Synthesis of a Macrocyclic Ligand Derived from 6,6′-Dihydrazino-2,2′-bipyridyl

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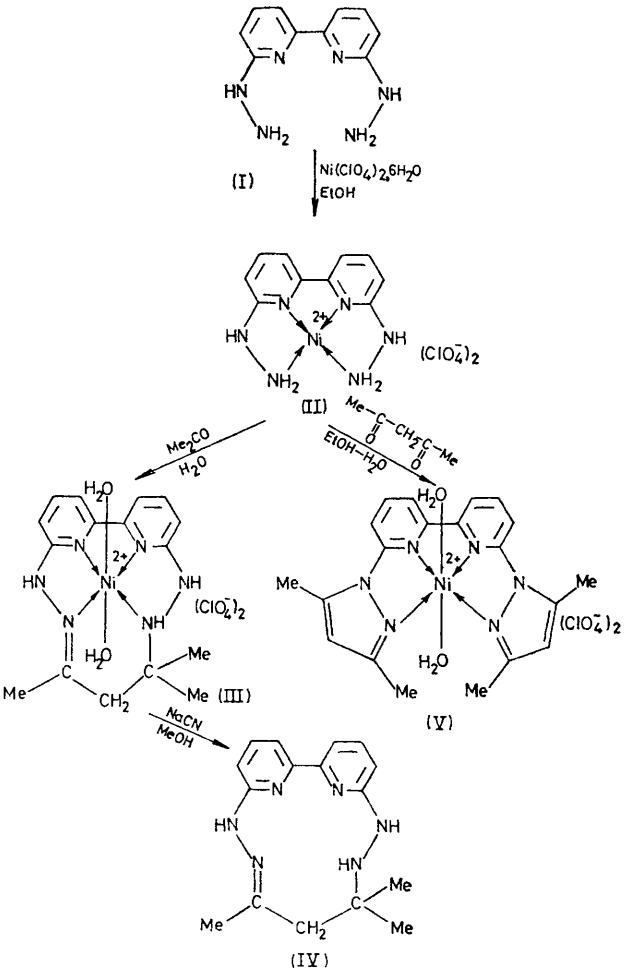
Summary A thirteen-membered macrocycle is very easily formed when nickel(II) or cobalt(II) complexes of 6,6′-dihydrazino-2,2′-bipyridyl are treated with aqueous acetone.

The tendency for α di-imine ligands to form stable complexes with transition metals in relatively low oxidation states has been well established.[1] We have used this property in synthesising a quadridentate ligand, 6,6′-dihydrazino-2,2′-bipyridyl (I), which acts as a highly reactive precursor in the formation of macrocyclic ligands. Upon complexation (I) chelates strongly through the α di-imine nitrogens of the bipyridyl residue, but because of its geometry bonds only weakly at two further coplanar co-ordination sites, leaving the co-ordinating terminal amines of the hydrazine groups in a state of unusually high lability and nucleophilicity. This is evident by inspection of molecular models of (I) where, assuming no distortion of bond angles, the minimum N–N through-space distance between the terminal amines is *ca.* 65% greater than the corresponding distance between the bipyridyl nitrogens. Ligand (I) therefore functions as a potential starting point in the synthesis of a whole family of macrocyclic ligands, containing the bipyridyl unit, which have not previously been reported. Two modes of attack have been observed corresponding to ring closure to give metal macrocyclics or ligand structural development by reaction with the hydrazine groupings. Thus reaction of the nickel(II) complex of (I) with refluxing aqueous acetone leads in a few minutes to the quantitative formation of a Curtis type macrocycle[2] under the mildest conditions yet observed. Treatment of 6,6′-dibromo-2,2′-bipyridyl[3] with hydrazine hydrate at reflux gave (I) as pale yellow needles (96%), m.p. 208°, after recrystallisation from water. Addition of hexaaquonickel(II) perchlorate to (I) in EtOH precipitated (II) as orange crystals (72%). Evidence for cyclisation of the co-ordinated ligand in (II) is given by characterisation of the displaced ligand, (IV), obtained from (III) by reaction with sodium cyanide. In the i.r. spectrum of (III) the primary amine deformation band present at 1626 cm^{-1} in (II), is absent and instead new absorption bands appear at 1611 cm^{-1} and 1372 cm^{-1} which are attributable to the C=N stretching mode and to the deformation mode of the geminal dimethyl group. Not only is the extreme ease of ring closure remarkable, but the rate enhancement which is brought about by the addition of water is significant and



contrasts strongly with the observations of Curtis.[4] Such rate enhancement by water possibly indicates the greater lability of the high spin di-aquo species derived from (II), which is known to be present in aqueous solution, from a study of the solution electronic spectrum of (II), over the more inert square planar species.

This macrocycle represents the first example of such a ligand having as part of its skeleton a bipyridyl residue. In the synthesis of the biologically interesting iron macrocycle complexes, (IV) readily combines with sources of iron(II) to form air-stable, high-spin complexes in almost quantitative yield, and without the problems of oxidation encountered by previous workers using saturated macrocycles.[5] Steric constraints preclude the possibility of (IV) forming metal complexes without the ligand assuming the square planar configuration.

Cobalt(II) forms high-spin analogues of (II) and (III), the analogue of (III) being formed either by reaction of the analogue of (II) with acetone under conditions equally as mild as those used with nickel(II), or alternatively by direct reaction of (IV) with a source of cobalt(II).

The alternative potential mode of reactivity of the complex (II) may be illustrated by reaction with β diketones which add to both hydrazine units to produce substituted pyrazole derivatives. Reaction of (II) with acetylacetone in aqueous EtOH gave (V).

Satisfactory elemental analyses have been obtained for all compounds described, together with satisfactory ^{1}H n.m.r., i.r. and m.s. data, where possible.

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