

Some Metal Complexes of Macrocyclic Ligands Incorporating the 1,10-Phenanthroline Group. X-Ray Crystal Structure of the Manganese(II) Complex

By M. M. BISHOP, JACK LEWIS, TIMOTHY D. O'DONOGHUE, and PAUL R. RAITBY
(Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW)

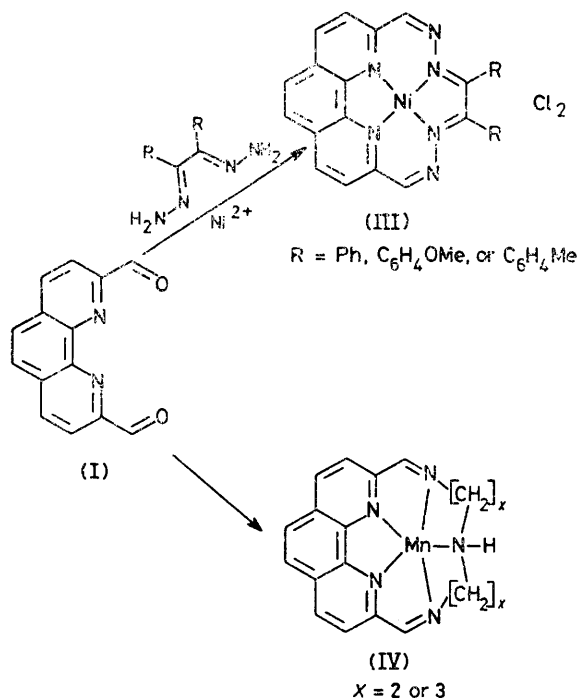
Summary The incorporation of 1,10-phenanthroline into metal macrocyclic systems is reported; the presence of π -delocalisation in these systems is considered and the X-ray structure of a six co-ordinate pentagonal pyramidal Mn^{II} complex incorporating the 1,10-phenanthroline group is consistent with this view.

1,10-PHENANTHROLINE (phen) forms complexes of great stability with transition metal ions, and has been used for many years as a co-ordinating ligand group. In particular it has been found to stabilise unusual metal ion oxidation states¹ and appears to act as a 'non-innocent' ligand, with considerable electron delocalisation between the metal ion and the nitrogen base system.² In this sense it behaves as a potential electron acceptor (*i.e.*, phen⁻¹ ion). We report the successful preparation of macrocyclic ligand complexes

involving phen as part of the ring system. The incorporation of this ligand into macrocyclic systems will lead to several potentially interesting redox situations, and oxidation states for the metal ions. In particular the possibility of complete π -electron delocalisation within the macrocycle leads to direct comparisons with metal-porphin systems and the effects of this, particularly on metal redox potentials is of obvious interest. The crystal structure of one of these new macrocycles shows that the metal ion has the unusual pentagonal pyramidal co-ordination geometry, consistent with such a π -electron delocalisation process.

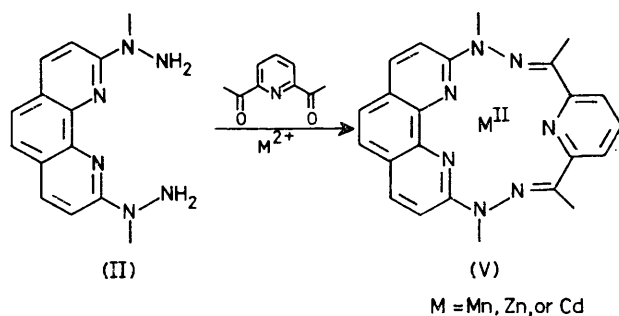
The macrocyclic ligands were prepared by reactions between 2,9-disubstituted phenanthrolines and other suitable species in the presence of a transition metal ion template. The most convenient phenanthrolines for these reactions are 1,10-phenanthroline-2,9-dicarboxaldehyde (I), prepared by the SeO_2 oxidation of neocuproine hemihydrate,

and 2,9-di(methylhydrazino)-1,10-phenanthroline (II) obtained from the reaction of the corresponding 2,9-dichloro derivative³ with methylhydrazine.



The condensations to give the macrocycle (III) occur at sites removed from the inner co-ordination sphere of the template, and the reaction therefore proceeds under mild conditions.⁴

These macrocycles are obtained in *ca.* 50% yield by combining methanolic solutions of the dialdehyde (I) with stoichiometric amounts of nickel(II) chloride hexahydrate and the dihydrazine. The reaction occurs at room temperature. Cobalt(II) and iron(II) templates also result in macrocyclic products but under similar conditions zinc(II) and manganese(II) do not.



The i.r. absorption spectra show no N-H or C=O stretching nor any NH₂ bending modes. Application of the Onsager law to the conductivities of methanol solutions

shows that the molecule is monomeric and a 1:1 electrolyte. The molecular weight in methanol confirms this.†

The dialdehyde (I) also reacts with diethylenetriamine or *NN*-(iminobispropylamine) in refluxing methanol in the presence of manganese(II) chloride tetrahydrate to give the compounds (IV) in yields of *ca.* 50 and *ca.* 10%, respectively. The physical properties of these yellow or orange crystalline solids are consistent with the Curry type⁵ of ring formation having occurred.

The macrocyclic ligand complexes (V) are prepared by the condensation of 2,6-diacetylpyridine and the dihydrazine (II) with Zn^{II} (60% yield), Cd^{II} (55%), or Mn^{II} (75%) templates. The Mn^{II} complex was precipitated as the tetrafluoroborate and the orange solid recrystallised from methanol. I.r. spectra confirm the ring closure and conductivity measurements establish that the complexes are 1:1 electrolytes in Me₂SO solution.

