Zinc(II) and cadmium(II) complexes of the potentially tridentate ligands 2-[[2-pyridinylmethyl)amino]methyl]phenol (HSALAMP) and 2-[[[2-(2-pyridinyl)ethyl]amino]methyl]phenol (HSALAEP). X-ray crystal structures of the $[Zn(SALAMP)(NO_3)]_2$ and the $[Cd(SALAEP)(NO_3)]_2$ dimers

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Abstract

Zinc(II) and cadmium(II) complexes with two potentially tridentate (NNO) ligands 2-[[(2-pyridinylmethyl)amino]methyl]phenol (HSALAMP) and 2-[[[2-(2-pyridinyl)ethyl]amino]methyl]phenol (HSALAEP) have been isolated and structurally characterized through ^{1}H, ^{13}C and 2-D NMR spectroscopy and in two cases by X-ray crystallography. HSALAMP behaves as a tridentate (NNO) or a bidentate (NN) ligand, depending upon the nature of the anion and the reaction conditions and on reaction with zinc(II) salts gives three types of complex: (a) $[Zn(SALAMP)X]_2 \cdot yC_2H_5OH$ ($X=Cl$, $y=0$ (**I**); $X=I$, $y=0$ (**II**); $X=NO_3$, $y=1$ (**III**); (b) $[Zn(HSALAMP)X_2] \cdot yH_2O$ ($X=Cl, y=1$ (**IV**); $X=I, y=0$ (**V**); (c) $[Zn(HSALAMP)_2](ClO_4)_2 \cdot C_2H_5OH \cdot H_2O$ (**VI**). However HSALAEP, a similar compound with one additional carbon atom in the chain, acts as a tridentate ligand irrespective of the nature of the anion and the reaction conditions, forming compounds with zinc(II) and Cd(II) salts, $[M(SALAEP)X]_2 \cdot yC_2H_5OH$ ($M=Zn, X=Cl, y=0$ (**VII**); $M=Zn, X=I, y=0$ (**VIII**); $M=Zn, X=NO_3$, $y=0$ (**IX**) and $M=Cd$, $X=NO_3$, $y=1$ (**X**)). The single crystal X-ray structures of the $[Zn(SALAMP)(NO_3)]_2$ (**III**) and the $[Cd(SALAEP)(NO_3)]_2$ (**X**) dimers have been determined. **III** crystallized in the monoclinic system, space group $P2_1/c$, with $a=10.156(4)$, $b=17.424(4)$, $c=8.090(4)$ Å, $\beta=107.56(2)°$, $V=1365(2)$ Å^3 and $Z=4$. **X** crystallized in the monoclinic system, space group $P2_1/n$, with $a=9.728(2)$, $b=15.132(4)$, $c=10.223(4)$ Å, $\beta=92.910(10)°$, $V=1502.9(8)$ Å^3 and $Z=2$. The structures of **III** and **X** are similar and consist of centrosymmetric dimers in which deprotonated phenolates bridge the two metal atoms and link the two halves of the dimer. In **III** and **X** the zinc(II) and cadmium(II) ions have a highly distorted six-coordinate structure, bonded to two oxygen atoms from a bidentate nitrate group, the pyridine nitrogen, an amine nitrogen and a phenolate oxygen. The metal–metal separations are quite short (3.063(1) Å (**III**), 3.429(1) Å (**X**)) with M–O–M angles of 98.33(9) (**III**) and 99.2(1)° (**X**). Compounds **I** and **II** and **VII–IX** have been proposed to have dimeric structures similar to those of **III** and **X**, with SALAMP or SALAEP acting as tridentate (NNO) ligands with the two zinc(II) ions bridged similarly by phenolate oxygens. Compounds **IV**, **V** and **VI** appear to have four-coordinate, monomeric structures with (HSALAMP) acting as a bidentate ligand (NN).

Key words: Crystal structures; Zinc complexes; Cadmium complexes; Tridentate ligand complexes

Introduction

The zinc(II) ion has been found to be essential for all forms of life and more than 80 zinc(II) containing metalloenzymes have been identified fulfilling specific roles in each of the six major biochemical categories, e.g. as oxidoreductases, transferases, hydrolases, lyases, isomerases and ligases [1, 2]. In most of these enzymes zinc(II) has been assumed to have distorted four- or five-coordinate stereochemistries. In these enzymes zinc is held in the protein matrix by at least three enzyme based ligands in such a way as to allow only one or two additional ligand sites to be available to solvent and substrate. In spite of great efforts, the structures of the active sites and the mode of their actions are not clear in many of these enzymes. In order to get

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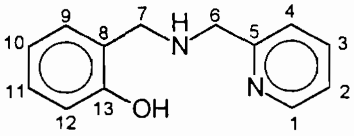
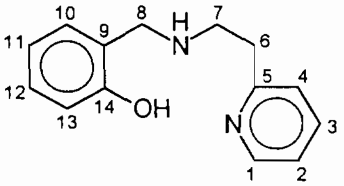


(HSALAMP)



(HSALAEP)

Fig. 1. HSALAMP and HSALAEP ligands.

a deeper insight into the structure–reactivity relationship of zinc(II) containing enzymes, the study of small molecules which are analogues of the metal binding sites in enzymes appears to offer an attractive opportunity to model the metal based chemistry without protein based complications inherently attendant on studying the enzymes themselves. For example in order to understand the mode of action of carboxypeptidase A, carboxypeptidase B [3–6] and thermolysin [7, 8], enzymes which have very similar ligation [9], in that the active site consists of a zinc(II) ion surrounded by a donor set of N_2O from the protein based ligands and a water molecule at the fourth site in a distorted tetrahedral geometry around the zinc(II) ion, model studies with tridentate and tetradentate ligands containing N, O and/or S atoms have been reported [2].

In our earlier communications [10, 11], we reported the synthesis and the ligating properties of the tripodal (N_2O) ligands HSALIMP, HSALIEP, HSALAMP and HSALAEP with copper(II) ions. The X-ray crystal structures of [Cu(SALIMP)(NO_3)] and [Cu(HSALAMP)Cl_2]·C_2H_5OH were also determined [11]. In these complexes, the tripodal systems behave either as tridentate (NNO) or bidentate (NN) ligands, depending upon the nature of the anions present. These complexes represent a class of very good models for understanding the nature of the active site in galactose oxidase. In the present publication, we report the results of our investigations on the ligating properties of the reduced Schiff base ligands HSALAMP and HSALAEP (Fig. 1) with zinc(II) and cadmium(II) ions. The X-ray crystal structures of dimeric zinc(II) (**III**) and cadmium(II) (**X**) complexes are also reported.

Experimental

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.

Synthesis of the ligands

2-[[2-Pyridinylmethyl)amino]methyl]phenol (HSALAMP)

2-Aminomethylpyridine (5.4 g, 50 mmol), dissolved in absolute ethanol (10 ml) was added to a solution of salicylaldehyde (6.2 g, 50 mmol) in the same solvent (15 ml) and the resulting dark yellow reaction mixture was stirred at room temperature for *c.* 30 min. A solution of sodium borohydride (3.0 g, 79 mmol) in water (40 ml) containing sodium hydroxide (0.40 g, 10 mmol) was added dropwise with constant stirring at room temperature over *c.* 15 min. The yellow colour of the Schiff base disappeared in *c.* 10 min, and the resulting colourless solution was stirred further for 1 h. It was concentrated under reduced pressure to *c.* 20 ml and the residue was extracted with chloroform (4×40 ml). The chloroform extract was dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure to give an oily mass. Petroleum ether (40–60 °C) (40 ml) was added to the oily residue, which on keeping in a refrigerator for a few days solidified to give a colourless crystalline compound. It was filtered off, washed with petroleum ether (3×10 ml) and recrystallized from hot ethylacetate. Yield 9.70 g, 96%. 2-[[[2-(2 – Pyridinyl)ethyl]amino]methyl]phenol (HSALAEP) was synthesized similarly by replacing 2-aminomethylpyridine with 2-(2-aminoethyl)pyridine. HSALAMP and HSALAEP were characterized through ^{1}H, ^{13}C and 2D NMR spectroscopy.

