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Bis complexes of zinc(II), cadmium(II) and mercury(II) with a potentially pentadentate N-donor ligand. Lewis acidity versus coordination tendency

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The dihydrazone of 2,6-diacetylpyridine is used as a N-donor ligand L to synthesise $[ZnL_2](ClO_4)_2$ (**1**), $[CdL_2](ClO_4)_2$ (**2**) and $[HgL_2](ClO_4)_2$ (**3**). The X-ray crystal structures of the three complexes have been determined. The asymmetric unit of **1** contains two independent cations of $[ZnL_2]^{2+}$ and four perchlorates. The metal atoms have distorted octahedral N_6 coordination sphere. The structure of **2** is a dimer $[Cd_2L_4]^{4+}$ containing a crystallographic centre of symmetry and associated with four perchlorate anions. The cadmium atoms are bonded to two tridentate L and in addition form a bond to a free NH_2 end of an adjacent CdL_2^{2+} unit. Thus Cd(II) in **2** is seven coordinate. The cation in **3** is a monomer with an HgN_6^{2+} core. The Lewis acidity in the three metal atoms follow the order Zn(II) > Cd(II) > Hg(II). The order of the tendency of acquiring a coordination number higher than six is Zn(II) < Cd(II) < Hg(II). A balance between these two counteracting factors is attained in Cd(II) making **2** a 7-coordinate dimer.

1. Introduction

Zn(II), Cd(II) and Hg(II) are non-transition, d^{10} metal ions. Of these, the chemistry of Zn(II) is most well developed as Zn is the most abundant metal in the living organisms after Fe. The other two ions, Cd(II) and Hg(II) have not received enough attention as these are not biologically important. For quite some time, we have been trying to develop their chemistry [1–4]. Here we have chosen the potentially pentadentate N-donor ligand L (Scheme 1) for a comparative study. Our main objective is to examine the variation of the coordinating properties of the zinc triad with the size of the metal ions. The d^{10} metal ions as such do not have any preference for a particular geometry as they do not have any crystal field stabilisation energies (CFSE) dependent on the geometry of the coordination sphere. Such a study is not possible for any transition metal triad as they will have CFSE. Thus the three metal ions Zn(II), Cd(II) and Hg(II) are ideal for our present purpose.

2. Results and discussion

The ligand L has been synthesised earlier by Busch and coworkers [5]. But the synthetic procedure is not given clearly. We have synthesised it by reacting 2,6-diacetylpyridine with excess of hydrazine hydrate in ethanol in presence of catalytic amount of acetic acid. We have prepared the bis L complexes of Zn(II), Cd(II) and Hg(II) as perchlorate salts by reacting metal perchlorates with L in 1:2 M proportion in methanol at room temperature. $[ZnL_2](ClO_4)_2$ (**1**) and $[CdL_2](ClO_4)_2$ (**2**) are colourless while $[HgL_2](ClO_4)_2$ (**3**) is yellowish. The X-ray crystal structures of these three complexes have been determined (Figs. 1–3). Selected bond distances and angles of the three complexes are given in Table 1.

The asymmetric unit of **1** contains two cations of $[ZnL_2]^{2+}$ named A and B and four perchlorates. The cations have similar structures and that of A is shown in Fig. 1. The metal atoms are six-co-ordinate with distorted octahedral environments being bonded to two terdentate ligands. The deviations from octahedral are primarily due to the small bite of the mer terdentate ligand, the angle subtended by the outer nitrogen atoms being on average 150.5° rather than the ideal trans angle of 180°. The bonds to the central pyridine nitrogen atoms range from 2.036(3) to 2.040(3) Å in the two cations, significantly shorter than the bonds to the outer nitrogen atoms 2.161(3)–2.244(3) Å. The two ZnN_3 planes intersect at an angle of 86.8(1)°. The NH_2 groups in **1** form strong hydrogen bonds with the perchlorate anions as listed in the Supplementary material Table S.

The structure of **2** is shown in Fig. 2. It is best considered as a dimer $[Cd_2L_4]^{4+}$ containing a crystallographic centre of symmetry and associated with four perchlorate anions. The cadmium atoms are bonded to two ligands L and in addition form a weak bond to N(10)\$1 from an adjacent CdL_2 unit thus forming a centrosymmetric dimer. The metal atoms are thus seven coordinate. As in the zinc structure, the two bonds to the central pyridine nitrogen atoms are the shortest at 2.285(2), 2.300(2) Å. The bonds to the outer nitrogens are Cd(1)–N(40) 2.350(3) Å, Cd(1)–N(31) 2.430(3)

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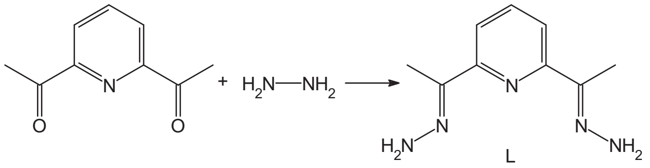

Scheme 1.

