		
O(1)–Zn(1)–O(2)	94.75(9)	O(1)–Zn(1)–N(1)	167.5(1)		

^a Atom designate code (from ORTEP).

Table 3

Bond lengths (Å) and angles (°) relevant to the manganese coordination spheres in [Mn(SALIEP)2](ClO4) (IX)

		ADC ^a			ADC ^a
Mn(1)–O(1)	1.884(3)	1	Mn(2)–O(2)	1.874(4)	1
Mn(1)-N(1)	2.019(4)	1	Mn(2)-N(3)	2.021(4)	1
Mn(1)–N(2)	2.368(4)	1	Mn(2)-N(4)	2.383(4)	1
O(1)-Mn(1)-O(1)	180.00	O(2)–Mn(2)–O(2)	180.00		
N(1)-Mn(1)-N(2)	82.1(2)	N(3)-Mn(2)-N(4)	81.3(2)		
N(1)-Mn(1)-N(2)	97.9(2)	N(3)-Mn(2)-N(4)	98.7(2)		

^a Atom designate code (from ORTEP).

Table 4 Bond lengths (Å) and angles (°) relevant to the zinc coordination sphere in $[Zn(AMP)_2(NO_3)_2]$ (X)

		ADC ^a			ADC ^a
Zn(1)–O(1)	2.317(2)	1	Zn(1)-N(1)	2.140(2)	1
Zn(1)-N(2)	2.071(2)	1		~ /	
O(1)-Zn(1)-O(1)	180.00	O(1)-Zn(1)-N(1)	89.19(7)		
O(1) - Zn(1) - N(1)	90.81(7)	O(1)-Zn(1)-N(2)	94.34(7)		
O(1) - Zn(1) - N(2)	85.66(7)	O(1)-Zn(1)-N(1)	90.81(7)		
O(1) - Zn(1) - N(1)	89.19(7)	O(1)-Zn(1)-N(2)	85.66(7)		
O(1)-Zn(1)-N(2)	94.34(7)	N(1)-Zn(1)-N(1)	180.00		
N(1)-Zn(1)-N(2)	79.60(7)	N(1)-Zn(1)-N(2)	100.40(7)		
N(1)-Zn(1)-N(2)	100.40(7)	N(1)-Zn(1)-N(2)	79.60(7)		
N(2)-Zn(1)-N(2)	180.00				

^a Atom designate code (from ORTEP).

3. Results and discussion

3.1. Synthesis of the complexes

Two Schiff bases 2-[[(2-pyridinylmethyl)imino]methyl]phenol (HSALIMP) and 2-[[[2-(2-pyridinyl)ethyl]imino]methyl]phenol (HSALIEP), which are potentially tridentate (N₂O) ligands, capable of forming two adjacent (6,5) and (6,6) membered chelate rings respectively on coordination with the same metal ion have been produced from 1+1 condensation of salicylaldehyde with 2-aminomethylpyridine and 2-(2aminoethyl)pyridine respectively. HSALIMP and HSALIEP are unstable and were used immediately to avoid noticeable degradation as evidenced by the isolation of $[Zn(AMP)_2(NO_3)_2]$, (AMP = 2-aminomethyl pyridine) as a minor product from the filtrate of complex I, where AMP is presumed to have been produced from the hydrolysis of HSALIMP. The coordination behaviour of HSALIMP, which has one carbon less than that of (HSALIEP), differs from the latter towards zinc(II) ion as has already been observed in case of zinc(II) and cadmium(II) complexes with the reduced Schiff base ligands [3]. Reactions between HSALIMP and zinc(II) salts produce two types of complex: (a) dimeric 1:1 complexes, $[Zn(SALIMP)X]_2 \cdot yH_2O$ (X = NO₃, y = 0 (I); X = I, y = 3 (II), in which SALIMP acts as a tridentate (N₂O) ligand and the deprotonated phenolate group links the two zinc(II) ions and the two halves of the dimer, as in case of (IV); and (b) a 1:1 monomeric complex, [Zn(HSALIMP)Cl₂]·2H₂O (III), in which HSALIMP acts as a bidentate (NN) ligand with no deprotonation of the phenolate oxygen, which remains uncoordinated, as was observed in the case of [Cu(HSALAMP)Cl₂]·C₂H₅OH [1]. The formation of the compounds of type a, or b depends on the nature of the anion. With nitrate and iodide anions, having moderate to weak coordinating ability, complexes of type a are formed whereas with chloride as anion the type b complex is formed. With nickel(II) ion the formation of a six-coordinate octahedral complex [Ni(SALIMP)₂Br₂] (VIII) of 1:2 metal:ligand stoichiometry takes place.