Synthesis of the complexes

[Zn(SALAMP)Cl]$_2$ (I)

(a) A reaction mixture of $ZnCl_2$ (1.0 mmol) and HSALAMP (1.0 mmol) was stirred in 20 ml of dry ethanol at room temperature. After 5 min, a white solid started separating out from a colourless solution. The mixture was stirred at room temperature for 6 h and the solid was filtered off, washed with dry ethanol (3×5 ml) and dried under vacuum at 60 °C for 12 h. Yield 20%.

(b) Triethylamine (a few drops) was added to a stirred mixture of $ZnCl_2$ (1.0 mmol) and HSALAMP (1.0 mmol) in dry ethanol (20 ml). A white solid separated out immediately from a colourless solution. It was filtered off and treated in the same way as in method (a). Yield 85%. *Anal.* Calc. for [Zn(SALAMP)Cl]$_2$ (**I**): C, 49.54; H, 4.13; Zn, 20.77. Found: C, 49.56; H, 4.60; Zn, 20.48%. λ_{max} (nm) (ϵ ($dm^3\ mol^{-1}\ cm^{-1}$)): 288 (3160), 271 (3240), 262 (4160).

[Zn(SALAMP)I]$_2$ (II)

II was obtained similarly by replacing $ZnCl_2$ with ZnI_2 using method (a) (yield 20%) and (b) (yield 93%). *Anal.* Calc. for [Zn(SALAMP)I]$_2$ (**II**): C, 38.48; H, 3.21; N, 6.91; Zn, 16.13. Found: C, 38.11; H, 3.36; N, 6.56; Zn, 15.86%. λ_{max} (nm) (ϵ (dm^3 mol^{-1} cm^{-1})): 370 (560), 290 (4325), 270 (4190), 260 (4660).

[Zn(SALAMP)(NO$_3$)]$_2 \cdot C_2H_5OH$ (III)

HSALAMP (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 room temperature. A white solid separated after 1 h. The mixture was stirred for a further 6 h and the solid was filtered off, washed with dry ethanol (3×3 ml) and dried under vacuum at 60 °C for 12 h. Yield 70%. *Anal.* Calc. for [Zn(SALAMP)(NO$_3$)]$_2 \cdot C_2H_5OH$ (**III**): C, 46.10; H, 4.25; Zn, 17.95. Found: C, 46.33; H, 4.41; Zn, 18.46%. λ_{max} (nm) (ϵ (dm^3 mol^{-1} cm^{-1})): 290 (4225), 270 (4675), 265 (5210). The crystals used for X-ray structure determination were obtained by the slow diffusion of ether into the solution of the complex in a mixture of *N,N'*-dimethylformamide/methanol (1:1). The recrystallized sample (X-ray) loses an ethanol molecule which was shown to be present (analysis) in the sample before recrystallization.

[Zn(HSALAMP)Cl$_2$]$\cdot H_2O$ (IV)

The filtrate from the preparation of compound **I** (method (a)), was concentrated nearly to dryness leaving an oily mass which solidified on standing at room temperature to produce a white crystalline compound. The product was filtered off, washed with a minimum amount of dry ethanol and dried under vacuum at 60 °C for 12 h. Yield 50%. *Anal.* Calc. for [Zn(HSALAMP)Cl$_2$]$\cdot H_2O$ (**IV**): C, 42.35; H, 4.34; Zn, 17.75. Found: C, 42.40; H, 3.79; Zn, 17.40%. λ_{max} (nm) (ϵ (dm^3 mol^{-1} cm^{-1})): [275], 270 (4110), 260 (3210).

[Zn(HSALAMP)I$_2$] (V)

This was obtained similarly from the filtrate of compound **II** (method (a)), as a pale yellow crystalline solid. Yield 50%. *Anal.* Calc. for [Zn(HSALAMP)I$_2$] (**V**): C, 29.25; H, 2.62; Zn, 12.26. Found: C, 29.57; H, 2.90; Zn, 12.07%. λ_{max} (nm) (ϵ (dm^3 mol^{-1} cm^{-1})): 365 (1240), 285 (4260), 270 (3910), 265 (4850).

[Zn(HSALAMP)$_2$](ClO$_4$)$_2 \cdot C_2H_5OH \cdot H_2O$ (VI)

A mixture of $Zn(ClO_4)_2 \cdot 6H_2O$ (1.0 mmol) and HSALAMP (1.0 mmol) was stirred in dry ethanol (20 ml) at ambient temperature for 20 h. The colourless solution was concentrated nearly to dryness and the oily mass which was left, was treated with dry petroleum ether (50 ml). The resulting mixture was kept at −5 °C for 10 days. A white crystalline solid separated, which was filtered off, washed with dry ethanol (2×3 ml) and dried *in vacuo* at ambient temperature for 48 h. Yield 40%. *Anal.* Calc. for [Zn(HSALAMP)$_2$](ClO$_4$)$_2 \cdot C_2H_5OH \cdot H_2O$ (**VI**): C, 44.42; H, 4.76; Zn, 8.85. Found: C, 44.21; H, 5.00; Zn, 8.52%. λ_{max} (nm) (ϵ (dm^3 mol^{-1} cm^{-1})): [295], 280 (5840), 270 (7260).

[Zn(SALAEP)Cl]$_2$ (VII)

HSALAEP (1.0 mmol) was dissolved in dry ethanol (10 ml) and added to a solution of zinc chloride in the same solvent (10 ml). The resulting mixture was stirred at ambient temperature for 16 h and concentrated to 5 ml. On standing at room temperature a white solid formed, which was filtered off, washed with dry ethanol (2×2 ml), then recrystallized from hot methanol and dried under vacuum at 60 °C for 8 h. Yield 50%. *Anal.* Calc. for [Zn(SALAEP)Cl]$_2$ (**VII**): C, 51.08; H, 4.56; Zn, 19.88. Found: C, 51.01; H, 4.62; Zn, 19.43%.

[Zn(SALAEP)I]$_2$ (VIII)

VIII was obtained in a similar manner to **VII** by replacing zinc chloride with zinc iodide. Yield 50%. *Anal.* Calc. for [Zn(SALAEP)I]$_2$ (**VIII**): C, 39.96; H, 3.57; Zn, 15.56. Found: C, 40.10; H, 3.79; Zn, 15.11%. λ_{max} (nm) (ϵ (dm^3 mol^{-1} cm^{-1})): 290 (2775), 270 (6875), 265 (8775).

[Zn(SALAEP)(NO$_3$)]$_2$ (IX)

A solution of HSALAEP (1.0 mmol) in dry ethanol (15 ml) was added dropwise with constant stirring to a solution of zinc nitrate (1.0 mmol) in the same solvent (10 ml). A white solid separated immediately. The resulting mixture was stirred at ambient temperature for 3 h and the solid was filtered off, washed with ethanol (2×3 ml) and dried under vacuum at 60 °C for 8 h. Yield 60%. *Anal.* Calc. for [Zn(SALAEP)(NO$_3$)]$_2$ (**IX**): C, 47.27; H, 4.22; Zn, 18.40. Found: C, 47.07; H, 4.60; Zn, 18.06%. λ_{max} (nm) (ϵ (dm^3 mol^{-1} cm^{-1})): 290 (2425), 270 (4850), 260 (13875).

[Cd(SALAEP)(NO$_3$)]$_2 \cdot C_2H_5OH$ (X)

X was prepared by a similar method to that used for **IX** by replacing zinc nitrate with cadmium nitrate. Yield 60%. *Anal.* Calc. for [Cd(SALAEP)(NO$_3$)]$_2 \cdot C_2H_5OH$ (**X**): C, 42.41; H, 4.22; Cd, 26.48. Found: C, 43.08; H, 3.75; Cd, 26.78%. λ_{max} (nm) (ϵ (dm^3 mol^{-1} cm^{-1})): 295 (1350), 280 (3250), 270 (6875), 265 (13050). The crystals suitable for X-ray analysis were obtained by the slow diffusion of ether into the solution of the complex in a mixture of *N,N'*-dimethylformamide/ethanol (1:1). The ethanol molecule present in the analytical sample was absent in the X-ray sample (i.e. after recrystallization).

