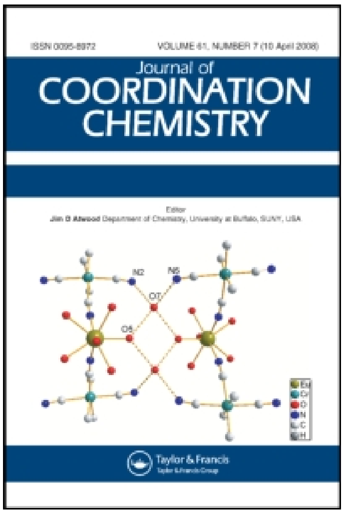

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THE INTERACTION OF Ag^I, Zn^{II} AND Pb^{II} WITH A PYRIDINYL-DERIVED N_5-MACROCYCLE

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The interaction of Ag^I , Zn^{II} and Pb^{II} with the macrocycle L^1 containing an N_5-donor set has been investigated. The ^1H nuclear magnetic resonance spectra of the complexes showed broad peaks, suggesting a slow exchange of metal ions between complexed and uncomplexed sites. The 1 : 1 (metal : ligand) stoichiometry was confirmed by first atom bombardment mass spectrometry and elemental microanalysis, solvent molecules being included when suggested by the infrared spectra. The X-ray crystal structures of $[AgL^1]ClO_4$, $[ZnL^1](ClO_4)_2$ and $[PbL^1(NO_3)_2]$ have been determined. The metal atoms in complexes are endomacrocyclic with the silver atom and zinc atom in a pentacoordinate environment comprising the ligand N_5-donor set. The lead atom prefers seven coordination derived from the full donor set of the macrocycle and two oxygens from dinitrate anions.

Keywords: Lead(II); Schiff-base penta-azamacrocycle; Zinc(II); Silver(I)

INTRODUCTION

A very large number of synthetic Schiff-base polyaza-macrocyclic and macroacyclic ligands have been prepared to mimic biologically occurring natural macrocycles. In addition to biological implications, aspects of the chemistry of these ligands and their complexes are of relevance in many other areas. The synthesis of new aza-macrocyclic complexes and their potential applications in areas such as electrocatalysis and electrochemical corrosion are themes of great interest [1–3].

In an earlier paper [4] we discussed the interaction of Cu^{II} and Ni^{II} with the macrocycle L^1 (Scheme 1) containing an N_5-donor set. Conductometric titration with chloride indicated the formation of 1:1 complexes.

The metal atoms in complexes are endomacrocyclic with the copper atom in a pentacoordinate environment comprising the ligand N_5-donor set. The nickel atom is in an approximately octahedral environment derived from the ligand N_5-donor set and a monodentate nitrate anion.

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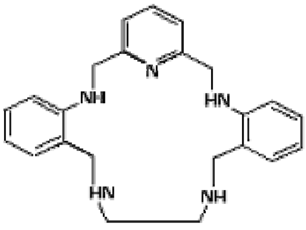

L^1

SCHEME 1

In the endomacrocyclic complexes the aliphatic nitrogen atom configurations are *S*,*S* (or *R*,*R*) whereas in the exomacrocyclic complexes the aliphatic nitrogen atom configurations are *R*,*S* (or *S*,*R*) [5, 6].

The ligand can form two diastereoisomeric species, each forming an enantiomeric pair for octahedral, square-based pyramidal and trigonal bipyramidal geometries. Molecular models suggest that one diastereoisomer (*R*,*R*,*R*,*R*) is less strained than the other (*R*,*R*,*R*,*S*) [7, 8].

In this paper we report the synthesis and properties of Ag^I , Zn^{II} and Pb^{II} complexes of the penta-azamacrocycle L^1 together with the crystal structure of the 1:1 complexes $[AgL^1]ClO_4$, $[ZnL^1](ClO_4)_2$ and $[PbL^1(NO_3)_2]$.

EXPERIMENTAL

Physical Measurements

Infrared (IR) spectra were recorded as KBr discs or NaCl plates, using a Perkin Elmer 1600 Fourier transform spectrometer. Electron impact and positive ion fast atom bombardment (FAB) mass spectra were obtained on Kratos MS80 and VG PROSPEC spectrometers. Proton nuclear magnetic resonance (NMR) spectra were run in deuterated solvents on a Bruker ACF-250 spectrometer. NMR titrations were run in deuterated chloroform on a Bruker AMX2-400 spectrometer. Elemental analyses were determined by the University of Sheffield microanalytical service. Crystal structure data were collected on a Siemens P4 four-circle X-ray diffractometer using molybdenum radiation. The structures were solved on a VIGLEN 486DX computer using the SHELX93 software package.