HSALIEP, which has one additional carbon atom in the chain, and is capable of forming two adjacent six membered chelate rings, reacts with zinc(II) and Cd(II) ions to form dimeric 1:1 complexes (IV-VII) and with manganese(III) ion to form a monomeric 1:2 complex [Mn(SALIEP)₂](ClO₄) (IX). In all these complexes, HSALIEP acts as a deprotonated, tridentate ligand irrespective of the nature of the anions, as has been seen with the corresponding saturated analogues. The difference in the coordination abilities of the two Schiff base ligands HSALIMP and HSALIEP could be attributed to the difference in the chelate ring sizes which are formed on coordination.

3.1.1. Description of the structures of

$[Zn(SALIEP)(NO_3)]_2$ (IV), $[Mn(SALIEP)_2](ClO_4)$ (IX) and $[Zn(AMP)_2(NO_3)_2]$ (X)

The structure of IV is very similar to the structures of [Zn(SALAMP)(NO₃)]₂ and [Cd(SALAEP)(NO₃)]₂ with the reduced ligands [3] with the only difference that in IV nitrate is acting as a monodentate ligand as against bidentate in the other complexes (Fig. 1). A perspective view of $[Zn(SALIEP)(NO_3)]_2$ (IV) is shown in Fig. 2, and selected bond distances and angles relevant to the zinc coordination sphere are given in Table 2. The structure consists of a centrosymmetric dimer (Fig. 2), comprising two zinc(II) ions, two monodentate nitrate anions and two tridentate SALIEP ligands bonded by the pyridine nitrogen, the imine nitrogen and the phenolate oxygen (N,N,O) atoms of SALIEP. The deprotonated phenolate bridges the two zinc atoms and links the two halves of the dimer together. The geometry about the five-coordinate zinc atom can best be described as slightly distorted trigonal bipyramidal, with equatorial angles in the range 113-130°, and an axial angle (O(1)-Zn(1)-N(1)) of 167.5°. The O(1) bridge forms an asymmetric linkage to the zinc atoms with markedly different zinc-oxygen distances (Zn(1)-O(1)



HSALIMP



Fig. 1. HSALIMP and HSALIEP ligands.



Fig. 2. Perspective view of [Zn(SALIEP)(NO₃)]₂ (IV).

1.994 Å and O(1)*–Zn(1) 2.103 Å). The Zn(1)–Zn(1)* separation of 3.184 (1) Å is significantly longer than that observed in the analogous zinc(II) complex of the reduced Schiff base ligand [Zn(SALAMP)(NO₃)]₂ (Zn–Zn = 3.063 Å). The nitrate group, acts as a monodentate ligand with a Zn–O distance (Zn(1)–O(2)) of 2.051 Å, typical for monodentate nitrate. The zinc–nitrogen and zinc–oxygen bond distances of Zn(1)–N(2) = 2.096 (pyridine), Zn(1)–N(1) = 2.087 Å (imino) and Zn(1)–O(1) = 1.994, and Zn(1)–O1* = 2.103 Å are considered normal, but significantly different from those observed for the analogous zinc(II) and cadmium(II) complexes with reduced ligands [3].