Physical measurements

NMR spectra were recorded with a JEOL XL-300 spectrometer ($SiMe_4$ internal standard) in dmso (d_6), and electronic spectra were recorded in DMF solution with a Varian DMS 100 UV–Vis spectrometer in the range 200–900 nm. IR 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 and cadmium were determined volumetrically using EDTA titrations.

Crystallographic data collection and refinement of the structures

[Zn(SALAMP)(NO$_3$)]$_2$ (III)

The crystals of **III** are colourless parallelepipeds. The diffraction intensities of an approximately 0.45×0.20×0.08 mm crystal were collected with graphite monochromatized Mo Kα radiation using a Rigaku AFC6S diffractometer at 26±1 °C and the ω–2θ scan technique to a $2\theta_{max}$ value of 51.1°. A total of 2692 reflections was measured, of which 2511 ($R_{int}=0.026$) were unique and 1896 were considered significant with $I_{net}>2.0\sigma(I_{net})$. An empirical absorption correction was applied, after a full isotropic refinement, using the program DIFABS [12], which resulted in transmission factors ranging from 0.79 to 1.00. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient = 0.2597E-06). The cell parameters were obtained from the least-squares refinement of setting angles of 18 carefully centred reflections with 2θ in the range 41.68–45.81°.

The structure was solved by direct methods [13, 14]. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 1896 observed reflections ($I>2.00\sigma(I)$) and 227 variable parameters and converged with unweighted and weighted agreement factors of $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|=0.031$ and $R_w=[(\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2)]^{1/2}=0.028$. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.49 and −0.25 electrons/Å^3, respectively. Neutral-atom scattering factors [15] and anomalous-dispersion terms [16, 17] were taken from the usual sources. All calculations were performed with the TEXSAN [18] crystallographic software package using a VAX 3100 work station. A summary of the crystal and other data is given in Table 1 and atomic coordinates are given in Table 2. Selected bond distances and angles are given in Table 3. For hydrogen atom atomic coordinates (Table SI), anisotropic thermal parameters (Table SII), a full listing of bond distances and angles (Table SIII), a listing of structure factors (Table SIV) and least-squares planes (Table SV) see 'Supplementary material'.

TABLE 1. A summary of crystallographic data for [Zn(SALAMP)(NO_3)]$_2$ (**III**) and [Cd(SALAEP)(NO_3)]$_2$ (**X**)

	III	**X**
Chemical formula	$C_{26}H_{24}N_6Zn_2O_8$	$C_{28}H_{30}N_6Cd_2O_8$
Formula weight	679.28	803.4
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$
a (Å)	10.156(4)	9.728(2)
b (Å)	17.424(4)	15.132(4)
c (Å)	8.090(2)	10.223(4)
β (°)	107.56(2)	92.910(10)
V (Å^3)	1365(2)	1502.9(8)
Z	4	2
$2\theta_{max}$ (°)	50.1	45.0
T (K)	299	173
λ (Mo Kα) (Å)	0.71069	0.71069
D_{calc} (g/cm^3)	1.653	1.775
μ(cm^{-1})	18.59	14.67
R^a	0.031	0.0239
$R_w{}^b$	0.028	0.0303
Max. shift/σ	0.00	0.01
F(000)	692	800
GOF	1.80	1.17
Crystal size (mm)	0.45×0.20×0.08	0.44×0.32×0.12

$^aR=\Sigma(|F_o|-|F_c|)/\Sigma|F_o|$. $^bR_w=[(\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o{}^2)]^{1/2}$.

TABLE 2. Final atomic positional parameters and B_{eq} values for [Zn(SALAMP)(NO_3)]$_2$ (**III**) with e.s.d.s in parentheses

Atom	x	y	z	$B_{eq}{}^a$
Zn(1)	0.37697(4)	−0.05216(2)	0.91426(5)	2.75(2)
O(1)	0.5796(2)	−0.0446(1)	0.9382(3)	2.99(9)
O(2)	0.2188(3)	−0.0951(1)	1.0227(3)	4.0(1)
O(3)	0.4210(3)	−0.1370(2)	1.1586(3)	5.2(1)
O(4)	0.2438(3)	−0.1798(1)	1.2265(3)	4.6(1)
N(1)	0.2601(3)	−0.0098(1)	0.6692(3)	2.9(1)
N(2)	0.3507(3)	−0.1546(1)	0.7576(3)	2.8(1)
N(3)	0.2945(3)	−0.1380(2)	1.1393(4)	3.5(1)
C(1)	0.2527(4)	0.0620(2)	0.6109(5)	3.4(2)
C(2)	0.1772(4)	0.0822(2)	0.4457(5)	3.9(2)
C(3)	0.1049(4)	0.0260(2)	0.3359(5)	3.9(2)
C(4)	0.1138(4)	−0.0480(2)	0.3925(4)	3.5(2)
C(5)	0.1926(3)	−0.0651(2)	0.5594(4)	2.8(1)
C(6)	0.2119(4)	−0.1455(2)	0.6307(5)	3.4(2)
C(7)	0.4596(4)	−0.1545(2)	0.6692(4)	3.2(1)
C(8)	0.6039(3)	−0.1613(2)	0.7924(4)	2.7(1)
C(9)	0.6586(3)	−0.1035(2)	0.9153(4)	2.6(1)
C(10)	0.7982(4)	−0.1082(2)	1.0101(4)	3.1(2)
C(11)	0.8796(4)	−0.1684(2)	0.9888(5)	3.4(2)
C(12)	0.8241(4)	−0.2260(2)	0.8736(5)	3.5(2)
C(13)	0.6867(4)	−0.2220(2)	0.7760(5)	3.1(1)

$^aB_{eq}=(8\pi^2/3)\Sigma_{i=1}^{3}\Sigma_{j=1}^{3}U_{ij}a^*_ia^*_j\mathbf{a}_i\cdot\mathbf{a}_j$.

[Cd(SALAEP)(NO$_3$)]$_2$ (X)

The crystals of **X** are colourless blocks. The diffraction intensities of an approximately 0.44×0.32×0.12 mm crystal were collected with graphite-monochromatized Mo Kα radiation using a Nicolet R3m four-circle dif-

TABLE 3. Bond distances (Å) and angles (°) relevant to the zinc coordination sphere in $[Zn(SALAMP)(NO_3)]_2$ (**III**)

		ADC[a]			ADC[a]
Zn(1)–O(1)	2.012(2)	1	Zn(1)–O(1)	2.036(2)	65703
Zn(1)–O(2)	2.182(3)	1	Zn(1)–N(1)	2.113(3)	1
Zn(1)–N(2)	2.159(3)	1	Zn(1)–Zn(1)	3.063(1)	65703
Zn(1)–O(3)	2.400(3)	1			
O(1)–Zn(1)–O(1)	81.67(9)		O(1)–Zn(1)–O(2)	147.06(9)	
O(1)–Zn(1)–N(1)	109.7(1)		O(1)–Zn(1)–N(2)	92.97(9)	
O(1)–Zn(1)–O(2)	95.98(9)		O(1)–Zn(1)–N(1)	102.8(1)	
O(1)–Zn(1)–N(2)	174.63(9)		O(2)–Zn(1)–N(1)	102.9(1)	
O(2)–Zn(1)–N(2)	88.7(1)		N(1)–Zn(1)–N(2)	78.7(1)	
Zn(1)–O(1)–Zn(1)	98.33(9)		Zn(1)–O(2)–N(3)	98.4(2)	
O(1)–Zn(1)–O(3)	91.70(9)		O(2)–Zn(1)–O(3)	55.56(9)	

[a]Atom designator code (from ORTEP).

fractometer at 173 K. Using 1.6° ω-scans at a scan rate of 5.33° $\min^{-1}$, a total of 2186 reflections was collected with $4 < 2\theta < 45°$. Of these 1965 reflections were unique and 1718, which had $F > 4.0\sigma(F)$, were used in the structure refinement. The data were corrected for Lorentz and polarization effects and an empirical absorption correction was applied, based on ψ-scan data ($T_{max} = 0.781$, $T_{min} = 0.644$). A Patterson calculation [19] revealed the position of the cadmium atom, and the remaining non-hydrogen atoms were located using the tangent expression program TEXP [19]. Hydrogen atoms were inserted at calculated positions using a riding model and having a common thermal parameter. The structure was refined using blocked-cascade least-squares methods [20] and converged with unweighted and weighted agreement factors of $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.0239$ and $R_w = [(\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2)]^{1/2} = 0.0303$. The maximum least-squares shift/error ratio was 0.012 and the final difference map showed no feature greater than 0.27 e $Å^{-3}$. The function minimized in the refinement was $2\Sigma w(|F_o| - |F_c|)^2$ where $w = [\sigma^2(F_o) + 0.00011F_o^2]^{-1}$. A summary of crystal and other data is given in Table 1 and final fractional coordinates for non-hydrogen atoms are given in Table 4. Selected bond distances and angles are given in Table 5. For hydrogen atom atomic coordinates (Table SVI), anisotropic thermal parameters (Table SVII), a full listing of bond distances and angles (Table SVIII) and a listing of structure factors (Table SIX) see 'Supplementary material'.