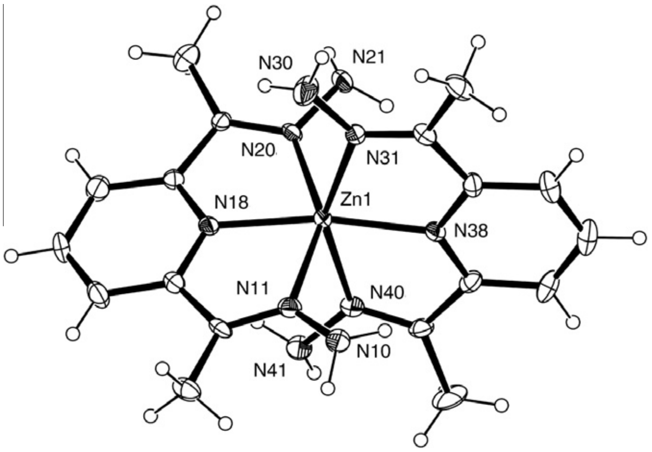

Fig. 1. The structure of cation A, $[ZnL_2]^{2+}$ with ellipsoids at 30% probability. The structure of cation B is similar. Selected bond lengths (Å) and angles (°) are given in Table 1.

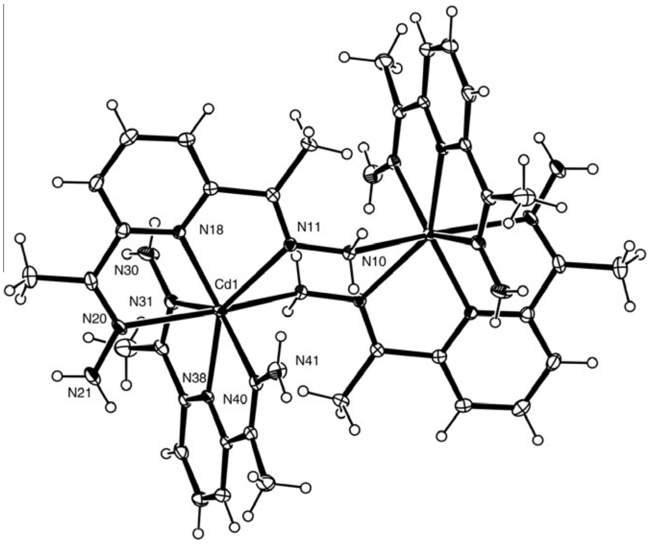

Fig. 2. The structure of the cation in **2** which contains a crystallographic centre of symmetry with ellipsoids at 30% probability. Selected bond lengths (Å) and angles (°) are given in Table 1.

Å, Cd(1)–N(11) 2.470(3) Å, and Cd(1)–N(20) 2.529(3) with the unique bond Cd(1)–N(10)$1 at 2.733(3) Å. The two CdN_3 planes intersect at an angle of 68.7(1)°. The plane containing N(11), N(18), N(20), Cd(1) shows an r.m.s. deviation of 0.236 Å compared to 0.012 Å for N(31), N(38), N(40), Cd(1) with the distortion no doubt due to the formation of the dimer. The N(11)–N(10) bond is longer at 1.413(3) Å than the other three N–N distances 1.378(4), 1.379(4), 1.361(4) Å. As is the case for the Zn cation, the NH_2 groups form hydrogen bonds with the perchlorates (details are given in Table S).

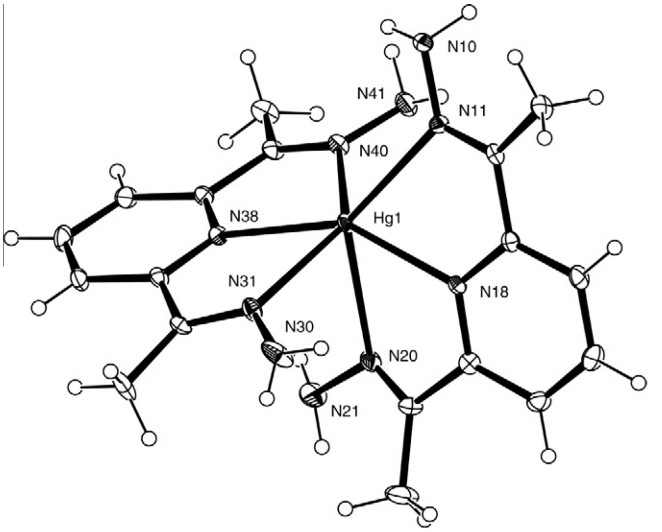

Fig. 3. The structure of the $[HgL_2]^{2+}$ cation in **3**, shown as a monomer, with ellipsoids at 30% probability. Selected bond lengths (Å) and angles (°) are given in Table 1.