The structure of the cation in $[Mn(SALIEP)_2](CIO_4)$ (IX) is shown in Fig. 3 and bond distances and angles relevant to the manganese coordination sphere are given in Table 3. Two slightly different molecules each with inversion symmetry are present in the unit cell. The structure consists of a centrosymmetric molecule with the center of symmetry at the manganese atom. The coordination sphere about the manganese atom consists of two phenolate oxygens, two pyridine nitrogens and two imino nitrogen atoms (N₄O₂) from two deprotonated SALIEP ligands. Each SALIEP acts as a tridentate ligand via a phenolate oxygen, and pyridine and imino nitrogen atoms. The geometry about the manganese atom is close to regular octahedral. The Mn1, N1, N2, N1* and N2* are nearly coplanar and the bond angles within the 'plane' are significantly distorted from those of a regular octahedron with N(1)-Mn(1)-N2 = 97.9 (2)° and $N(1)-Mn(1)-N^{*}(2) =$ $82.1(2)^{\circ}$. The angles $O(1)-Mn(1)-O(1^{*})$ (180.0°), $N(1)-Mn(1)-N^{*}(1)$ (180.00°), and $N(2)-Mn(1)-N^{*}(2)$ (180.00°) are linear however. The Mn atom resides in the N_4 plane (angle sum 360°). The Mn(1)–O(1) distance of 1.884 Å is much shorter than the metal oxygen distance found in IV and other zinc(II) and cadmium(II) complexes of the reduced ligands [3], and can be attributed to the higher metal oxidation state. However the manganese-imino nitrogen bond distance of Mn-N(1) (2.019 Å) is similar to that observed for zinc(II) complex (IV) but the Mn(1)-N(2) (2.368 (4) Å) (pyridine) distance is surprisingly much longer than the comparable distance observed for complex IV. The perchlorate group is disordered and is uncoordinated.

The structure of $[Zn(AMP)_2(NO_3)_2]$ (X) is shown in Fig. 4 and bond distances and angles relevant to the zinc coordination sphere are given in Table 4. The molecule is centrosymmetric with the center of inversion at the zinc atom. The coordination around the pseudo-octahedral zinc atom (N_4O_2) consists of two



Fig. 3. Perspective view of [Mn(SALIEP)₂](ClO₄) (IX).



Fig. 4. Perspective view of [Zn(AMP)₂(NO₃)] (X).

pyridine nitrogens, two amino nitrogens, and two oxygen atoms from two monodentate nitrate anions. The Zn, N1, N2, N1* and N2* atoms are coplanar and the bond angles within the 'plane' vary significantly from each other and from those of a regular octahedron with N(1)–Zn–N2 = 79.60(7)° and N(1)–Zn–N*(2) = 100.60(2)°. Other bond angles are close to those expected for regular octahedral geometry.

3.2. Spectroscopic properties

All the complexes display an absorption at 1617-1645 cm⁻¹ which is assigned to the C=N stretch of the coordinated Schiff base ligands [10]. Strong well resolved-sharp bands in the regions 1597-1605, 1460-1485, 1420-1445, 1040-1055 and 1005-1015 cm⁻¹ are assigned to the coordinated pyridine ring [11]. The mode of the coordination of the nitrate group can be determined by infrared spectroscopy, in a region of the spectrum where combination $(v_1 + v_3)$ bands occur for coordinated nitrate [12]. In compounds I, IV and X the single absorption band at 1736-1739 cm⁻¹, is associated with the monodentate nitrate in agreement with the structural data for IV and X, which suggests that compound I has dimeric structure analogous to IV. The perchlorate v_3 band in IX appears at 1084 cm⁻¹ indicating the presence of uncoordinated perchlorate group in agreement with the X-ray crystal structure of IX.

The electronic spectra of compounds I-VII are characterized by the presence of two to three high energy transitions which can be assigned to charge transfer from the ligand to the metal and vice versa. The transitions of very strong intensity at 367–394 nm and 266–269 nm, have been attributed to the charge transfer from the pyridine and imino nitrogens to the metal centers [1].