TABLE 4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($A^2 \times 10^3$) for $[Cd(SALAEP)(NO_3)]_2$ (**X**)

	x	y	z	U_{eq} [a]
Cd	791(1)	−74(1)	1533(1)	13(1)
N(1)	2994(3)	−593(2)	1292(3)	17(1)
C(1)	3183(4)	−1128(3)	264(4)	18(1)
C(2)	4450(4)	−1459(3)	−18(4)	24(1)
C(3)	5579(4)	−1212(3)	772(4)	27(1)
C(4)	5390(4)	−655(3)	1814(4)	25(1)
C(5)	4094(4)	−355(3)	2068(4)	18(1)
C(6)	3874(4)	235(3)	3231(4)	22(1)
C(7)	3197(4)	1121(3)	2924(4)	22(1)
N(2)	1675(3)	1046(2)	2797(3)	18(1)
C(8)	1001(4)	1893(3)	2390(4)	21(1)
C(9)	1317(4)	2184(2)	1020(4)	17(1)
C(10)	2120(4)	2932(2)	850(4)	22(1)
C(11)	2354(4)	3266(3)	−377(4)	24(1)
C(12)	1733(4)	2851(2)	−1463(4)	22(1)
C(13)	947(4)	2102(3)	−1321(4)	18(1)
C(14)	762(3)	1730(2)	−102(4)	14(1)
O(1)	63(2)	963(2)	37(2)	16(1)
N(11)	−1058(3)	−433(2)	3532(3)	19(1)
O(11)	162(3)	−711(2)	3675(3)	23(1)
O(12)	−1372(3)	52(2)	2549(3)	22(1)
O(13)	−1939(3)	−629(2)	4314(3)	27(1)

[a]Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Results and discussion

Synthesis of the complexes

2-[[(2-Pyridinylmethyl)amino]methyl]phenol (HSALAMP) and 2-[[[2-(2-pyridinyl)ethyl]amino]methyl]phenol (HSALAEP) are potentially tridentate (N_2O) ligands, capable of forming two adjacent (6,5)- and (6,6)-membered chelate rings, respectively, on coordination to the same metal ion. The coordination behaviour of HSALAMP, which has one carbon less than that of HSALAEP, differs markedly from the latter towards zinc(II) ion as has already been observed with the copper(II) ion [10, 11]. HSALAMP, on reaction with zinc(II) salts, results in the formation of three types of complex: (a) dimeric complexes of 1:1 (metal:ligand) stoichiometry, in which SALAMP acts as a tridentate (N_2O) ligand and the deprotonated phenolate group links the two zinc(II) ions and the two halves of the dimer, as in the case of **III** and **X** and can be represented as $[Zn(SALAMP)X]_2\cdot$

TABLE 5. Bond lengths (Å) and angles (°) relevant to the cadmium coordination spheres in [Cd(SALAEP)(NO$_3$)] (**X**)

Cd–N(1)	2.307(3)	Cd–N(2)	2.274(3)
Cd–O(1)	2.279(2)	Cd–N(11)	2.842(3)
Cd–O(11)	2.497(3)	Cd–O(12)	2.401(3)
Cd–Cda	3.429(1)	Cd–O(1a)	2.224(2)
N(1)–Cd–N(2)	89.3(1)	N(1)–Cd–O(1)	114.9(1)
N(2)–Cd–O(1)	87.9(1)	N(1)–Cd–N(11)	129.6(1)
N(2)–Cd–N(11)	88.2(1)	O(1)–Cd–N(11)	115.3(1)
N(1)–Cd–O(11)	103.5(1)	N(2)–Cd–O(11)	83.8(1)
O(1)–Cd–O(11)	140.6(1)	N(11)–Cd–O(11)	26.3(1)
N(1)–Cd–O(12)	155.9(1)	N(2)–Cd–O(12)	90.5(1)
O(1)–Cd–O(12)	89.2(1)	N(11)–Cd–O(12)	26.3(1)
O(11)–Cd–O(12)	52.6(1)	N(1)–Cd–O(1a)	91.8(1)
N(2)–Cd–O(1a)	168.0(1)	O(1)–Cd–O(1a)	80.8(1)
N(11)–Cd–O(1a)	100.1(1)	O(11)–Cd–O(1a)	107.5(1)
O(12)–Cd–O(1a)	93.3(1)	Cd–O(1)–Cda	99.2(1)

yC$_2$H$_5$OH (X = Cl, y = 0 (**I**); X = I, y = 0 (**II**); X = (NO$_3$), y = 1 (**III**)); (b) monomeric complexes of 1:1 (metal:ligand) stoichiometry in which HSALAMP acts as a bidentate (N$_2$) ligand with no deprotonation of the phenolate oxygen, which remains uncoordinated, as was observed in the case of [Cu(HSALAMP)Cl$_2$]·C$_2$H$_5$OH [11] and are represented as [Zn(HSALAMP)X$_2$]·yH$_2$O (X = Cl, y = 1 (**IV**); X = I, y = 0 (**V**)); (c) a monomeric complex [Zn(HSALAMP)$_2$(ClO$_4$)$_2$]·C$_2$H$_5$OH·H$_2$O (**VI**) of 1:2 (metal:ligand) stoichiometry, in which the phenolate oxygen remains protonated and uncoordinated. The formation of the compounds of type (a) (b) or (c) is dictated by a number of factors. The most important of these is the nature of the anion. For example with Cl or I as anions, with moderate to weak coordinating ability, complexes of type (a) and (b) are formed. With nitrate as anion only a type (a) complex is formed, whereas with perchlorate as anion, which has very weak or non-coordinating ability, only the formation of complex of type (c) takes place. Secondly the reaction conditions affect the ratio of (a) and (b) type compounds, which are produced in the same reaction mixture (e.g. **I**, **II**). By using anhydrous solvent and/or a base like triethylamine (see 'Experimental'), which enhances the deprotonation of the phenolate oxygen, the percentage of type (a) over (b) is increased.

HSALAEP, which has one additional carbon atom in the chain, and is capable of forming two adjacent six-membered chelate rings, on reaction with zinc(II) and cadmium(II) ions, results in the formation of only dimeric complexes of 1:1 (metal:ligand) stoichiometry, **VII**–**X**, irrespective of the nature of the anions and the reaction conditions. In these compounds SALAEP acts as a tridentate, deprotonated, (N$_2$O) ligand, which links the two metal centres and the two halves of the dimer, as confirmed by the X-ray structure determination of **X**. This difference in the behaviour of HSALAMP and HSALAEP has been attributed to the difference in the chelate ring sizes which are formed on coordination.

