Chemistry of Polydentate Ligands. Part 9.[1] Preparation and Properties of Group 2B Cation Complexes with Multidentate Ligands based on 2,2′-Bipyridyl

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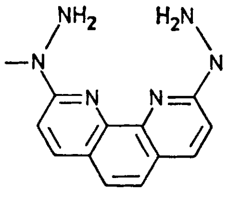
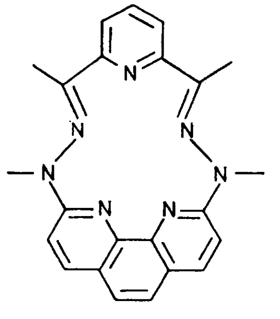
Complexes of Group 2B metal ions with 6,6′-di-(1-methylhydrazino)-2,2′-bipyridyl and with the quinquedentate macrocycle prepared by condensation of this compound with 2,6-diacetylpyridine are reported. Infrared spectra are consistent with the linear ligand adopting either a *cis*-α or *cis*-β conformation in octahedral complexes. The cavity of the macrocycle is of sufficient size to incorporate a Zn^{II} ion bound to two axial ligands, but the larger Cd^{II} ion gives a six-co-ordinate complex with a chloride ion occupying the axial site in a pentagonal pyramid. Hydrogen-1 n.m.r. spectral parameters for the complexes are presented: signals from two of the bipyridyl hydrogens move downfield in passing from the linear to the cyclic ligands, while the third resonance shifts upfield. This behaviour is discussed in terms of a change in the dihedral angle about the 2,2′ bond and an alteration in the extent of π conjugation in the two ligands.

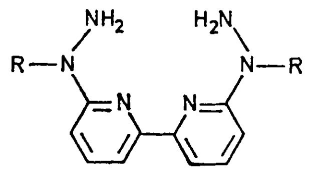
An earlier paper in this series [2] compares the ^1H n.m.r. spectra of $[M(L^1)]^{2+}$, M = Zn^{II} and Cd^{II}, with those of $[M(L^2)]^{2+}$ and discusses the downfield movement of the phenanthroline-hydrogen resonances in $[M(L^2)]^{2+}$ relative to the equivalent signals in $[M(L^1)]^{2+}$. An explanation was proposed where the increased ring currents from the greater extent of π delocalisation in the macrocyclic rings compared to the open-chain ligands are responsible for the shifts. We now report the results of a similar study on Group 2B complexes of L^4 and L^6, which differ from L^1 and L^2 in that the phenanthroline segments have been replaced with 2,2′-bipyridyl residues. Details of the syntheses of L^3, L^4, and $[Zn(L^5)(OH_2)_2][NO_3]_2$ have already been published,[3-5] and a route similar to that used in the preparation of the last compound was followed in the formation of complexes with L^6.



L^1

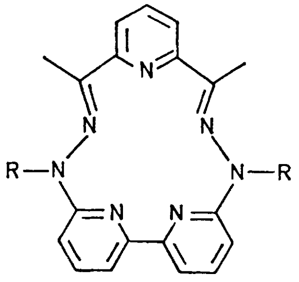


L^2



L^3 R = H

L^4 R = Me



L^5 R = H

L^6 R = Me

RESULTS AND DISCUSSION

The Group 2B metal-ion complexes of L^4, which are intermediates in the preparation of derivatives of the macrocycle L^6, were isolated by addition of $[NH_4][NCS]$ to aqueous or methanolic solutions of a salt of the appropriate metal ion and L^4. Complexes with L^6 were prepared by condensing 2,6-diacetylpyridine with the above compounds, in the presence of a mineral acid catalyst. Ring closure was accompanied by a deepening in the yellow colour of the solution over 4 h refluxing. Analytical and electrical conductance data for the complexes isolated are presented in Table 1.