¹H, ¹³C and 2D NMR spectroscopy has been used to extract information regarding the mode of coordination of the ligands with the metal ions. The assignments in proton and ¹³C NMR spectra have been made on the basis of hetcore and cosy experiments and comparison of these data with those of the free, freshly isolated Schiff base ligands HSALIMP and HSALIEP and the dimeric zinc(II) complex (IV), for which the single crystal X-ray structure has been determined. ¹H NMR spectra of compounds I and II are very similar but are slightly different from that of III (Table 5), pointing to the fact that the structures of I and II are similar but different from that of III. In compounds I-III, the hydrogens of the methylene group (H6) (Fig. 1) adjacent to the imino nitrogen of SALIMP, form a singlet and show a downfield shift (0.13 ppm (I, II), 0.05 ppm (III)) in its position from that in the free ligand and the singlet due to H7 (Fig. 1) shows an upfield shift (0.05-0.10 ppm) (Table 5) compared to its position in the free ligand, reflecting the coordination of the HSALIMP

ligand to the zinc(II) ion through imino nitrogen. The signals due to the pyridine hydrogens show minor to significant shifts (0.01-0.02 (H1), 0.14-0.26 (H2), 0.15-0.29 (H3) and 0.10-0.22 ppm (H4)) in their positions from those in the free ligand indicating the participation of the pyridine nitrogen in coordination with the metal ion. The phenyl hydrogens also show significant shifts (0.17 (H9), 0.27-0.32 (H10), 0.08-0.10 (H11) and 0.16-0.17 ppm (H12)) in their positions from those in the free ligand suggesting the involvement of phenolate oxygen in coordination with the metal ion (I and II) thus supporting the conclusions drawn from analytical and other spectroscopic data.

Compounds IV, V and VII exhibit very similar ¹H NMR spectra (Table 5), which differ markedly from that of VI. In compounds IV, V and VII the hydrogens of the methylene group (H7) and the enamine hydrogen (H8) which are present adjacent to the imino group show significant shifts (0.08-0.17 (H7), 0.15-0.42 (H8) in their positions compared with the free ligand, and are clearly influenced by proximity of the coordinated metal ions. H6 and the hydrogens of the pyridine and phenyl rings also show small to significant changes in their positions indicating the coordination of the SALIEP ligand and the retention of the structures in DMSO solutions.

In the ¹³C NMR spectra of the compounds I–VII, the signal due carbon atoms adjacent to the donor sites show very significant changes in their positions as compared with the free Schiff base ligands (Table 6) clearly indicating the coordination of the ligands through these donor sites and the retention of their structures in the DMSO solutions. In compounds I-III the signal due to C6 which is adjacent to the imino nitrogen shows a drastic upfield shift (20.98-21.17 ppm), whereas the signal due to C7 shows a relatively small downfield shift (1.71-2.31 ppm) from their positions in the free ligand, thus demonstrating the participation of the imino nitrogen in coordination with the zinc(II) ions. The signals due to carbon atoms C1 and C5 which are adjacent to the pyridine nitrogen also show small (1.02-1.47 ppm (C1)) to significant upfield shifts (4.17-4.66 ppm (C5)) from their positions in the free ligand, indicating the participation of pyridine N in coordination to the zinc(II) ion. In compounds I and II the carbon atom C13, to which the phenolate oxygen is linked, shows a very large downfield shift (34.1-34.14 ppm) from its position in the free ligand showing the participation of phenolate oxygen in coordination with the zinc(II) ion. The signal due to C13 in compound III could not be detected. This may be indicative of nonparticipation of a protonated phenolate oxygen in coordination and a monomeric structure for III. The signals due to other carbon atoms also show small to significant variations from their positions in the free ligand establishing the coordination of the ligands to the metal ions and the retention of the structures in the solutions.

