Template Condensations: Metal Ion Directed Syntheses of Macrocyclic, Tricyclic, and Quadricyclic Metal Complexes From Butane-2,3-dione Dihydrazone and Formaldehyde

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Summary Metal complexes of the ligand, butane-2,3-dione dihydrazone, react with formaldehyde to yield simple octa-aza-macrocyclic ligand complexes, dihydro-octa-aza-annulene complexes, and clathrochelates of a quadricyclic ligand.

Metal ions are known to affect the steric course of reactions; the template synthesis of macrocyclic ligands are among the best examples.[1] Secondary amines of complexed ligands are known to react with formaldehyde to form polydentate ligands[2] or macrocyclic ligands.† We report the preparation of novel macrocyclic tricyclic and quadricyclic ligand complexes involving metal ion directed condensation of butane-2,3-dione dihydrazone with formaldehyde. The free amino-groups of the co-ordinated butane 2,3-dione dihydrazone are ideally oriented for ring closure giving six-membered chelate rings and ultimately, fourteen-membered ring octa-aza-macrocyclic ligand complexes, such as (I). However, the simple condensation product (I), still has secondary nitrogen atoms which are capable of further condensation with formaldehyde to yield either a tricyclic ligand complex (II) with two cyclic ethers fused to the macrocyclic ring or with another molecule of butane-2,3-dione dihydrazone and formaldehyde to yield the quadricyclic ligand complexes, (III) (Scheme).‡

The nickel(II) complex (I; M=Ni) has properties consistent with low-spin, square planar nickel(II): diamagnetic; n.m.r. δ 2·15 (–Me), 4·51 (–CH_2); i.r., single N–H absorption at 3240 cm^{-1}; u.v., 430 nm (2·3 × 10^3), 350 (5·6 × 10^3), 287 (1·98 × 10^3), 226 (8 × 10^3). The nickel(II) complex (II; M=Ni) is of similar appearance to that of (I) but the i.r. spectrum does not indicate the N–H group. The n.m.r. spectrum yields only a weak broad absorption at the frequency where the methyl groups were observed for (I), yet is diamagnetic in the solid state. However, the preferred chair conformation of the six-membered chelate rings may bring the oxygen atom close enough to an axial bonding site of the nickel in (I) to produce transient fluctuations between the singlet and triplet ground state, resulting in a rapid relaxation of the ligand proton nuclei. A similar tricyclic ligand complex of iron(II) can be isolated with acetonitrile in the two axial sites, $[Fe^{II}(MeCN)_2](ClO_4)_2$

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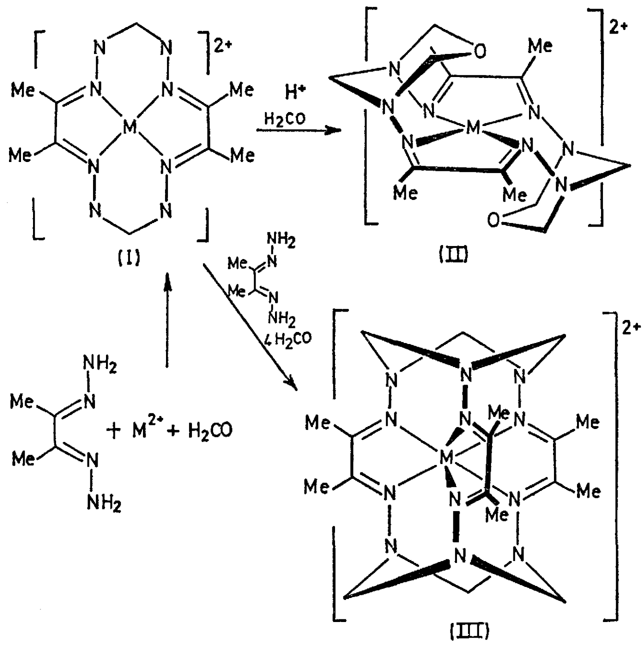
† V. Goedken, unpublished results. Ethylenediamine, formaldehyde and methylamine condense under the directing influence of nickel(II) perchlorate to give 3,10-dimethyl-1,3,5,8,10,12-hexa-azacyclotetradecane nickel(II) perchlorate.