Synthetic Procedures

Chemical reagents and solvents used were of commercial reagent quality unless otherwise stated. Solvents for physical measurements were redistilled and dried prior to use.

Ligand Precursors

2,6-Diformylpyridine was prepared using the literature method [4]; the α,ω-diamine compound, *N*,*N*′-bis(2-aminobenzyl)-1,2-diaminoethane was prepared by selective reduction of *N*,*N*′-bis(2-nitrobenzyl)-1,2-diaminoethane. The identity and purity of the precursors were judged by ^{1}H NMR and mass spectrometry.

The Macrocycle L^1

N,*N*′-bis(2-aminobenzyl)-1,2-diaminoethane (10 mmol) was added to a gently refluxing solution of manganese(II) nitrate (10 mmol) and 2,6-diformylpyridine (10 mmol) in methanol (400 cm^3) and refluxed for 15 min. After cooling, sodium borohydride (100 mmol) was added carefully. When the effervescence stopped, the volume was reduced to *ca.* 50 cm^3 by rotary evaporation, water (200 cm^3), sodium hydroxide (8 g) and chloroform (100 cm^3) were added and then the solution was filtered through a well-packed filter aid which was washed with more chloroform (100 cm^3). The combined chloroform solutions were separated, dried over magnesium sulfate and the solvent was removed on a rotary evaporator. The crude product was recrystallized from ethyl acetate, then ethanol. Yield: 50%. IR (KBr disc): $\upsilon_{NH} = 3425$, 2255 cm^{-1}. MS (FAB): 374 (L^1H^+) amu. Microanalysis found (calcd. for $C_{23}H_{27}N_5$): 74.0% (74.0%) C, 7.5% (7.3%) H, 18.7% (18.8%) N. ^1H NMR ($CDCl_3$): 7.61 (1H, t, PyrH), 7.03 (2H, d, PyrH), 7.20–6.65 (8H, m, ArH), 4.42 (4H, s, $PyrCH_2$), 3.86 (4H, s, $ArCH_2$), 2.70 (4H, s, $NHCH_2$), 1.60 (4H, b, NH) ^{13}C NMR ($CDCl_3$): 157.7, 147.8, 136.4, 129.6, 128.3, 124.7, 120.8, 116.2, 110.5, 53.4, 48.9, 48.6 ppm.

Metal Complexes of L^1

The appropriate metal salt (0.5 mmol) was added to a suspension of the corresponding macrocycle $\mathbf{L^1}$ (0.5 mmol) in ethanol (15 cm^3) and stirred for 0.5h, the precipitated products were filtered off, washed with ethanol, dried and recrystallized from different solvents.

Analyses for $AgL^1(ClO_4)$ 1 ($C_{23}H_{23}N_5O_4ClAg$)

Pale yellow crystals. IR (KBr disc): $\upsilon_{NH} = 3315\,m^{-1}$, $\upsilon_{ClO_4} = 1090$, 620 cm^{-1}. MS (FAB): 480 $[AgL^1]^+$ amu. Microanalysis found (calcd.): 47.6% (47.9%) C, 4.01% (4.02%) H, 12.06% (12.14%) N.

Analyses for $ZnL^1(ClO_4)_2$ 2 ($C_{23}H_{23}N_5O_8Cl_2Zn$)

White crystals. IR (KBr disc): $\upsilon_{NH} = 3254\,cm^{-1}$, $\upsilon_{ClO_4} = 1100$, 625 cm^{-1}. MS (FAB): 436 $[ZnL^1–H]^+$ amu. Microanalysis found (calcd.): 43.54% (43.59%) C, 3.62% (3.66%) H, 11.01% (11.05%) N.

Analyses for $PbL^1(NO_3)_2$ 3 ($C_{23}H_{23}N_7O_6Pb$)

White crystals. IR (KBr disc): $\upsilon_{NH} = 3145\,cm^{-1}$, $\upsilon_{NO_3} = 1383$, 1306 cm^{-1}. MS (FAB): 579 $[PbL^1–H]^+$ amu, 374 $[L1H^+]$ amu. Microanalysis found (calcd.): 39.40% (39.43%) C, 3.10% (3.31%) H, 13.82% (13.99%) N.