Description of the structures of [Zn(SALAMP)(NO$_3$)]$_2$ (III) and [Cd(SALAEP)(NO$_3$)]$_2$ (X)

A perspective view of [Zn(SALAMP)(NO$_3$)]$_2$ (**III**) is shown in Fig. 2, and selected bond distances and angles relevant to the zinc coordination sphere are given in Table 3. The structure consists of a centrosymmetric dimer (Fig. 2), comprising two zinc(II) ions, two nitrate anions and two tridentate SALAMP ligands. The coordination sphere about each zinc consists of two oxygen atoms from a bidentate nitrate ligand, and the pyridine nitrogen, the amine nitrogen and the phenolate oxygen (N,N,O) atoms of SALAMP. The deprotonated phenolate bridges the two zinc atoms and links the two halves of the dimer. The geometry about the six-coordinate zinc atom can best be described as highly distorted octahedral. The zinc atom is displaced by 0.124 Å from the mean plane of the four atoms N1, O1, O2 and O3 which are approximately coplanar (maximum deviation 0.192 Å from the mean plane). The bond angles within the 'plane' vary markedly from those of a regular octahedron with O(2)–Zn(1)–N(1) 102.9°, O(1)–Zn(1)–O(1)* 81.67(9)°, O(2)–Zn(1)–(O(3) 55.56(9)° and O(1)–Zn(1)–O(3) 91.70(9)°. The bonds Zn(1)–O(2) and Zn(1)–O(1)* are close to colinear (N(2)–Zn(1)–O(1)* = 174.63°). The O(1) bridge forms an asymmetric linkage to the zinc atoms with Zn(1)–O(1) = 2.012 and O(1)*–Zn(1) = 2.036 Å. The Zn–Zn separation of 3.063 Å is reasonably short. The

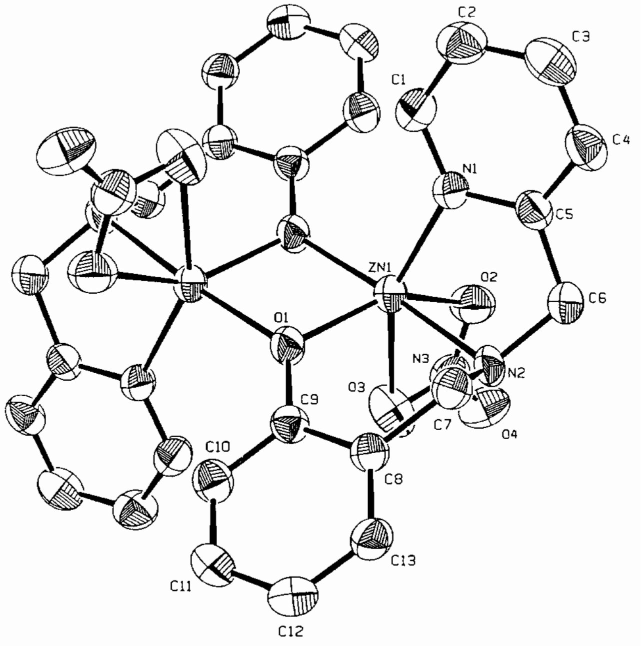


Fig. 2. Perspective view of [Zn(SALAMP)(NO$_3$)]$_2$ (**III**).

nitrate group acts as an asymmetric bidentate ligand with Zn(1)–O(2) = 2.182 and Zn(1)–O(3) = 2.400 Å. These distances are somewhat similar to those reported for the cadmium(II) complex **X** involving bidentate nitrate. The bite angle of 55.56° is slightly larger than that observed for **X** (52.6°). The zinc–nitrogen and zinc–oxygen bond distances of Zn(1)–N(1) = 2.113(3) (pyridine), Zn(1)–N(2) = 2.159(3) Å (amino) and Zn(1)–O(1) = 2.012 Å are normal, but significantly shorter than those observed for the analogous cadmium(II) complex **X**.

The structure of $[Cd(SALAEP)(NO_3)]_2$ (**X**), which is very similar to that of **III**, is shown in Figs. 3 and 4, and bond distances and angles relevant to the cadmium coordination sphere are given in Table 5. The structure consists of a centrosymmetric dimer (Fig. 3), comprising two cadmium(II) ions, two nitrate anions and two tridentate SALAEP ligands. The coordination sphere about each cadmium consists of two oxygen atoms from a bidentate nitrate ligand, and the pyridine nitrogen, the amine nitrogen and the phenolate oxygen (N,N,O) atoms of SALAEP. The deprotonated phenolate bridges the two cadmium atoms and links the two halves of the dimer. The geometry about the six-coordinate cadmium atoms is highly irregular. Although Cd, N1, O1, O11 and O12 are approximately coplanar (maximum deviation 0.125 Å from the mean plane), the bond angles within the 'plane' vary markedly from those of a regular octahedron with N(1)–Cd–O(11) = 103.5° and N(7)–Cd–O(1) = 114.9°. The angle N(2)–Cd–O(1a) (168.0°) is close to linear. The O(1) bridge forms an asymmetric linkage to the cadmium atoms with Cd–O(1) = 2.279 and O(1a)–Cd = 2.224 Å. The Cd–Cda distance of 3.429 Å is quite short. The nitrate group acts as an asymmetric bidentate ligand, with Cd–O(11) = 2.497 and Cd–O(12) = 2.401 Å. These distances are somewhat similar to those reported for the cadmium(II) complex $[Cd(L)(NO_3)_2]$ (**A**) (L = 1,4,7,10-tetraoxa-13-azacyclopentadecane) involving bidentate nitrate [21]. The bite angle of 52.6° is comparable with that reported for compound **A** (50.08°) [21]. The cadmium–nitrogen bond lengths of Cd–N(1) = 2.307(3) (pyridine) and Cd–N(2) = 2.274(3) (amino) Å are similar to those observed in **A**, but significantly shorter than those reported for other cadmium(II) complexes of the ligand 1,7,10,16-tetraoxa-4,10-diazacyclooctadecane ligand (2.482 Å) [22]. The Cd–O(1) distance of 2.279(2) Å is somewhat shorter than those reported for cadmium(II) complexes of these macrocyclic ligands [21, 22].

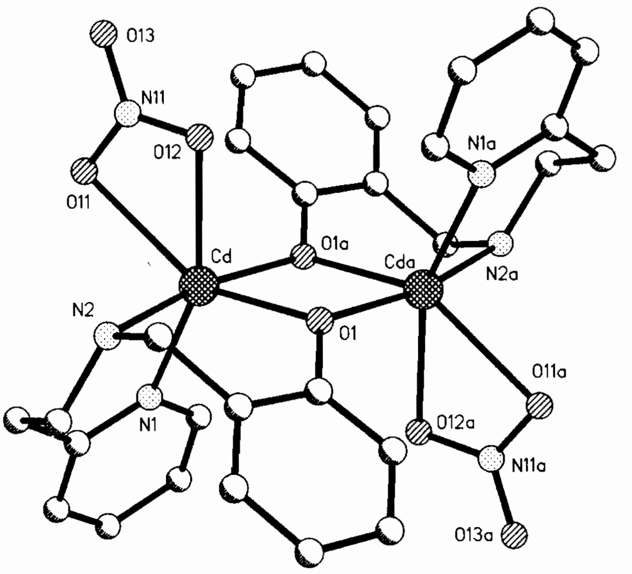


Fig. 3. Perspective view of $[Cd(SALAEP)(NO_3)]_2$ (**X**).

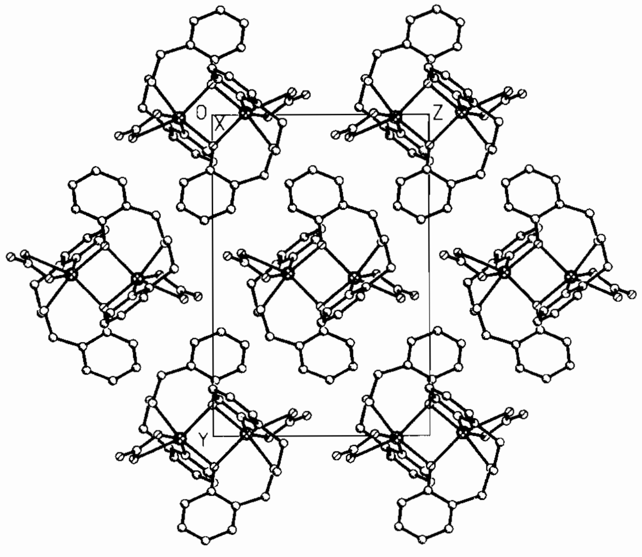


Fig. 4. Packing diagram of $[Cd(SALAEP)(NO_3)]_2$ (**X**).