Table 5				
¹ H NMR	spectral	data	with	assignments

Complex ^a	$\delta(\text{ppm}) \text{ (DMSO)}(d_6)$
H(SALIMP)	5.01 (2H, s, H6); 7.0 (1H, d, <i>J</i> = 7.5 Hz, H12); 7.01 (1H, t, <i>J</i> = 7.5 Hz, H10); 7.39 (1H, t, <i>J</i> = 6.0 Hz, H2); 7.44 (1H, t, <i>J</i> = 8.1 Hz, H11); 7.49 (1H, d, <i>J</i> = 7.8 Hz, H4); 7.59 (1H, d, <i>J</i> = 7.2 Hz, H9); 7.88
	(1H, t, J = 7.8 Hz, H3); 8.65 (1H, d, J = 4.2 Hz, H1); 8.83 (1H, s, H7).
H(SALIEP)	3.19 (2H, t, J = 6.9 Hz, H6); 4.08 (2H, t, J = 6.9 Hz, H7); 6.93–6.98 (2H, m, H11 & H13); 7.29 (1H,
	d, <i>J</i> = 7.5 Hz, H2); 7.36–7.42 (2H, m, H4 & H12); 7.46 (1H, d, <i>J</i> = 8.1 Hz, H10); 7.78 (1H, t, <i>J</i> = 7.5
	Hz, H3); 8.59 (1H, s, H8); 8.62 (1H, d, J = 4.5 Hz,H1).
$[Zn(SALIMP)(NO_3)]_2$ (I)	5.14 (2H, s, H6); 6.69 (1H, t, J = 5.4 Hz, H10); 6.84 (1H, d, J = 8.4 Hz, H12); 7.36 (1H, t, J = 7.8 Hz,
	H11); 7.42 (1H, d, J = 7.5 Hz, H9); 7.65 (1H, t, J = 6.3 Hz, H2); 7.71 (1H, d, J = 8.1 Hz, H4); 8.17
	(1H, t, J = 7.8 Hz, H3); 8.67 (1H, d, J = 5.1 Hz, H1); 8.77 (1H, s, H7).
$[Zn(SALIMP)I]_2 \cdot 3H_2O$ (II)	5.14 (2H, s, H6); 6.69 (1H, t, <i>J</i> = 7.0 Hz, H10); 6.83 (1H, d, <i>J</i> = 8.7 Hz, H12); 7.35 (1H, t, <i>J</i> = 6.9 Hz,
	H11); 7.42 (1H, d, <i>J</i> = 7.5 Hz, H9); 7.63 (1H, t, <i>J</i> = 8.4 Hz, H2); 7.69 (1H, d, <i>J</i> = 7.8 Hz, H4); 8.14
	(1H, t, J = 6.9 Hz, H3); 8.67 (1H, d, J = 4.8 Hz, H1); 8.78 (1H, s, H7).
[Zn(HSALIMP)Cl ₂]·H ₂ O (III)	5.06 (2H, s, H6); 6.74 (1H, t, J = 7.2 Hz, H10); 6.83 (1H, d, J = 8.1 Hz, H12); 7.34 (1H, t, J = 7.8 Hz, H12); 7.34 (1H, t
	H11); 7.42 (1H, d, $J = 7.5$ Hz, H9); 7.53 (1H, t, $J = 6.0$ Hz, H2); 7.59 (1H, d, $J = 7.5$ Hz, H4); 8.03
	(1H, t, J = 7.8 Hz, H3); 8.66 (1H, d, J = 4.5 Hz, H1); 8.73 (1H, s, H7).
$[Zn(SALIEP)(NO_3)]_2$ (IV)	3.33 (2H, t, <i>J</i> = 4.5 Hz, H6); 3.95 (2H, t, <i>J</i> = 4.5 Hz, H7); 6.59 (1H, t, <i>J</i> = 7.2 Hz, H11); 6.76 (1H, d,
	J = 8.7 Hz, H13); 7.29–7.34 (2H, m, H10 & H12); 7.60 (1H, t, $J = 6.0$ Hz, H2); 7.62 (1H, d, $J = 6.9$
	Hz, H4); 8.08 (1H, t, $J = 7.5$ Hz, H3); 8.44 (1H, s, H8; 8.81 (1H, d, $J = 5.0$ Hz, H1).
$[Zn(SALIEP)Cl)]_2 \cdot 2H_2O(V)$	3.38 (2H, t, J = 6.9 Hz, H6); 4.00 (2H, t, J = 6.9 Hz, H7); 6.52 (1H, t, J = 7.5 Hz, H11); 6.66 (1H, d, H12) = 7.5 Hz, H12) = 7.5 Hz, H11); 6.66 (1H, d, H12) = 7.5 Hz, H11); 6.66 (1H, d, H12) = 7.5 Hz, H11); 6.66 (1H, d, H12) = 7.5 Hz, H12) =
	J = 8.4 Hz, H13); /.14 (1H, d, $J = 8.1$ Hz, H10); /.26 (1H, t, $J = 6.6$ Hz, H12); /.39 (1H, t, $J = 9.0$
	Hz, H2); $/.46$ (1H, d, $J = 8.1$ Hz, H4); $/.85$ (1H, t, $J = 8.1$ Hz, H3); $8.1/$ (1H, s, H8); 8.69 (1H, d, $J = 8.1$ Hz, H3); $8.1/$ (1H, s, H8); 8.69 (1H, d, H2); $J = 8.1$ Hz, H3); $8.1/$ (1H, s, H8); 8.69 (1H, d, H3); $8.1/$ (1H, s, H8); $8.1/$ (1H, s,
	J = 4.5 Hz, H1.
$[Zn(SALIEP)I]_2 \cdot H_2O(VI)$	2.00 (2H, I, $J = 1.8$ HZ, H6); 4.04 (2H, DS, H7); 6.87 (2H, DS, H11 & H15); 7.30–7.30 (4H, M, H2, H4, H10, H12); 7.00 (1H, h_2 , H1); 8.60 (1H, h_2 , L12); 8.60 (1H, h_2 , H2); 8.60 (1H, h_2, H2); 8.60 (1H, h_2, H2); 8.60 (1H, h_2; 8.60 (1H, h_2);
	$H_{10}, H_{12}; 1.90$ (1H, 05, H1); 8.00 (1H, 1, $J = 5.9$ Hz, H3); 8.09 (1H, 5, H8).
$[Ca(SALAEP)(NO_3)]_2 C_2H_5OH$	5.50 (2H, t, $J = 4.6$ Hz, H0; 5.51 (2H, t, $J = 4.6$ HZ, H7); 6.48 (1H, t, $J = 6.9$ HZ, H11); 6.59(1H, (VII) d, $J = 8.4$ Hz, H13); 7.18–7.22 (2H, m, H10 & H12); 7.55–7.61 (2H, m, H2 & H4); 8.04 (1H, t, $J = 7.2$ Hz, H3); 8.32 (1H, s, H8); 8.57 (1H, bs, H1).