Crystal Structure Data and Determination

The molecular structures of $[AgL^1]ClO_4$, $[ZnL^1](ClO_4)_2$ and $[PbL^1(NO_3)_2]$ (**1**, **2** and **3**) are illustrated in Figs. 1, 2 and 3, respectively. Selected bond lengths and angles with standard deviations in parentheses are presented in Tables I, II and III. Crystal data and experimental conditions for complexes are listed in Table IV.

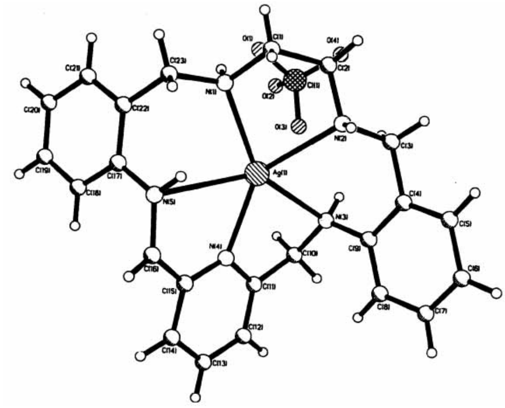

FIGURE 1 The structure of the cation $[AgL^1]^+$.

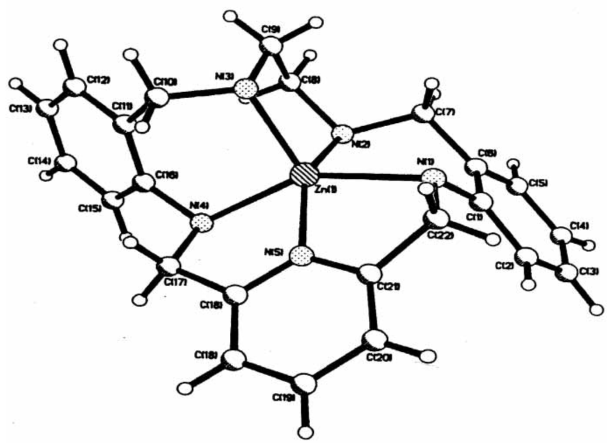

FIGURE 2 The structure of the cation $[ZnL^1]^{2+}$.

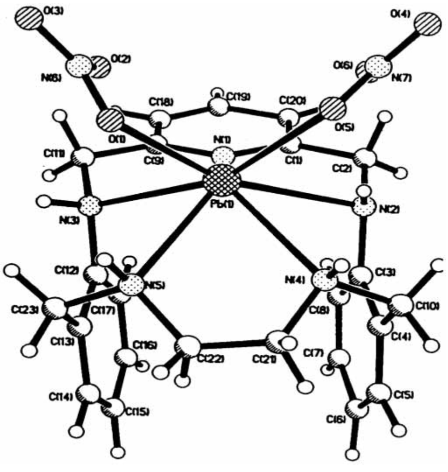

FIGURE 3 The structure of $[PbL^1(NO_3)_2]$.

TABLE I Bond lengths and angles in silver complex

Bond lengths (Å)			
Ag(1)–N(4)	2.308(7)	Ag (1)–N(1)	2.357(7)
Ag(1)–N(2)	2.471(7)	Ag (1)–N(3)	2.563(7)
Ag(1)–N(5)	2.732(7)		
Bond angles (°)			
N(1)–Ag(1)–N(4)	141.4(2)	N(4)–Ag(1)–N(2)	141.8(2)
N(1)–Ag(1)–N(2)	76.3(2)	N(4)–Ag(1)–N(3)	71.4(2)
N(1)–Ag(1)–N(3)	137.6(2)	N(2)–Ag(1)–N(3)	80.8(2)
N(1)–Ag(1)–N(5)	80.2(2)	N(4)–Ag(1)–N(5)	68.1(2)
N(2)–Ag(1)–N(5)	132.4(2)	N(3)–Ag(1)–N(5)	139.4(2)

TABLE II Bond lengths and angles in zinc complex

Bond lengths (Å)			
Zn(1)–N(5)	2.033(5)	Zn(1)–N(4)	2.204(4)
Zn(1)–N(2)	2.084(5)	Zn(1)–N(3)	2.058(5)
Zn(1)–N(1)	2.271(5)		
Bond angles (°)			
N(4)–Zn(1)–N(1)	150.5(2)	N(2)–Zn(1)–N(1)	141.8(2)
N(3)–Zn(1)–N(1)	112.7(2)	N(5)–Zn(1)–N(1)	71.4(2)
N(2)–Zn(1)–N(4)	101.2(2)	N(3)–Zn(1)–N(4)	80.8(2)
N(5)–Zn(1)–N(4)	78.8(2)	N(3)–Zn(1)–N(2)	68.1(2)
N(5)–Zn(1)–N(2)	149.6(2)	N(5)–Zn(1)–N(3)	139.4(2)