Spectroscopic properties

The IR spectra of all the compounds are characterized by the presence of two to three bands in the region 3200–3500 cm^{-1}, which have been assigned to νNH and νOH of the water or ethanol molecules present in the compounds or the phenolic OH group of the ligand. The mode of coordination of the nitrate group can be determined by IR spectroscopy, in a region of the spectrum where combination $(\nu_1 + \nu_3)$ bands occur for coordinated nitrate [23]. In compounds **III**, **IX** and **X** the absorption bands at 1767, 1734 (**III**), 1765, 1738 (**IX**) and 1765, 1738 (**X**) cm^{-1} are associated with the bidentate nitrate in agreement with the structural data for **III** and **X**, which suggests that **IX** has an analogous dimeric structure also. The perchlorate ν_3 band in **VI** shows some minor splitting (1105 and 1090 cm^{-1}) suggesting involvement of the perchlorate group either in an H-bonding interaction with the water molecule or the phenolic –OH, or some very weak interaction with the metal ion. In the far-IR region the absorption frequencies have been assigned tentatively on the basis of reported data [24]. The absorption frequencies at 380–400 and 270–315 cm^{-1} in compounds **I**, **III**, **VII**, **IX** and **X** may be associated with νMO (phenolic) and νMN stretches, respectively. In compounds **I** and **VII** two frequencies in the region 240–280 cm^{-1} have been assigned to zinc chlorine stretches. In **IX** and **X** a strong band at 350–360 cm^{-1} has been assigned to the $M(ONO_2)$ stretching mode. Thus the IR and far-IR spectral data support the coordination of ligands through nitrogen and oxygen atoms and the involvement of anions in coordination.

The electronic spectra of these compounds exhibit three to four high energy transitions which could be assigned to charge transfer from the filled d orbitals of the metals to antibonding (π^*) orbitals of the phenolic residues [10] and also to π–π^* CT. In compounds **II** and **V** the transition at 365–370 nm, which is absent in other compounds with this ligand, clearly indicates the involvement of the iodine ligands in the charge transfer process. Similarly a very intense band in **IX** and **X** at 260–265 nm has been attributed to involvement of the nitrate ion in the charge transfer process. Earlier [10] we observed that the location and the intensity of the charge transfer band in copper(II) complexes of Schiff base ligands HSALIMP and HSAMIEP differ significantly from those of the reduced ligands HSALAMP and HSALAEP.

^1H, ^{13}C and 2D NMR spectroscopy has been used for structure elucidation and deciding the mode of coordination of the ligands with the metal ions. The assignments in proton and ^{13}C NMR spectra have been made on the basis of hetcore and cosy experiments and comparison of these data with those of the free ligands and the dimeric zinc(II) (**III**) and cadmium(II) (**X**) complexes, for which the single crystal X-ray structures have been determined. In compounds **I–III**, which show similar ^1H and ^{13}C NMR spectra, the hydrogens of the two methylene groups (H6, H7) (Fig. 1) flanking the amine group of SALAMP, form three to four signals in the form of singlets, doublets and/or quartets in the region 3.54–4.49 ppm (Table 6), reflecting the coordination of SALAMP to the metal centre through all three (N_2O) donor sites, which results in the formation of two adjacent (6,5) chelate rings thus forcing the ligand to undergo a major conformational change in which the two hydrogens in each methylene group, as well as the two methylene groups themselves, become non-equivalent, and appear at different chemical shifts, compared with their appearance as a singlet at 3.91 ppm in the free ligand. In zinc(II) and cadmium(II) complexes of the seven-membered (1,4,5-thiadiazepine) heterocyclic ligands, where the thiadiazepine ring undergoes a conformational change upon coordination with metal ions, the hydrogens of the methylene groups flanking the sulfur appear as a singlet compared with an AB quartet in the free ligand [25]. Compounds **IV–VI** exhibit similar NMR spectra, which differ slightly from those of **I–III**. In compounds **IV–VI**, the hydrogens of each methylene group appear either as a broad singlet in the regions 3.95–4.05 (H6) and 4.15–4.18 (H7) ppm or a multiplet at 3.86–4.17 ppm, pointing to the fact that the two hydrogens of each methylene group are somewhat equivalent, but the two methylene groups are themselves non-equivalent. In these compounds HSALAMP coordinates to the zinc(II) ion through the two nitrogen donors, resulting in the formation of a single five-membered chelate ring, and the phenolate group, which remains protonated and uncoordinated, must move in the opposite direction, making room for the metal ion to coordinate. A similar situation was observed in $[Cu(HSALAMP)Cl_2]C_2H_5OH$ [11].

In compounds **I–III**, H10 (Fig. 1) shows an upfield shift (0.26–0.38 ppm) compared to its position in the free ligand and in compounds **IV–VI** (H10 appears nearly at the same position as in the free ligand), thus indicating the involvement of the phenolate oxygen in coordination to the zinc(II) ion in **I–III**, but not in **IV–VI**, thus supporting the conclusions drawn from analytical and other spectroscopic data. The signals due to other hydrogens of the pyridine and phenyl groups show small to significant shifts from their positions in the free ligand (Table 6), reflecting the coordination of SALAMP through either N_2O (**I–III**) or N_2 (**IV–VI**) and the retention of the structures in DMSO solutions.

In the ^{13}C NMR spectra of the compounds **I–IV** and **VI**, the signal due to C6 shows an upfield shift (0.85–3.24 ppm) whereas the signal due to C7 shows a downfield shift (0.4–1.27 ppm) (except **IV** which shows an upfield shift of 2.54 ppm) from their positions in the free ligand. The signals due to other carbon atoms also show small to significant shifts (Table 7) from their positions in the free ligand, indicating the coordination of the ligand with the metal ion and the retention of the structures in solutions.

The electrical conductance measurements carried out on compounds **I** and **VII** (chloro derivatives) and compounds **III**, **IX** and **X** (nitrate derivatives) in *N*,*N*-dimethylformamide show values in the ranges 1–3 and 47–58 Ω^{-1} cm^2 mol^{-1}, respectively, which are lower than the value reported for 1:1 electrolytes (65–90 Ω^{-1} cm^2 mol^{-1}) [26]. The conductance data indicate that in the halogen derivatives (**I**, **II**, **VII** and **VIII**), which have similar spectral properties, the same structure is present in the solid and the solution states. In the nitrate derivatives (**III**, **IX** and **X**) a conductance value of 47–58 Ω^{-1} cm^2 mol^{-1} is indicative of partial replacement of the nitrate ion with the solvent molecule.