‡ All the compounds described gave satisfactory elemental analyses.

which is low-spin and possesses the required n.m.r. spectrum; δ 2·80 (–Me) 1·98 (MeCN), 4·7—5·7 multiplet (two types of –CH_2) and appear in the ratio 12:6:12.

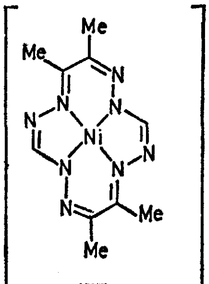


Scheme

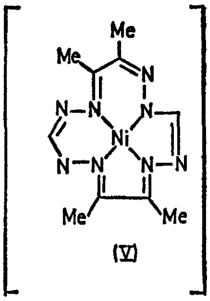
The iron(II) complex (III; M=Fe), a dodeca-aza-quadricyclic crown capped clathrochelate, is very stable in acidic solution:[3] n.m.r.; δ 2·58 (–Me); 3·71 and 5·69, J 13 Hz (–CH_2); visible and u.v.; 523 nm (1·16 × 10^4), 310 (8·4 × 10^3). The large AB splitting pattern of the –CH_2 group is produced by the locked conformation of the 1,3,5-triazacyclohexane crown and the anisotropy of the magnetic field about the low-spin d^6 electronic configuration of the iron(II).

The product obtained by reaction of the individual components of (I), (butane-2,3-dione, hydrazine, and formaldehyde) with nickel(II) perchlorate and molecular oxygen is a molecular complex of nickel(II) containing a di-anionic dihydro-octa-aza[14]annulene ligand, (IV), of C_{2h} symmetry.[4] This intensely coloured red product has the following physical characteristics: n.m.r., δ 2·16 and 2·36 (–Me), 7·09 (–CH); visible and u.v., 560 nm (4·4 × 10^3), 532 (4 × 10^3), 425 (5·7 × 10^3) 320 (1·13 × 10^4); mass spectrum: parent peak ($Ni^{58}C_{10}H_{14}N_8$) 304·0586. The i.r. spectrum does not show an N–H group or isolated imine linkages but does contain strong absorptions near 153 cm^{-1} characteristic of a highly delocalized ring system. This 16π electron system has the predominant resonance structure indicated by (IV) as confirmed by a single crystal X-ray structural determination.[5]

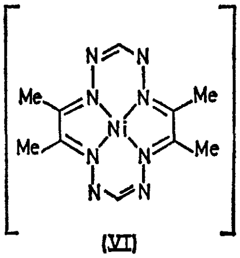
We have isolated two isomers of (IV), (V) and (VI). (VI) has been obtained by oxidation of (I) by molecular oxygen in acetonitrile solution which has been made basic with hydrazine and (V) is prepared in the same manner as (IV), with the exception that hydrazine must be the last ingredient added. The physical properties of both (V) and (VI) are similar to those of (IV); the parent peak of the mass spectrum of each have the same mass as that of (IV), the i.r. spectra and u.v. and visible spectra are also very similar. The n.m.r. spectra of each provide the clearest evidence for the structures indicated: the methyl groups of (VI) appear as a singlet at δ 2·49, whereas for (V), each methyl group is in a different chemical environment and the n.m.r. of the methyl region consists of four singlets at δ 2·54, 2·57, 2·65, and 2·83. Structure (IV) is the most stable isomer; both (V) and (VI) undergo thermal and photochemical isomerization to (IV).



(IV)



(V)



(VI)

It appears that the metal directed syntheses of ligands in structures (I), (II), and (III) is a general reaction for iron(II), cobalt(II), and nickel(II). The synthesis and study of the complete series are in progress. Zinc(II) and manganese(II) have failed to yield cyclization products under similar reaction conditions.

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[4] Similar complexes of C_{2h} symmetry have been prepared by the insertion of divalent transition metal ions into macrocyclic ligands formed by the condensation of bis-hydrazone with orthoesters; J. E. Baldwin, R. H. Holm, R. W. Harper, J. Huff, S. Koch, and T. J. Trues, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 393.

[5] V. Goedken and S. Peng, to be published.