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COMMUNICATION

HELICAL GROUP 12 CO-ORDINATION. THE X-RAY CRYSTAL STRUCTURE OF A FIVE-CO-ORDINATE ZINC(II) COMPLEX

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Abstract—The templated diimine-containing complexes, $[M(SpyNpy_2)](ClO_4)_2 \cdot 0.5H_2O$ {where M = Zn^{II}, Cd^{II} or Hg^{II}}, exhibit chirality in solution (NMR) which is consistent with, and may be diagnostic of, a helical coordination array in these complexes as verified by the X-ray crystal structure of an enantiomer of the zinc(II) derivative.

In the topical area of supramolecular chemistry, co-ordination chemistry has found relevance as a means of directing ligand assemblies through the recognition of conformations, such as helices, coded in an appropriate disposition of donors.[1] Recently, one of us has demonstrated how octahedral zinc(II) was used to template the first structurally characterised double-helical macrocyclic complex.[2] In general, tetrahedral and octahedral metal centres feature prominently as co-ordination motifs for doubly and triply stranded helical complexes, with by far the most commonly studied genre of ligands being of the oligomeric pyridyl variety.[1] Interestingly, the more simple mono-helical structures have received much less attention. Structurally characterised mono-helical complexes containing ten-co-ordinate europium(III),[3] seven-co-ordinate cobalt(II)[4] and five-co-ordinate silver (I)[5] and zinc(II)[6] are known. We now report our preliminary findings of what is only the second example of a structurally characterised trigonal bipyramidal zinc(II) motif for the helical co-ordination of a multidentate ligand, in this case the potentially septadentate ligand $SpyNpy_2$.

The complexes, $[M(SpyNpy_2)](ClO_4)_2 \cdot 0.5H_2O$, were isolated as yellow-coloured crystals from the [1+2] Schiff-base condensation reaction between 2,6-bis(2-aminothiophenoxymethyl)pyridine[7] and 2-pyridine carboxaldehyde in methanol in the presence of the appropriate metal perchlorate salt {see Scheme 1}. In each case the complexes were charac-

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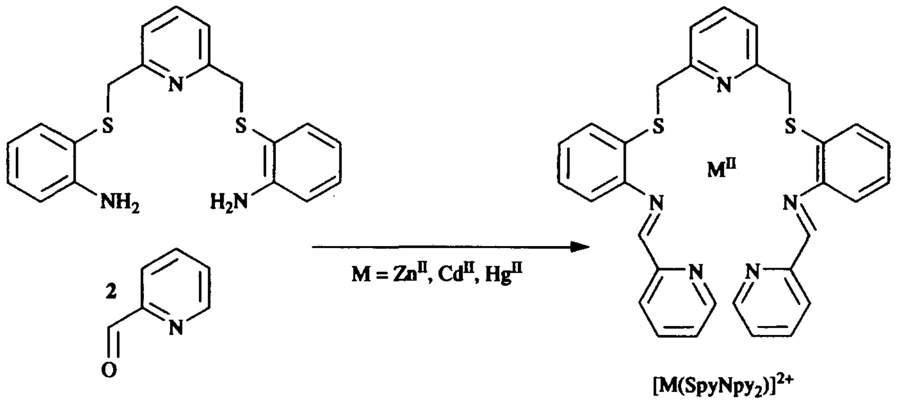

Scheme 1.

terised using IR and NMR spectroscopy, fast atom bombardment (FAB) mass spectrometry and elemental analysis. The ^{1}H NMR spectrum of the most soluble complex, [Hg(SpyNpy$_2$)] (ClO$_4$)$_2$ · 0.5H$_2$O, is typical and is reproduced in Fig. 1 by way of example. Notably in each case the methylene regions of the spectra contain well-resolved AB doublet-of-doublets, indicative of an inequivalence in these geminal protons in each half of a molecule. The AB spin pattern implies that: (i) co-ordination has removed the erstwhile enantiotopic nature of the methylene protons to make them diastereotopic and the complex chiral; (ii) the complexes are kinetically inert on the NMR time-scale, a view reinforced by the observation of satellites allied to the main imine resonance and ascribed to