The i.r. spectra of complexes with L^4 contain two ν(N–H) bands at *ca.* 3 300 cm^{-1} and 3 200 cm^{-1} along with a bending mode [6] at *ca.* 1 640 cm^{-1}. Two ν(C≡N) signals of equal intensity, at roughly 2 098 and 2 075 cm^{-1} in each spectrum, indicate *cis* co-ordination of the thiocyanate ligands. Complexes containing hydrazone derivatives of L^3 exhibit similar pairs of signals owing to the quadridentate ligands assuming *cis*-α or *cis*-β conformations; an explanation that is equally valid here.[7] Molecular models demonstrate that this type of co-ordination is possible only if there is some rotation of the two pyridyl rings relative to each other *i.e.* the dihedral angle about the 2,2′ bond is not zero. Solutions of the compounds $[M(L^4)]^{2+}$ in dmso (dimethyl sulphoxide) are 2 : 1 electrolytes.[2]

The absence of any signals attributable to either N–H or carbonyl vibrations in the i.r. spectra of compounds with L^6 indicates that condensations have occurred, but does not distinguish between ring closure and formation

TABLE 1

Analytical and electrical conductance data for complexes of L^4 and L^6

Compound	Analysis (%) Found C	Found H	Found N	Calc. C	Calc. H	Calc. N	Λ [a] S cm^2 mol^{-1}
$[Zn(L^4)(NCS)_2]$ [b]	39.6	4.1	26.7	39.5	3.8	26.3	63
$[Cd(L^4)(NCS)_2]$ [c]	35.7	3.5	23.6	35.6	3.4	23.7	60
$[Zn(L^6)(NCS)_2]\cdot H_2O$ [d]	48.1	3.7	22.5	48.4	4.1	22.1	60
$[Cd(L^6)Cl][BF_4]$	41.4	3.8	15.8	41.6	3.5	16.2	27
$Hg_2(L^6)Cl_4\cdot 4H_2O$	25.3	2.5	10.0	25.6	3.0	9.9	25

[a] Measured at room temperature on 10^{-3} mol dm^{-3} solutions in dmso. [b] $\nu(C{\equiv}N)$ of 2 084 and 2 098 cm^{-1}. [c] $\nu(C{\equiv}N)$ of 2 071 and 2 096 cm^{-1}. [d] The $\nu(C{\equiv}N)$ region consists of a broad band at 2 044 cm^{-1}.

of long polymeric chains. Proof of cyclisation comes from (i) the combination of analytical, infrared, and electrical conductance data as described in an earlier paper,[2] and (ii) the similarity of the i.r. spectra to those of complexes containing L^2 where crystallography has demonstrated that monomeric ring systems are present.[1,8] The macrocyclic cavity of L^5 is large enough to encompass the seven-co-ordinate metal ion in $[Zn(L^5)(OH_2)_2][NO_3]_2$,[5] and it is likely that the zinc(II) in $[Zn(L^6)(NCS)_2]$ is also seated in the plane of the equatorial donors. In contrast, chemical evidence indicates that the Cd^{II} ion is six-co-ordinate in $[Cd(L^6)Cl][BF_4]$. Both the retention of one chloride ion per molecule, and the conductivity, which corresponds to a 1 : 1 electrolyte in dmso, provide evidence for some differentiation between the two axial sites. This is best accounted for by the cadmium(II) being out of the macrocyclic plane, with the six donor atoms at the vertices of a pentagonal pyramid. Thus the cavity in L^6 is of sufficient size to girdle Zn^{II} but the larger Cd^{II} ion [9] has to sit above the quinquedentate ligand. As with L^2, the size of the macrocyclic hole in L^6 controls the co-ordination environment of different size cations.[2,8] Consideration of the zinc(II) complexes with these two ligands shows up a difference between them; in $[Zn(L^6)(NCS)_2]$ the donor atoms are at the vertices of a pentagonal bipyramid about the seven-co-ordinate metal ion, while the geometry of $[Zn(L^2)Cl][BF_4]$ is a pentagonal pyramid and the zinc(II) is out of the macrocyclic plane. The flexibility of the 2,2′-bipyridyl (bipy) unit relative to 1,10-phenanthroline (phen) results in L^5 and, by analogy, L^6 having slightly larger cavities than L^2.* This small difference has a marked effect on the co-ordination of the metal ions. High-spin Fe^{II}, which is smaller than Zn^{II},[9b] is the only metal ion that has so far been found to sit at the centre of L^2, in $[Fe(L^2)(OH_2)_2][BF_4]_2$.[1]

