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New Planar Quinquedentate Macrocycles which contain Pyridine Donor Atoms. The X-ray Structure Determination of {8,15-Dihydro-2,6-dimethyltripyrido[*c,d:i,j:l,m*][1,4,7,8,10,13,15]-heptaazapentadecin-N^1, N^{2b}, N^7, N^{8b}, N^{12}}diaquozinc(II) Dinitrate

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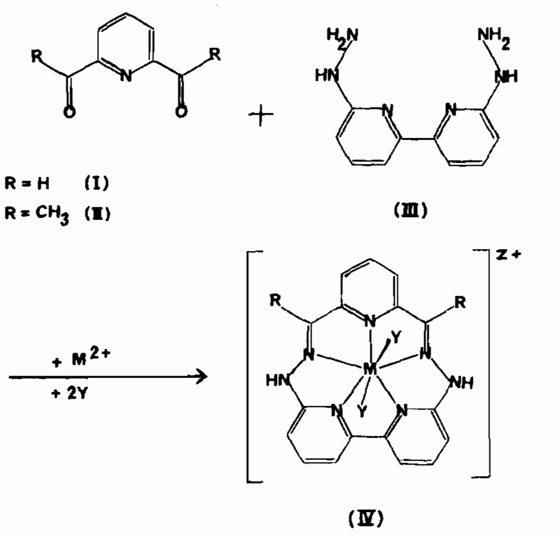
It has been demonstrated recently [1, 2] that metal complexes of quinquedentate macrocyclic ligands can be isolated from Schiff Base condensations of 2,6-diformylpyridine (I) and 2,6-diacetylpyridine (II) which are carried out in the presence of certain metal ions. Such complexes have approximately pentagonal-bipyramidal coordination geometries, with equatorial donors provided by the quinquedentate ligand and with two monodentate ligands defining the axial sites. In an attempt to prepare complexes with more regular coordination polyhedra, synthetic routes have been successfully modified as shown in the reaction scheme to incorporate more donor atoms into fused rings, and thus provide a more rigid and more planar equatorial 'N_5' donor set.



In the presence of zinc(II) salts of weakly coordinating anions (*e.g.* NO_3^-) the reactions of the dihydrazine (III) resulted in cationic zinc(II) complexes with water molecules occupying axial coordination positions. {8,15-Dihydro-2,6-dimethyl-tripyrido-[*c,d:i,j:l,m*][1,4,7,8,10,13,15]-heptaazapentadecin-N^1,N^{2b},N^7,N^{8b},N^{12b}}diaquozinc(II) dinitrate (IV, M = Zn, R = CH_3, Y = H_2O, z = 2 as nitrate salt) separated from ethanol as pale yellow plates, $[ZnC_{19}H_{17}N_7(H_2O)_2](NO_3)_2$, M = 568.37, monoclinic, space group Pn, a = 14.132(4), b = 9.226(4), c = 8.739(2) Å, β = 94.50(1)°, U = 1139.41 $Å^3$, D_m = 1.62, D_c = 1.65 g cm^{-3}, Z = 2. The crystals diffracted only weakly and the X-ray structure determination was undertaken using 1403 data with $I \geqslant 2\sigma(I)$ obtained on a Philips PW1100 4-circle diffractometer equipped with graphite monochromatised MoK_α radiation (λ = 0.71069 Å). Refinement [3] of positional and temperature parameters (Zn anisotropic) for all non-hydrogen atoms was performed using full-matrix least-squares procedures and has converged at a conventional R factor of 0.097.

The complex cation (Figure 1) has a pentagonal-bipyramidal coordination geometry with water molecules (O(1) and O(2)) occupying axial coordination positions. The equatorial 'N_5' donor set of the macrocycle is very nearly planar, with no nitrogen deviating by more than 0.01 Å from the 'ZnN_5' best (least-squares) plane.

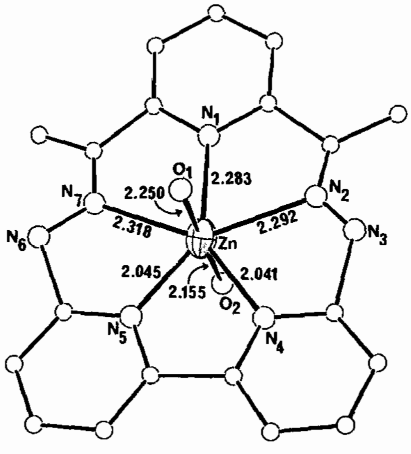


Fig. 1. The macrocyclic dication, showing bond lengths in the coordination sphere. Estimated standard deviations on the bondlengths shown vary from 0.004 to 0.006 Å.

Whilst the rigidity of the macrocycle has resulted in a more planar arrangement of the donor atoms than in any previous examples of macrocyclic quinquedentate ligands, it also prevents the movement of N atoms relative to the Zn atom to allow Zn–N bonds to be of equal length. Thus the

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[a] Some results of this study were presented at the 7th Coordination and Metal-Organic Chemistry Conference, La Trobe University, Australia, February, 1977.

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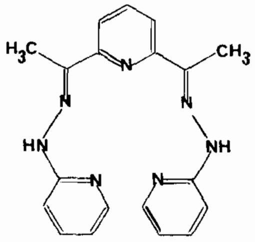
chemically equivalent bonds Zn–N(4) and Zn–N(5) are equal in length within experimental error, but are much shorter than the bonds to the imine nitrogen atoms N(2) and N(7). These effects of "hole size" and ligand rigidity on fixing Zn–N bond lengths are particularly striking when compared with the lengths observed in a diaquozinc(II) complex with the closely related linear quinquedentate ligand (V) which is not macrocyclic. In this complex the coordinate bonds to the nitrogen atoms equivalent to N(1), N(2), N(4), N(5) and N(7) are much more equal in length, being 2.251(4), 2.314(4), 2.305(4), 2.288(4) and 2.286(4) Å respectively [4].



(V)

When the reactions of III (see scheme) are carried out in the presence of coordinating anions (*e.g.* Y = NCS^-) they result in neutral zinc(II) complexes which have very low solubilities and cannot be satisfactorily recrystallized. The formulation of such products as complexes of the macrocyclic ligands is based upon elemental analyses and infrared data and the fact that they can be prepared from ethanol solutions of the nitrate salts of the diaquodications (*vide supra*) on addition of lithium salts of the appropriate anion.

These results and other work which is in progress on similar complexes demonstrate that III is a useful precursor in macrocyclic syntheses, and extend its application from quadridentate systems which have been reported [5] previously.

Acknowledgments

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References

1 N. W. Alcock, D. C. Liles, M. McPartlin and P. A. Tasker, *Chem. Comm.*, 727 (1974).
2 M. G. B. Drew, A. H. Othman, P. D. A. McIlroy and S. M. Nelson, *J. Chem. Soc. Dalton*, 2507 (1975); M. G. B. Drew, J. Grimshaw, P. D. A. McIlroy and S. M. Nelson, *ibid.*, 1389 (1976) and M. G. B. Drew, A. H. Othman and S. M. Nelson, *ibid.*, 1394 (1976).
3 "SHELX-76", G. M. Sheldrick, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW, U.K.
4 D. Wester and G. J. Palenik, *Inorg. Chem., 15,* 755 (1976).
5 J. Lewis and K. P. Wainwright, *Chem. Comm.*, 169 (1974).