^a Compounds: I is light brown, II–IV, VI, VII are very pale yellow, V is yellow and VIII is purple. s = singlet, d = doublet, bs = broad singlet, t = triplet, m = multiplet.

The ¹³C NMR spectra of compounds IV, V and VII are very similar (Table 6) and the signals due to carbon atoms C1, C5, C7, C8 and C14 present in the vicinity of donor sites show minor to significant changes (0.00–0.66 (C1), 0.04–0.55 (C5), 0.23–1.6 (C7), 3.95–4.21 (C8) and 11.49–32.89 (C14) ppm) in their positions from the free ligand indicating the coordination of

these sites to the metal ions and pointing to the fact that the compounds V and VII have dimeric structures similar to IV. The signals due to the carbon atoms C1, C5 and C7 show only minor changes (0.00-1.6 ppm) in their positions as compared with much larger changes in corresponding zinc(II) complexes with the HSALIMP ligand. This has been attributed to more

Table 6								
¹³ C NMR	spectral	data	(δ	(PPM),	DMSO	(d_6)	with	assignments

	I	II	III	IV	V	VI	VII	SALIMP	SALIEP
IC1	147.98	147.85	148.30	149.82	149.30	149.13	149.70	149.32	149.16
C2	123.75	123.64	123.29	122.82	121.86	123.58	123.55	122.53	121.51
C3	139.54	139.54	138.78	139.83		137.08	139.64	137.02	136.38
C4	123.20	123.04	122.68	125.15	124.09	124.35	125.21	122.13	123.38
C5	155.99	155.95	156.44	160.67			161.28	160.61	160.73
C6	42.96	42.77	42.87	35.70		34.26	36.93	63.94	38.74
C7	169.65	169.76	169.16	58.10	58.60	57.64	59.47	167.45	57.87
C8	118.62	118.92	118.93	170.04	169.94		170.20	118.80	165.99
C9	134.38	133.82	133.42	118.45	118.46	119.60	119.27	131.85	118.60
C10	119.68	119.63	119.63	133.82	133.76	133.36	132.88	118.69	131.58
C11	134.72	134.95	134.19	112.95	112.81	117.31	111.98	132.55	118.41
C12	117.47	117.32	117.36	135.62	135.63	136.55	136.46	116.54	132.21
C13	191.96	191.99		122.24	122.31	122.20	122.84	157.85	116.49
C14				170.52		191.92	172.17		159.03