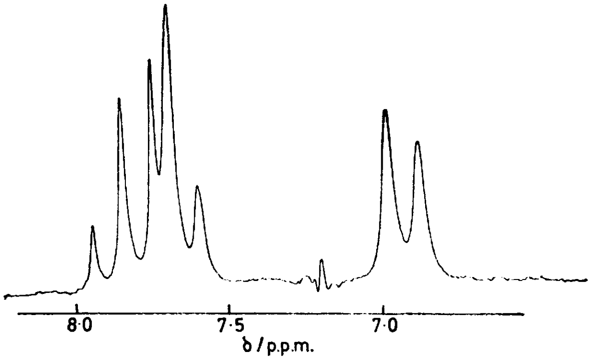


FIGURE 1 The aromatic region of the ^1H n.m.r. spectrum of $[Cd(L^4)(NCS)_2]$

Hydrogen-1 N.M.R. Spectra of the Complexes.—The hydrogen atoms of the bipy residues in L^4 and L^6 form ABC spin systems.[10] Three multiplets, two of which are superimposed, are present in the aromatic regions of the spectra [see Figures 1 and 2(*c*)] and each has an integrated intensity of two atoms; the pyridyl segments are equivalent. Spectral parameters were obtained by fitting calculated spectra to the observed signals with the iterative least-squares program NUMARIT.[11] The pyridine hydrogens in L^6 form an AB_2 spin system and signals from these atoms were analysed by published procedures.[10] Figure 2, part of the spectrum of $[Zn(L^6)(NCS)_2]$, illustrates the superpositioning of signals from the ABC and AB_2 spin systems, and also indicates how the spectrum was analysed; the spin systems were treated separately. Chemical shifts and coupling constants for the spectra are contained in Table 2 and the numbering scheme adopted is given in the accompanying diagram. The relative positions of H^3 and H^5 were assigned by reference to their positions in the spectrum of bipy.[12] In all the spectra $J(H^3H^5)$ was found to be very small, and treating it as zero made little difference to the chemical shifts and other coupling constants obtained.

Consideration of the chemical shifts for L^4 and for the complexes of this open-chain ligand demonstrates that only slight variations occur on complex formation. However, marked differences are apparent when spectral parameters of the linear and cyclic complexes are compared. The coupling constants $J(H^3H^4)$ and $J(H^4H^5)$ decrease on passing to the macrocycle. A downfield movement of 0.5 p.p.m. for the chemical shift of the N-methyl groups between compounds with L^4 and L^6 is similar to the difference measured between analogous

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* The comparison is made from in-plane values of M–N(py) (py = pyridine) and M–N(phen/bipy) for the complexes $[Mn(L^2)Cl][BF_4]$ and $[Zn(L^5)(OH_2)_2][NO_3]_2$. The figures are 2.10 and 2.12 Å respectively in the former compound and 2.29(1) and 2.06(1) Å in the latter. Considering the N(py)–N(phen) and N(py)–N(bipy) separations gives a measure of the relative sizes of the two cavities: the respective values of 4.0 and 4.1 Å show that L^2 has the smaller hole.