TABLE 6. ^{1}H NMR spectral data with assignments

Complex[a]	δ (ppm) (DMSO-d$_6$)[b]
HSALAMP	3.91 (4H, s, H6 and H7); 6.85 (1H, t, $J=8.1$ Hz, H10); 6.88 (1H, d, $J=7.5$ Hz, H12); 7.20 (1H, t, $J=8.7$ Hz, H11); 7.21 (1H, d, $J=7.5$ Hz, H9); 7.35 (1H, t, $J=6.0$ Hz, H2); 7.51 (1H, d, $J=7.8$ Hz, H4); 7.84 (1H, t, $J=7.5$ Hz, H1 and H3); 8.63 (1H, d, $J=3.9$ Hz, H1)
HSALAEP	3.00 (4H, t, $J=3.0$ Hz, H6 and H7); 3.94 (2H, s, H8); 6.17 (1H, bs, NH); 6.79 (1H, d, $J=8.1$ Hz, H13); 6.80 (1H, t, $J=7.5$ Hz, H11); 7.15 (1H, d, $J=8.1$ Hz, H10); 7.16 (1H, t, $J=6.9$ Hz, H12); 7.29 (1H, t, $J=6.3$ Hz, H2); 7.35 (1H, d, $J=7.8$ Hz, H4); 7.78 (1H, t, $J=7.8$ Hz, H3); 8.57 (1H, d, $J=6.6$ Hz, H1)
[Zn(SALAMP)Cl$_2$] (**I**)	3.54 (1H, AB q, $J=3.9$ Hz, H6a); 3.79 (1H, d, $J=16.2$ Hz, H7b); 4.10 (1H, d, $J=11.7$ Hz, H6b); 4.49 (1H, q, $J=7.2$ Hz, H7a); 4.88 (1H, bs, NH); 6.47 (1H, t, $J=7.2$ Hz, H10); 6.89 (1H, t, $J=7.8$ Hz, H11); 7.00 (1H, d, $J=11.1$ Hz, H12); 7.03 (1H, d, $J=10.5$ Hz, H9); 7.18 (1H, d, $J=7.8$ Hz, H4); 7.34 (1H, t, $J=6.6$ Hz, H2); 7.79 (1H, t, $J=7.5$ Hz, H3); 8.87 (1H, d, $J=4.8$ Hz, H1)
[Zn(SALAMP)I]$_2$ (**II**)	3.82 (2H, s, H6 or H7); 3.97 (1H, d, $J=13.2$ Hz, H6 or H7); 4.34 (1H, d, $J=16.00$ Hz, H6 or H7); 4.54 (1H, d, $J=5.4$ Hz, NH); 6.54 (1H, t, $J=7.2$ Hz, H10); 6.75 (1H, d, $J=8.1$ Hz, H12); 7.08 (1H, t, $J=7.8$ Hz, H11); 7.11 (1H, d, $J=6.9$ Hz, H9); 7.61 (1H, t, $J=6.6$ Hz, H2); 7.67 (1H, d, $J=7.8$ Hz, H4); 8.14 (1H, t, $J=6.9$ Hz, H3); 8.64 (1H, d, $J=3.9$ Hz, H1)
[Zn(SALAMP)(NO$_3$)]$_2$·C$_2$H$_5$OH (**III**)	3.86 (2H, s, H6 or H7); 4.00 (1H, d, $J=17.4$ Hz, H6 or H7); 4.36 (1H, d, $J=13.5$ Hz, H6 or H7); 4.72 (1H, bs, NH); 6.59 (1H, t, $J=6.9$ Hz, H10); 6.77 (1H, d, $J=7.5$ Hz, H12); 7.09 (1H, t, $J=7.2$ Hz, H11); 7.16 (1H, d, $J=6.9$ Hz, H9); 7.56 (1H, t, $J=6.3$ Hz, H2); 7.66 (1H, d, $J=8.1$ Hz, H4); 8.12 (1H, t, $J=7.5$ Hz, H3); 8.55 (1H, d, $J=2.4$ Hz, H1)
[Zn(HSALAMP)Cl$_2$]·H$_2$O (**IV**)	4.05 (2H, s, H6); 4.18 (2H, s, H7); 6.89 (1H, t, $J=6.9$ Hz, H10); 6.98 (1H, t, $J=8.1$ Hz, H11); 7.27 (1H, t, $J=7.8$ Hz, H2); 7.35 (1H, d, $J=7.5$ Hz, H4); 7.58–7.63 (2H, m, H9 and H12); 8.07 (1H, t, $J=6.9$ Hz, H3); 8.69 (1H, d, $J=3.3$ Hz, H1)
[Zn(HSALAMP)I$_2$] (**V**)	3.86–4.17 (4H, m, H6 and H7); 6.88 (1H, bs, H10); 6.95 (1H, d, $J=7.5$ Hz, H12); 7.26 (1H, t, $J=7.5$ Hz, H2); 7.33 (1H, d, $J=6.0$ Hz, H4); 7.61–7.64 (2H, m, H9 and H11)[e]; 8.10 (1H, t, $J=7.2$ Hz, H3); 8.71 (1H, d, $J=3.9$ Hz, H1); 10.05 (1H, bs, NH)
[Zn(HSALAMP)$_2$](ClO$_4$)$_2$·C$_2$H$_5$OH·H$_2$O (**VI**)	3.95 (2H, bs, H6); 4.15 (2H, bs, H7); 6.82–6.89 (2H, m, H10, H12); 7.20–7.28 (2H, m, H9, H11); 7.60 (2H, d, $J=7.2$ Hz, H2 and H4); 8.07 (1H, t, $J=7.5$ Hz, H3); 8.68 (1H, bs, H1)
[Zn(SALAEP)Cl]$_2$ (**VII**)	2.94–3.07 (4H, m, H6 and H7); 3.88 (2H, bs, H8); 5.15 (1H, bs, NH); 6.46 (1H, t, $J=7.2$ Hz, H11); 6.56 (1H, d, $J=6.0$ Hz, H13); 6.99–7.03 (2H, m, H10 and H12); 7.50–7.52 (2H, m, H2 and H4); 8.02 (1H, t, $J=7.2$ Hz, H3); 8.61 (1H, d, $J=2.4$ Hz, H1)
[Zn(SALAEP)I]$_2$ (**VIII**)	2.93 (1H, bs, H6); 3.08 (3H, m, H6 and H7); 3.97 (2H, s, H8); 4.65 (1H, bs, NH); 6.50 (1H, t, $J=10.8$ Hz, H11); 6.54 (1H, d, $J=7.2$ Hz, H13); 6.97 (1H, t, $J=7.5$ Hz, H12); 7.11 (1H, d, $J=7.2$ Hz, H10); 7.50 (1H, t, $J=6.3$ Hz, H2); 7.53 (1H, d, $J=8.1$ Hz, H4); 8.05 (1H, t, $J=6.9$ Hz, H3); 8.56 (1H, bs, H1)
[Zn(SALAEP)(NO$_3$)]$_2$ (**IX**)	2.81–2.92 (1H, m, H6); 3.10–3.27 (3H, m, H6 and H7); 3.46 (2H, bs, H8); 4.64 (1H, bs, NH); 6.56 (1H, d, $J=7.5$ Hz, H13); 6.57 (1H, t, $J=6.9$ Hz, H11); 6.97 (1H, t, $J=7.5$ Hz, H12); 7.14 (1H, d, $J=6.6$ Hz, H10); 7.46 (1H, t, $J=6.3$ Hz, H2); 7.57 (1H, d, $J=7.8$ Hz, H4); 8.04 (1H, t, $J=7.8$ Hz, H3); 8.51 (1H, bs, H1)
[Cd(SALAEP)(NO$_3$)]$_2$·C$_2$H$_5$OH (**X**)	2.90–3.48 (4H, m, H6 and H7); 3.93 (2H, bs, H8); 6.48 (1H, bs, H11)[c]; 6.74 (1H, bs, H13)[d]; 7.01–7.06 (2H, m, H10 and H12)[e]; 7.43–7.49 (2H, m, H2 and H4)[e]; 7.95 (1H, t, $J=6.6$ Hz, H3); 8.56 (1H, bs, H1)

[a] Compounds **I–IV**, **VI**, **VII** and **X** are colourless; **V**, **VIII** and **IX** are pale yellow. [b] s = singlet, d = doublet, bs = broad singlet, t = triplet, m = multiplet. In **X**: [c] splits into triplet on D$_2$O exchange; [d] splits into doublet on D$_2$O exchange. In **V** and **X**: [e] splits into doublet and triplet on D$_2$O exchange.

TABLE 7. ^{13}C NMR spectral data with assignments

	I	II	III	IV	VI	VII	VIII	IX	X	SALAMP	SALAEP
C1	148.22	147.81	147.67	148.16	148.04	149.08	149.28	149.18	149.63	148.94	149.04
C2	122.86	124.10	124.25	124.07	124.10	123.00	122.96	122.91	122.58	122.14	121.40
C3	138.75	139.97	140.43	139.10	139.41	139.98	140.22	140.26	139.12	136.63	136.44
C4	122.49	123.94	124.07	123.75	123.92	125.09	125.36	124.71	125.01	122.14	123.18
C5	155.94	156.28	156.25	156.02		160.17	160.48	160.77	161.13	159.25	159.78
C6	51.97	52.47	52.53	50.18	50.14	34.28	34.06	34.03	35.17	53.38	37.41
C7	50.14	50.71	51.01	47.20	50.14	46.89	47.40	47.54	47.86	49.74	48.04
C8	122.08	123.07	123.96	122.89	129.80	52.50	53.20	53.17	53.29	124.58	50.59
C9	130.92	130.56	130.76	131.11	131.22	123.15	124.02	125.41	124.35	128.88	124.19
C10	115.39	117.99	115.11	115.48	116.22	130.87	130.68	130.77	131.55	118.65	128.48
C11	129.05	129.15	129.23	129.76	131.22	119.49	119.44	119.51	119.96	127.98	11.48
C12	118.61	119.67	119.55	118.99	118.36	129.23	129.05	128.99	128.94	115.46	127.90
C13	162.66			162.72		113.88	114.62	115.60	113.80	157.13	115.43
C14											157.48

The NMR and other spectral data for compounds **I–III** are similar suggesting the presence of similar structures, in which the ligand binds to the metal centre via all three donor sites and an anion (Cl, I or NO_3) also binds to the metal ion. These complexes have been assigned dimeric structures, as observed for **III** and **X**, where the phenolate oxygen is deprotonated and links the two metal centres and the two halves of the dimer. Compounds **IV** and **V**, which have very similar spectral data, are assigned mononuclear structures (Fig. 5), similar to $[Cu(HSALAMP)Cl_2]\cdot C_2H_5OH$ [11, 12], where HSALAMP acts as a bidentate (N_2) ligand, and the phenolate oxygen remains protonated and uncoordinated. Compound **VI** is assigned a four-coordinate structure (Fig. 6) in which HSALAMP acts as a bidentate ligand.