Table 1
Dimensions in the metal coordination spheres (distances, Å; angles, °) in complexes **1**–**3**.[a]

	1 (M=Zn)		**2** (M=Cd)	**3** (M=Hg)
	Cation A	Cation B		
M(1)–N(18)	2.040(3)	2.037(3)	2.285(2)	2.274(3)
M(1)–N(38)	2.036(3)	2.039(3)	2.300(2)	2.305(4)
M(1)–N(40)	2.187(3)	2.192(3)	2.350(3)	2.362(4)
M(1)–N(31)	2.206(3)	2.242(3)	2.430(3)	2.495(4)
M(1)–N(11)	2.244(3)	2.202(3)	2.470(3)	2.455(4)
M(1)–N(20)	2.161(3)	2.183(3)	2.529(3)	2.569(4)
M(1)–N(10)$1	–	–	2.733(3)	2.999(4)
N(38)–M(1)–N(18)	169.04(13)	175.64(12)	147.15(9)	148.32(13)
N(18)–M(1)–N(40)	99.23(12)	103.46(12)	122.25(8)	127.88(12)
N(38)–M(1)–N(40)	75.81(12)	75.11(12)	69.16(9)	69.55(13)
N(18)–M(1)–N(31)	109.98(11)	108.56(11)	93.59(8)	91.43(12)
N(38)–M(1)–N(31)	74.87(12)	75.67(12)	68.61(9)	67.88(13)
N(40)–M(1)–N(31)	150.62(12)	150.64(12)	137.75(9)	137.35(12)
N(18)–M(1)–N(11)	74.06(13)	75.17(11)	68.24(8)	69.27(12)
N(38)–M(1)–N(11)	95.88(12)	100.66(11)	144.56(8)	141.77(12)
N(40)–M(1)–N(11)	88.81(11)	91.01(11)	90.27(8)	91.43(12)
N(31)–M(1)–N(11)	96.03(12)	97.11(11)	126.26(8)	121.21(12)
N(18)–M(1)–N(20)	76.08(12)	75.60(11)	67.30(9)	67.90(13)
N(38)–M(1)–N(20)	114.07(12)	108.56(11)	81.79(8)	84.54(12)
N(20)–M(1)–N(40)	98.17(11)	96.02(12)	94.45(9)	98.35(13)
N(20)–M(1)–N(31)	91.98(11)	90.53(11)	78.44(9)	80.19(13)
N(20)–M(1)–N(11)	150.06(12)	150.77(11)	129.90(8)	132.17(12)
N(18)–M(1)–N(10)$1	–	–	115.92(8)	113.12(11)
N(38)–M(1)–N(10)$1	–	–	86.16(8)	83.26(12)
N(40)–M(1)–N(10)$1	–	–	105.04(8)	102.26(12)
N(31)–M(1)–N(10)$1	–	–	73.33(8)	70.41(12)
N(11)–M(1)–N(10)$1	–	–	71.24(8)	68.31(11)
N(20)–M(1)–N(10)$1	–	–	151.71(9)	150.57(12)

[a] $1 symmetry element $1-x$, $-y$, $-z$. For atom labelling scheme, see Figs. 1–3.

The structure of **3** is isomorphous with **2** in spacegroup $P2_1/c$ but there is a significant difference in that the unique bond from Hg(1) to N(10)$1 is significantly weaker at 2.999(4) Å and for that reason, Fig. 3 shows the structure as a monomer. Bond lengths from the metal to the central nitrogen atoms are 2.274(3) and 2.305(4) Å, while those to the outer nitrogen atoms are 2.362(4), 2.495(4), 2.455(4) and 2.569(4) Å. As in **2**, The N(11)–N(10) bond is longer at 1.393(5) Å than the other three N–N distances 1.381(5), 1.366(6), 1.352(5) Å. The two HgN_3 moieties are far from perpendicular intersecting at an angle of 68.6(1)°. The two planes