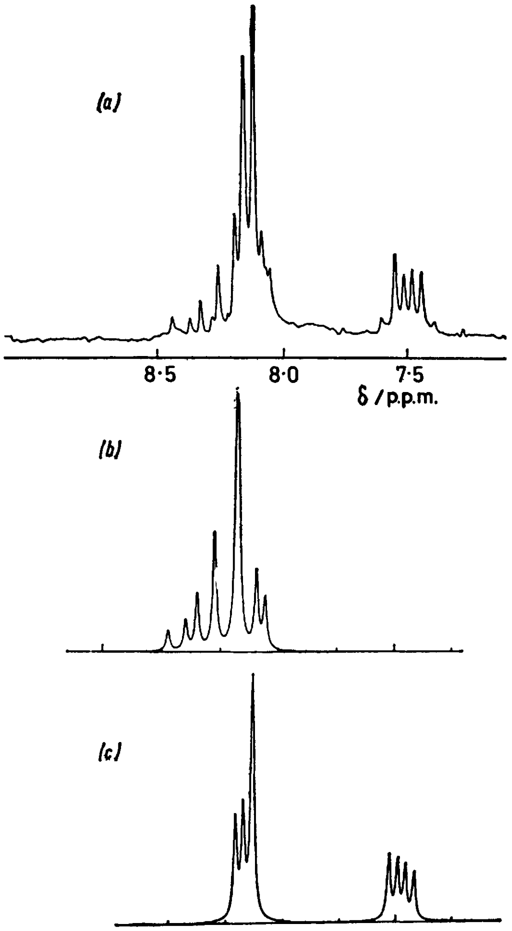


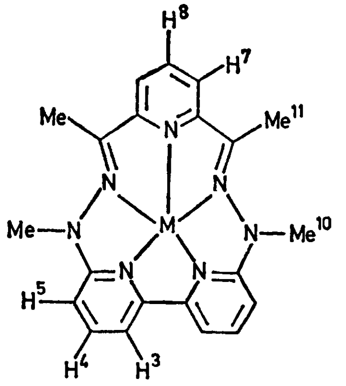
FIGURE 2 The aromatic region of the ^1H n.m.r. spectrum of $[Zn(L^6)(NCS)_2]$: (*a*) observed spectrum, (*b*) calculated AB_2 contribution, (*c*) calculated ABC contribution

groups in complexes of L^1 and L^2. For this latter pair the greater π delocalisation, and hence larger ring currents, available in the cyclic ligand is an explanation for the downfield shifts of the phen hydrogen signals on ring closure. The relative movements of the hydrogen resonances in the complexes with L^4 and L^6 are less uniform. The H^3/H^5 signals move downfield by 0.5 and 1.1 p.p.m., while the H^4 multiplet is displaced upfield by 0.4 p.p.m. This movement of signals in opposite directions accounts for the different appearances of the ABC spectra [Figures 1 and 2(*c*)]. The order of chemical shifts in the former figure is $H^5 < H^3 < H^4$ and in the latter $H^4 < H^3 \simeq H^5$.

These unusual changes are difficult to account for in terms of the simple ring current arguments used with the phen based compounds. The flexibility of the bipy unit, where rotation about the 2,2′ bond is possible, introduces a parameter (the dihedral angle ϕ between the pyridyl rings) that is absent in L^1 and L^2. This dihedral angle varies between complexes of L^4 and L^6 as the co-ordination geometries adopted by the ligands differ. Rigidity present in the macrocycle restricts the donor atoms in L^6 to equatorial co-ordination sites, but L^4 is known to adopt either a *cis*-α or *cis*-β configuration where at least one nitrogen donor occupies an axial site. Ring closure should decrease the dihedral angle. The influence of ϕ on hydrogen-atom chemical shifts in bipy has been investigated,[12] and movements of signals in opposite directions on altering this parameter were both predicted and encountered. However, the changes were smaller than those observed here, particularly for H^4 and H^5. It is possible that the shifts evident in the data in Table 2 are the result of a combination of alterations in the π conjugation and the dihedral angle.

TABLE 2

Chemical shifts [a] and coupling constants [b] for ^1H n.m.r. spectra of L^4, and of complexes of L^4 and L^6



Compound	H^3	H^4	H^5	H^7	H^8	H^{10}	H^{11}	$J(H^4H^5)$	$J(H^3H^4)$	$J(H^7H^8)$
L^4 [c]	7.67	8.08	7.21			3.51		8.0	7.0	
$[Zn(L^4)(NCS)_2]$	7.66	7.90	7.04			3.33		8.2	7.5	
$[Cd(L^4)(NCS)_2]$	7.65	7.82	6.95			3.32		8.6	7.5	
$[Zn(L^6)(NCS)_2]\cdot H_2O$	8.15	7.48	8.17	8.13	8.35	3.81	2.75	5.9	3.1	8.0
$[Cd(L^6)Cl][BF_4]$	8.08	7.46	8.11	8.27	8.43	3.80	2.75	6.8	2.3	7.9
$Hg_2(L^6)Cl_4\cdot 4H_2O$	8.15	7.57	8.16	8.33	8.43	3.84	2.76	5.4	3.6	7.0

[a] Values are in p.p.m. relative to $SiMe_4$. [b] Values are in Hz. [c] Run with D_2O + 1 drop of CD_3COOD as the solvent.