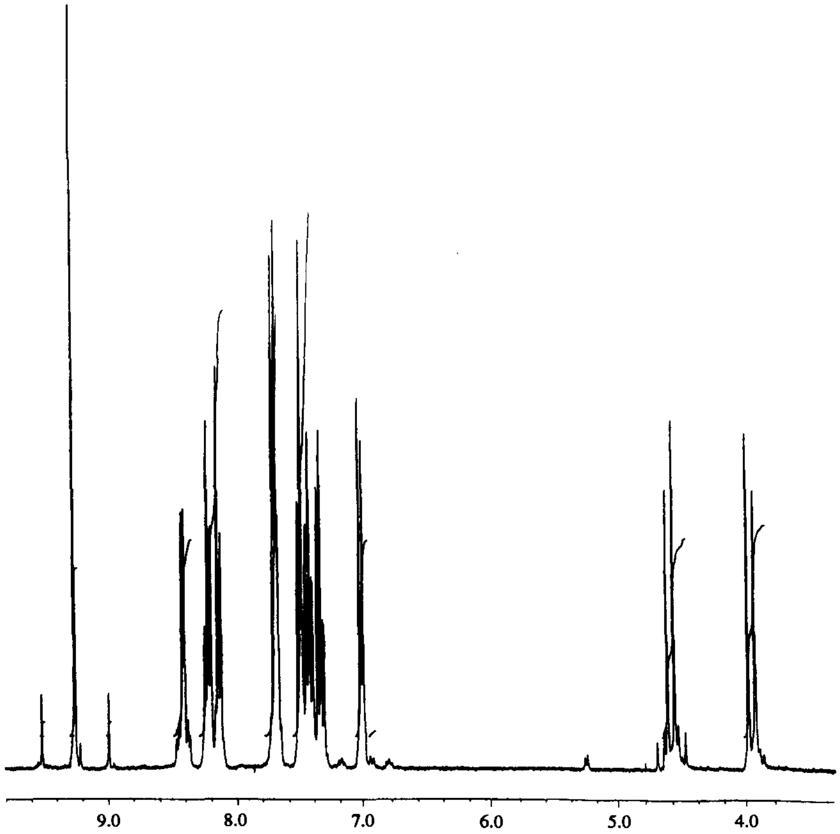

Fig. 1. ^{1}H NMR spectrum (300 MHz; 3.4–9.6 ppm range) of CD$_3$CN solution of [Hg(SpyNpy$_2$)] (ClO$_4$)$_2$·0.5H$_2$O.