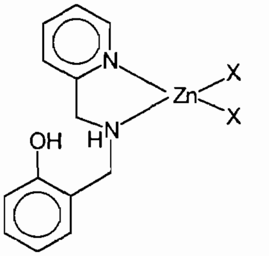


Fig. 5. Proposed structure for monomeric compounds **IV** and **V**.

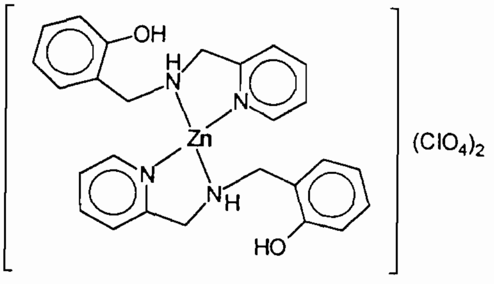


Fig. 6. Proposed structure for **VI**.

The ^1H and ^{13}C NMR spectra of compounds **VII–X** are very similar and show similar splitting patterns and chemical shifts (Tables 6 and 7), indicating similar structures in all cases. The hydrogens of the two methylene groups (H6, H7), which in the free ligand appear as triplets at the same chemical shifts (3.00 ppm), appear as complex multiplets in the region 2.90–3.48 (**VII**, **X**) or two multiplets at 2.81–2.93 (1H, H6) and 3.08–3.27 (3H, H6, H7) ppm, indicating the non-equivalence of the two hydrogens of each methylene group as well as the two methylene groups themselves, after coordination with the metal ions. The hydrogen atoms of the other methylene group (H8) appear as a broad singlet nearly at the same chemical shift as in the free ligand. The hydrogen atom of the secondary amine shows an upfield shift (1.02–1.53 ppm) (**VII–IX**) as compared to its position in the free ligand. The hydrogens of the pyridine and phenyl groups also show small to significant shifts from their positions in the free ligand (Table 6). In the ^{13}C NMR spectra of **VII–X**, the signals due to C6 and C7 show upfield shifts (2.24–3.38 (C6), 0.18–1.15 (C7) ppm) whereas the signal due to C8 shows a downfield shift of 1.91–2.70 ppm (Table 7), reflecting the involvement of NH in coordination with the metal ions. The signals due to other carbon atoms also show minor to significant shifts in their positions from those in the free ligand (Table 7). From the spectral (**VII–X**) and the conductance (**IX** and **X**) data which are very similar, it is reasonable to assume that they exist in a dimeric form as found for **III** and **X**, in which SALAMP and SALAEP act as deprotonated tridentate ligands (N_2O). On the basis of spectral and conductance data, compounds **VII** and **VIII**, and **IX** have been assigned five- and six-coordinate arrangements, respectively, in dimeric structures similar to the one found in **X**.

Conclusions

We have demonstrated that by changing the anions and the reaction conditions we can dictate the course of the reaction and can achieve the formation of specific products. For example the interaction between HSALAMP and the zinc(II) ion results in the formation of three types of compounds: (a) dimeric, five- or six-coordinate compounds involving an anion and a tridentate ligand with deprotonated phenolate oxygen, which bridges the two metal centres and links the two halves of the dimer, as we have seen in case of the cadmium complex **X**; (b) four-coordinate monomeric complexes involving two coordinated anions (Cl, I) and a bidentate (N_2) SALAMP ligand, in which the phenolate oxygen remains protonated and uncoordinated; (c) a four-coordinate 1:2 complex with (HSALAMP) acting as a bidentate ligand. The four- and five-coordinate complexes, which have one or two vacant sites for interaction with substrates or solvent molecules, are potentially good models for various zinc containing enzymes involving N_2O donor sites. The structure of the dimeric cadmium(II) complex is unusual, with a short Cd–Cd separation. There are few examples of dinuclear and polynuclear cadmium(II) complexes.

Supplementary material

Tables of atomic coordinates for hydrogen atoms, a complete listing of bond lengths and bond angles, anisotropic thermal parameters and calculated and observed structure factors are available on request from the authors.

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References

1 A. Galdes and B.L. Vallee, in H. Sigel (ed.), *Role of Metal Ions in Biological Systems,* Vol. 15, Marcel Dekker, New York, 1983, p. 1.
2 R.S. Brown, J. Huguet and N.J. Curtis, in H. Sigel (ed.), *Role of Metal Ions in Biological Systems,* Vol. 15, Marcel Dekker, New York, 1983, p. 55.
3 W.N. Lipscomb, *Tetrahedron, 30* (1974) 1625, and refs. therein.
4 W.N. Lipscomb, *Acc. Chem. Res., 3* (1970) 81.
5 F.A. Quiocho and W.N. Lipscomb, *Adv. Protein Chem., 25* (2971) 1.
6 M.F. Schmidt and J.R. Herriott, *J. Mol. Biol., 103* (1976) 175.
7 W.R. Kester and B.W. Matthews, *J. Biol. Chem., 252* (1977) 7704.
8 B.W. Matthews, J.N. Jansonius and P.M. Colement, *Nature (London), 238* (1972) 37.
9 M.K. Pangburn and A. Walsh, *Biochemistry, 14* (1975) 4050.
10 J.M. Latour, G.A. Leonard, D. Limosin, D.C. Povey and S.S. Tandon, in K.D. Karlin and J. Zubieta (eds.), *Biological and Inorganic Copper Chemistry,* Adenine, Guilderland, NY, 1985, p. 221.
11 J.M. Latour, S.S. Tandon and D.C. Povey, *Acta Crystallogr., Sect. C, 45* (1989) 7.
12 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A, 39* (1983) 158.
13 C.J. Gilmore, *J. Appl. Crystallogr., 17* (1984) 42.
14 P.T. Beurskens, *DIRDIF, Tech. Rep.* 1984/1, Crystallography Laboratory, Toernooiveld, 6525 Ed Nijmegen, Netherlands, 1984.
15 D.T. Cromer and J.T. Waber, *International Tables for X-ray Crystallography,* Vol. IV, Kynoch, Birmingham, UK, 1974, Table 2.2A.
16 J.A. Ibers and W.C. Hamilton, *Acta Crystallogr., 17* (1974) 781.
17 D.T. Cromer, *International Tables for X-ray Crystallography,* Vol. IV, Kynoch, Birmingham, UK, 1974, Table 2.3.1.
18 *Texsan-Texray Structure Analysis Package,* Molecular Structure Corporation, The Woodlands, TX, 1985.
19 G.M. Sheldrick, *SHELXS-86,* A program for crystal structure solution, Göttingen University, Germany, 1986.
20 G.M. Sheldrick, *SHELXTL User Manual,* Revision 4.1, Nicolet XRD Corporation, Madison, WI, 1984.
21 K.A. Byriel, K.R. Dunster, L.R. Gahan, C.H.L. Kennard, J.L. Latten, I.L. Swann and P.A. Duckworth, *Inorg. Chim. Acta, 205* (1993) 191.
22 L.A. Malmsten, *Acta Crystallogr., Sect. B, 35* (1979) 1702.
23 A.B.P. Lever, E. Mantovani and B.S. Ramaswamy, *Can. J. Chem., 49* (1971) 1957.
24 J.R. Ferraro, *Low Frequency Vibrations of Inorganic and Coordination Compounds,* Plenum, New York, 1971.
25 S.S. Sandhu, S.S. Tandon and H. Singh, *J. Inorg. Nucl. Chem., 40* (1978) 1967.
26 W.J. Geary, *Coord. Chem. Rev., 7* (1971) 81.