TABLE III Bond lengths and angles in lead complex

Bond lengths (Å)			
Pb(1)–N(5)	2.608(10)	Pb(1)–N(4)	2.645(11)
Pb(1)–N(2)	2.778(10)	Pb(1)–N(3)	2.764(11)
Pb(1)–N(1)	2.603(11)	Pb(1)–O(1)	2.659(14)
Pb(1)–O(5)	2.750(2)		
Bond angles (°)			
N(4)–Pb(1)–O(1)	150.5(5)	N(5)–Pb(1)–O(5)	141.8(5)
N(4)–Pb(1)–O(5)	112.7(8)	N(5)–Pb(1)–O(1)	71.4(6)
O(1)–Pb(1)–N(3)	101.2(7)	O(1)–Pb(1)–O(5)	80.8(10)
N(5)–Pb(1)–N(4)	78.8(4)	O(5)–Pb(1)–N(3)	68.1(2)
N(5)–Pb(1)–N(3)	149.6(3)	N(4)–Pb(1)–N(3)	139.4(9)

TABLE IV Summary of crystallographic data

Empirical formula	$C_{24}H_{30}N_5ClAgO_{4.5}$	$C_{23}H_{27}N_7PbO_6$	$C_{23}H_{27}C_{l2}N_5O_8Zn$
Formula weight	603.83	704.71	637.76
Temperature	293(2) K	293(2) K	293(2) K
Wavelength	0.710 73 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	*P*21/*c*	*P*1	*P*21/*n*
Unit cell dimensions	$a = 16.263(6)$ Å, $\alpha = 90°$ $b = 9.131(6)$ Å, $\beta = 102.29°$ $c = 18.405(7)$ Å, $\gamma = 90°$	$a = 9.051(3)$ Å, $\alpha = 77.31°$ $b = 11.002(4)$ Å, $\beta = 78.62°$ $c = 14.026(8)$ Å, $\gamma = 66.83°$	$a = 10.882(5)$ Å, $\alpha = 90°$ $b = 16.641(7)$ Å, $\beta = 102.24°$ $c = 15.016(8)$ Å, $\gamma = 90°$
Volume	2671(2) Å^3	1243(9) Å^3	2657(2) Å^3
Z	4	2	4
Density (calculated)	1.502 Mg m^{-3}	1.883 Mg m^{-3}	1.594 Mg m^{-3}
Absorption coefficient	0.900 mm^{-1}	6.840 mm^{-1}	6.840 mm^{-1}
F(000)	1236	688	1312

Three-dimensional, room-temperature X-ray data were collected in the range $3.5° < 2\theta < 45°$ on a Siemens P4 diffractometer by the ω scan method. For the three structures complex scattering factors were taken from the program package SHELXL93 [9] as implemented on the Viglen 486DX computer.

RESULTS AND DISCUSSION

Metal complexes of L^1 were first isolated from ethanolic solution and then recrystallized from different solvents. The 1:1 metal:ligand stoichiometry was confirmed by FAB mass spectrometry and elemental microanalysis, solvent molecules being included when suggested by IR spectra. The IR spectra showed bands corresponding to NH stretches in the region 3100–3400 cm^{-1} for each complex; anion stretches were difficult to assign owing to ligand stretches in the same region and were generally broadened or split as a result of complexation and/or hydrogen bonding.

The ^1H NMR spectra of the corresponding complexes showed broad peaks, suggesting a slow exchange of the metal ions between the complexed and uncomplexed sites; further work is in progress in order to obtain a full study of the behavior of these complexes in solution. However, FAB mass spectrometry has been used to characterize the solid products. The mass spectral data indicate complex formation since all the products show a main peak corresponding to each complex. Each of the complexes has a 1:1 (ligand:metal) stoichiometry. The spectrum of **3** is interesting because in addition to the base-ion peak at $m/z = 579$ corresponding to **3**, there is a peak at $m/z = 374$ which corresponds to metal-free L^1 suggesting that the lead ion is less strongly held than in **1** or **2** where no signal due to uncomplexed ligand is observed.

X-ray crystallographic studies were possible as the recrystallization of the complexes from different solvents resulted in formation of suitable crystals.