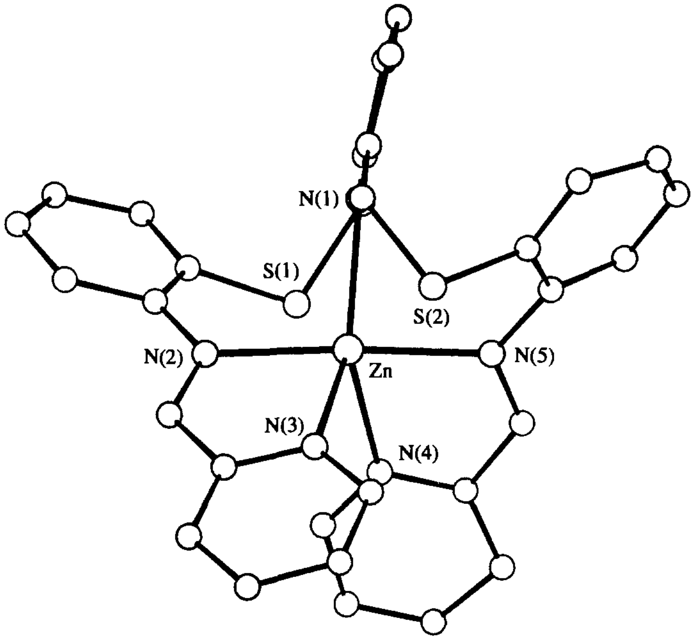

Fig. 2. The X-ray crystal structure and atom-numbering scheme of the cation $[Zn(SpyNpy_2)]^{2+}$. Co-ordination-sphere interactions (Å): Zn—N(1) 2.276(19); Zn—N(2) 2.159(20); Zn—N(3) 2.171(19); Zn—N(4) 2.217(23); Zn—N(5) 2.180(21); Zn···S(1) 2.761(11); Zn···S(2) 3.024(13). Co-ordination-sphere bond angles(°): N(1)—Zn—N(2) 95.8(7); N(1)—Zn—N(5) 87.2(7); N(4)—Zn—N(2) 100.5(8); N(4)—Zn—N(5) 75.1(8); N(3)—Zn—N(2) 76.9(8); N(3)—Zn—N(5) 103.3(8); N(1)—Zn—N(3) 135.5(9); N(1)—Zn—N(4) 141.7(8); N(3)—Zn—N(4) 82.2(8); N(2)—Zn—N(5) 175.5(9).

coupling between the imino protons and the naturally abundant $I = 1/2$ nuclei of ^{113}Cd, ^{111}Cd and ^{199}Hg.† We[2] and others[8] have noted a similar AB spin behaviour of methylene protons in other ligand systems and have used it as a diagnostic probe of helicity. In view of the suspected helical conformation of the complex, and of the rarity of structurally characterised mono-helical co-ordination environments, the X-ray crystal structure of $[Zn(SpyNpy_2)](ClO_4)_2 \cdot 0.5H_2O$ was undertaken.

Suitable, pale yellow crystals were obtained by recrystallisations from aqueous methanol. The X-ray crystal structure‡ of one of the enantiomers is presented in Fig. 2. The structure is consistent with the solution data. The cation is mononuclear with a five-co-ordinate zinc(II) centre surrounded by a helically co-ordinated (and potentially septadentate) ligand of C_2 symmetry. The zinc environment is distorted trigonal bipyramidal with only the five nitrogens of the ligand co-ordinated to the metal, leaving the two weakly basic thioether sulfur atoms unco-ordinated. The Zn—N bond lengths are typical for interactions between a first-row *d*-block ion and these donors.[9] In contrast, the Zn—S distances are long in comparison, and significantly longer than the range of distances {2.385(3)–2.407(3) Å} obtained for the interaction of these same thioether sulfurs in related acyclic and macrocyclic ligand complexes of nickel(II).[9] The non-co-ordination of these relatively weakly basic thioether sulfurs is presumed to be a consequence of strains within the co-ordination sphere arising from constriction of the helix around the zinc(II) ion. The ligand itself is helical but with a kink at the central pyridyl group. The perspective in Fig. 2 shows how the terminal pyridines overlap to complete one turn of the helix.

Whether the sulfurs remain unco-ordinated in

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† The intensities of the NMR satellites relative to the central imine singlet are: 1:6 for $[Cd(SpyNpy_2)](ClO_4)_2 \cdot 0.5H_2O$ and 1:10 for $[Hg(SpyNpy_2)](ClO_4)_2 \cdot 0.5H_2O$, corresponding closely to the natural abundances of the respective $I = 1/2$ nuclei ($^{113}Cd + ^{111}Cd = 25\%$; $^{119}Hg = 16.84\%$).

‡ *Crystal data for* $C_{31}H_{25}Cl_2O_8N_5S_2Zn \cdot 0.5H_2O$: $M = 804.98$, trigonal, $R\bar{3}c$ (no. 167), $a = b = 26.201(4)$, $c = 52.941(9)$ Å, $U = 31474.46$ Å^3, $Z = 36$, $D_c = 1.529$ g cm^{-3}, $F(000) = 14796$. A pale yellow crystal of size 0.16 × 0.18 × 0.24 mm was used for data collection (Philips PW1100 diffractometer, Mo-K_α radiation). The method of data collection and processing were similar to those previously described.[10] Final residual factors were $R = 0.0695$ and $R' = 0.0693$.

the cadmium(II) and mercury(II) derivatives is not certain. We have recently observed that co-ordination of the same thioether group is very sensitive to co-ordination-sphere constraints even in the presence of large, soft, heavy-metal ions such as mercury(II) and lead(II).[7] What is certain is that a helical environment, as evidenced by the AB spin behaviour of the methylene protons, is retained in solution even for these labile metal ions. We are currently investigating the interaction of $\mathrm{SpyNpy_2}$ and related ligands with a wide range of co-ordinating metal ions.

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