strained structures in complexes with HSALIMP ligand, because of the formation of a five-membered chelate ring in comparison with the formation of a six-membered chelate ring, leading to less strained structures. The signals due to C8 and C14 show significant to very large upfield shifts (3.95-4.21 ppm (C8), 11.49-32.89 ppm (C14)) in their positions from those of the free ligand clearly establishing the participation of imino nitrogen and phenolate oxygen to the metal ions. ¹H and ¹³C NMR spectra of compound VI are some what different from those of other three compounds with SALIEP which could be attributed either to dissociation of the compound in DMSO or a structure different from other three. From the ¹H and ¹³C NMR spectral data, compounds I, II, IV, V and VII, which have very similar structural features, have been assigned dimeric structures, similar to that of IV, which has been determined from X-ray crystallography. In this structure the deprotonated phenolate oxygen links the two metal centers and the two halves of the dimer. In compound III, in which the phenolate oxygen of the HSALIMP remains protonated and uncoordinated, the ligand seems to coordinate to the zinc(II) ion through the two nitrogen donors, resulting in the formation of a single five-membered chelate ring in a four coordinate arrangement. A similar situation was observed in the zinc(II) and copper(II) complexes of reduced Schiff base ligand HSALAMP [1,3].

The magnetic moment measurements on a powdered sample of compound VIII were carried out in the temperature range 300-93 K. The magnetic moment of 3.11 BM at 300 K which remains nearly unchanged (3.06 BM at 93 K) down to 93 K is consistent with a six-coordinate octahedral geometry around the nickel ion and a mononuclear structure [13]. The electronic spectrum of VIII in DMF solution can be interpreted in terms of a distorted octahedral stereochemistry around the nickel center. The ${}^{3}A_{2g} \rightarrow {}^{3}T_{2g}$ transition in VIII appears as a doublet at 876 and 817 nm, with the splitting most likely caused by a distortion from regular octahedral geometry. The transition due to ${}^3\mathrm{A}_{2g}\!\rightarrow{}^3\mathrm{T}_{1g}$ (F) could not be observed. A strong band at 394 nm $(\varepsilon = 10975 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})$ is assigned to a combination of ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}$ (P) and charge transfer transitions [14,15]. A very strong band at 269 nm ($\varepsilon = 21500 \text{ dm}^3$ mol^{-1} cm⁻¹), which appears nearly at the same position (266-269 nm) in Zn(II) and Cd(II) complexes of SALIMP and SALIEP ligands, is ascribed to a charge transfer transition. Thus, the electronic spectrum and magnetic data are indicative of a distorted octahedral stereochemistry for VIII, in which each HSALIMP acts as a bidentate ligand through imino and pyridine nitrogens and it seems reasonable to assume that the two axial positions are occupied by bromine atoms.

4. Conclusion

Zinc(II) ions react with SALIMP to form two types of compounds: (a) dimeric, five-coordinate compounds (I and II) involving an anion and a tridentate ligand with deprotonated phenolate oxygen, which bridges the two metal centers and links the two halves of the dimer, as in the case of IV and (b) a four-coordinate monomeric complex III involving two coordinated chloride ions and a bidentate (N_2) SALIMP ligand, in which the phenolate oxygen remains protonated and uncoordinated. SALIEP reacts with zinc(II) and cadmium(II) ions to form dimeric 1:1 compounds IV-VII in which SALIEP behaves as tridentate ligand (N₂O) with a deprotonated phenolate oxygen, which bridges two metal centers, and links the two halves of the dimer as determined by crystallographically in case of IV. On reaction with nickel(II) and manganese(III) ions, HSALIEP forms six-coordinate octahedral complexes VIII and IX with 1:2 metal:ligand stoichiometry.

5. Supplementary material

Tables of atomic coordinates, a complete listing of bond lengths and bond angles, anisotropic thermal parameters and calculated and observed structure factors have been deposited. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam. ac.uk or www: http://www.ccdc.cam.ac.uk).

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