The silver complex **1** crystallized from ethanol as pale yellow needles. The structure of the cation $[AgL^1]^+$ is illustrated in Figure 1; bond lengths and angles with estimated standard deviations are given in Table I. The silver ion is coordinated by the five nitrogen atoms of the macrocycle with the Ag–N(3) and Ag–N(5) bonds the longest at 2.56 and 2.73 Å. The shortest of the Ag–N bonds is that to the pyridyl fragment (2.31 Å), and the other bonds to the secondary amines are very unequal (2.36 and 2.47 Å). These bond lengths are similar to those found for the related complex AgL^2ClO_4 (range 2.37–2.55 Å) [10].

The molecule is twisted with the two phenyl rings (r.m.s. deviation 0.010 Å) displaced from the Ag atom 0.298 Å. The silver atom, pyridyl nitrogen and, in turn, each pair of chemically equivalent secondary amino nitrogen atoms form planes (r.m.s. deviations 0.036 and 0.037 Å), which are mutually inclined at 40°. Thus the coordination geometry of the Ag ion is a twisted 1:2:2 polyhedron.

The configurations of the aliphatic nitrogen atoms are *R*,*S*,*S*,*R*, with alternate protons being mutually *trans* to each other. The perchlorate anion is ordered with tetrahedral geometry and here it forms a hydrogen bond to atom *N*(4) of the macrocycle (O···N 2.998, O···H 2.33 Å).

The ethanol molecules do not form hydrogen bonds but lie in channels along the twofold screw axis parallel to the crystallographic *b* axis (0.25, *y*, 0.25). Their adjacent sites along this axis are mutually incompatible (shortest O···Me 2.86, C···C 3.15 Å); thus the maximum occupancy of any one site is 50%. The high thermal parameters found for these atoms suggest an occupancy which may be substantially less than this; however, no alternative combination of occupancy and thermal parameter produced such good convergence and the high apparent vibration must be attributed to the looseness of the packing in these channels. The shape of the channel in $[AgL^1](ClO_4) \cdot (1/2)EtOH$ shows constrictions and is 'twisted'. This together with the 'cranked' shape of the ethanol molecule inhibits the loss of solvent, once encapsulated.

From a sample of the zinc complex **2**, recrystallized from ethanol, a single crystal, with dimensions 0.64 mm × 0.44 mm × 0.23 mm, was selected and studied by X-ray. The molecular structure of this complex is illustrated in Figure 2; bond lengths and angles, with their estimated standard deviations, are summarized in Table II.

The structure consists of five-coordinate zinc with metal bound to the full donor set of the macrocycle. The zinc is present in a square pyramidal geometry as shown by the τ value of 0.015, expected for a d^{10} metal ion such as zinc(II). The small distortions from idealized geometry may be related to the five-membered chelate rings to the N1, N4 and N5 donor atoms (N5–Zn–N1 78.0° and N5–Zn–N4 78.8°) and the five-membered chelate ring with N2 and N3 donor atoms (N5–Zn–N3 88.1°).

The molecular structure of **3** is illustrated in Fig. 3; bound lengths and angles, with their estimated standard deviations, are summarized in Table III. The structure consists of seven-coordinate lead with the full donor set of the macrocycle taking up five of the sites of the coordination polyhedron while the remaining two sites are occupied by the oxygens from monodentate nitrate anions.

Factors such as the number of counter-ions and the stereochemical requirements of chelating ligands are probably decisive and *a priori* arguments are unreliable in predicting the geometry of a particular complex. $[PbL^1(NO_3)_2]$ has the capped trigonal prismatic structure. The stereochemical disposition in this complex demonstrates the coordination preferences of the metal ions.

In comparing the structures of the Zn(II), Ag(I) and Pb(II) complexes it is clear that the zinc atom is content to interact with the five nitrogen donor atoms of the macrocycle with distorted trigonal-bipyramidal geometry. The crystal structure of the Ag complex shows the metal to be in a distorted square-pyramidal geometry coordinated by the full donor set of the macrocycle. The structure of the silver complex is more flat, suggesting that the metal fits in the cavity of the ligand. In contrast, the lead complex is placed out of the main plane because it is too large for the cavity so the ligand sits on one side and the anions sit on the other side, coordinating the full donor set of the macrocycle and two oxygens of dinitrate anions.

Acknowledgments

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Supplementary Material

Atomic coordinates and equivalent isotropic displacement parameters (bonds, lengths and angles), anisotropic thermal vibrational parameters (hydrogen atom position parameters) and observed structure amplitudes and calculated structure factors have been deposited at the CCDC under nos 277/20 (Ag), 277/21(Zn) and 277/22 (Pb).

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