EXPERIMENTAL

Infrared spectra were measured as Nujol mulls supported between sodium chloride discs using Perkin-Elmer 257 and 457 spectrometers, over the range 625—4 000 cm^{-1}. Conductance measurements were made with a Wayne–Kerr universal bridge. The ^{1}H n.m.r. spectra were run at 80 MHz on a Varian CFT-20 spectrometer, with [^{2}H$_6$]dmso as the solvent. Microanalyses were performed by the Cambridge University Chemical Laboratory Microanalytical Department.

Reagents, of analytical grade where possible, were used without further purification. The compound 6,6′-di-(1-methylhydrazino)-2,2′-bipyridyl, L^4, was prepared by a published procedure.[4]

Complexes of L^4.—An appropriate salt (0.2 mmol) and 0.2 mmol of L^4 were dissolved in hot methanol (30 cm^3) and the mixture warmed for 10 min. An aqueous solution containing excess of [NH$_4$][NCS] was then added dropwise. After cooling, the precipitate was filtered off, washed with methanol and water, and dried in air. Yields were quantitative.

Complexes of L^6.—The example given here is the synthesis of [Cd(L^6)Cl][BF$_4$]. Cadmium acetate (0.3 mmol) and L^4 (0.3 mmol) were dissolved in aqueous methanol (50 cm^3) and the solution refluxed for 10 min before 2,6-diacetylpyridine (0.3 mmol) was added, followed by 2 cm^3 of 40% aqueous HBF$_4$. Heating was continued for 3 h before the solution was allowed to cool. Dropwise addition of an aqueous solution containing excess of NaCl gave a bright yellow precipitate. The solid was filtered off, washed with water, methanol, and ether, and dried in air. Yield: 65%.

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REFERENCES

[1] Part 8, M. M. Bishop, J. Lewis, T. D. O'Donoghue, P. R. Raithby, and J. N. Ramsden, *J.C.S. Dalton*, 1980, 1390.

[2] Part 6, J. Lewis and T. D. O'Donoghue, *J.C.S. Dalton*, 1980, 743.

[3] J. Lewis and K. P. Wainwright, *J.C.S. Dalton*, 1977, 734.

[4] J. Lewis and K. P. Wainwright, *J.C.S. Dalton*, 1978, 440.

[5] Z. P. Haque, D. C. Liles, M. McPartlin, and P. A. Tasker, *Inorg. Chim. Acta*, 1977, **23**, L21.

[6] K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds,' 2nd edn., Interscience, New York, 1970.

[7] J. Lewis and K. P. Wainwright, *J.C.S. Dalton*, 1977, 739.

[8] M. M. Bishop, J. Lewis, T. D. O'Donoghue, and P. R. Raithby, *J.C.S. Chem. Comm.*, 1978, 476.

[9] (*a*) M. B. Hursthouse, 'Molecular Structure by Diffraction Methods,' *Specialist Periodical Reports*, The Chemical Society, London, 1976, vol. 4, and refs. therein; (*b*) G. J. Palenik and D. W. Wester, *Inorg. Chem.*, 1978, **17**, 864.

[10] J. A. Pople, W. G. Schneider, and H. J. Bernstein, 'High Resolution Nuclear Magnetic Resonance,' McGraw-Hill, New York, 1959.

[11] J. S. Martin, R. A. Quirt, and K. M. Worvill, 'NUMARIT. High Resolution Spectral Analysis,' Science Research Council, Bulletin no. 9, Daresbury, 1975.

[12] S. Castellano, H. Gunther, and S. Ebersole, *J. Phys. Chem.*, 1965, **69**, 4166.