Crystal data: [C₂₃H₂₁ClMnN₇]⁺[BF₄]⁻, *M* 572.7; monoclinic, *a* = 11.717(8), *b* = 14.403(9), *c* = 15.316(9) Å, β = 116.42(6)°; *U* = 2314.8 Å³; *D_c* = 1.64 g cm⁻³, *Z* = 4, space group *P2₁/n*. Graphite monochromated Mo-*K_α* radiation, λ = 0.71069 Å, μ = 6.82 cm⁻¹. The structure was solved by using Patterson and Fourier methods on the 1709 unique observed intensities [*I* > 2.50 σ(*I*)], collected on a Syntex *P2₁* four-circle diffractometer (3.0 < 2θ < 55.0°). Full-matrix least-squares refinement yielded the final residuals *R* = 0.099, *R_w* [= Σ*w*²Δ/Σ*w*²|*F_o*|] = 0.069. [Mn and Cl were refined anisotropically, C, N, and B isotropically, and the H(ring), H(methyl), and F atoms were assigned common isotropic temperature factors]. The ring and methyl hydrogens were constrained to lie in geometric idealised positions (C-H, 1.08 Å), the methyl groups being treated as rigid bodies, pivoted about the carbon atoms. The BF₄⁻ anion was disordered about one of its 'three-fold axes.' It was successfully refined by employing two sets of positions for three fluorine atoms, and treating it as a rigid group. The Figure shows the molecular geometry of the cation, and includes some important bond lengths.‡

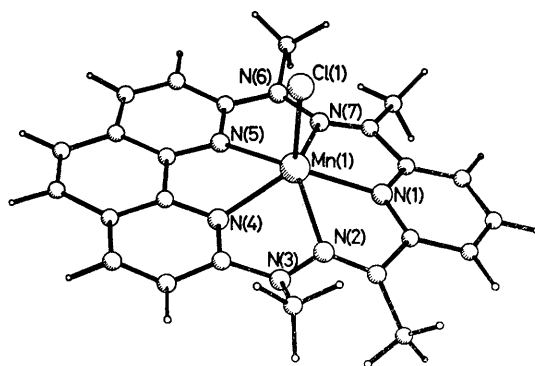


FIGURE. The molecular structure of [MnC₂₃H₂₁N₇Cl]⁺. Bond distances are: Mn(1)-Cl(1), 2.353(4); Mn(1)-N(1), 2.167(9); Mn(1)-N(2), 2.348(9); Mn(1)-N(4), 2.204(9); Mn(1)-N(5), 2.186(9); and Mn(1)-N(7), 2.312(9) Å.

† Satisfactory elemental analyses were obtained for all the compounds in this communication.

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

The X-ray structure of the Mn^{II} derivative provides an interesting stereochemical arrangement of ligand groups about the metal ion. The co-ordination polyhedron can best be described as a distorted pentagonal pyramid. The five nitrogen atoms are approximately coplanar (maximum deviation 0.09 Å) with the Mn atom 0.53 Å above this plane, while the axial position is occupied by a chlorine atom. The angles subtended by adjacent nitrogen donors at the metal ion fall in the range 67–73°; two Mn–N distances are significantly longer than the others. The phenanthroline reduces the flexibility in the ligand although it is still slightly folded. The pyridine ring makes an angle of 13.5° with the plane through the remaining four nitrogen donors, compared with *ca.* 40° in a related but less conjugated macrocycle.⁶ The N–N bond, 1.360(12) Å, is significantly shorter than the mean value of the N–N bond of 1.417 Å in a similar macrocycle in which π -delocalisation around the

ring is not possible.⁷ This indicates that such delocalisation occurs in our molecule. This structure is related to that observed⁸ for a macrocyclic system with Cd²⁺ ions, but the important difference which may be associated with delocalisation of π -electron density within the macrocycle is the planarity of the ligand reported here.⁹ The first reduction potentials of the Zn²⁺, Cd²⁺, and Mn²⁺ complexes of (V) are virtually identical which implies a partial reduction of the macrocyclic group rather than the metal centre, as anticipated from the behaviour of other phenanthroline compounds.^{1,2}

Financial support from the S.R.C. (T.D.O'D. and P.R.R.) and the British Council and the Association of Commonwealth Universities (M.M.B.) is gratefully acknowledged.

(Received, 27th October 1977; Com. 044.)

¹ W. R. McWhinnie and J. D. Miller, *Adv. Inorg. Chem. Radiochem.*, 1969, **12**, 135 and references therein.

² D. H. Busch and J. C. Bailar Jr., *J. Amer. Chem. Soc.*, 1956, **78**, 1137.

³ S. Ogawa and N. Gotoh, *Kogyo Kagaku Zasshi*, 1971, **74**, 83.

⁴ L. F. Lindoy, *Chem. Soc. Rev.*, 1975, **4**, 421.

⁵ J. D. Curry and D. H. Busch, *J. Amer. Chem. Soc.*, 1964, **86**, 592.

⁶ M. G. B. Drew, A. H. bin Othman, S. G. McFall, P. D. A. McIlroy, and S. M. Nelson, *J.C.S. Dalton*, 1977, 438.

⁷ P. A. Tasker, personal communication.

⁸ S. M. Nelson, S. G. McFall, M. G. B. Drew, A. H. bin Othman, and N. B. Mason, *J.C.S. Chem. Comm.*, 1977, 167.

⁹ Z. P. Haque, D. C. Liles, M. McPartlin, and P. A. Tasker, *Inorg. Chim. Acta*, 1977, **23**, L21.