Template Synthesis of Metal Complexes of Corrin Analogues

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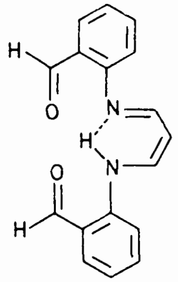
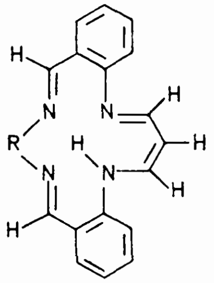
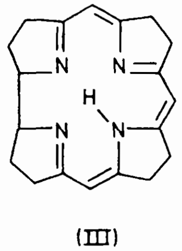
Summary Nickel(II), copper(II), and cobalt(III) complexes of the corrin analogue 3,12-dihydro-1,4,8,12-tetra-aza-2(*H*)-dibenzo[*f*,*m*]cyclopentadecine (IIa) have been prepared by a ready metal template process, together with similar complexes of related macrocyclic ligands.

We report the synthesis of the nickel(II) complex iodides, [Ni(ligand)]I, of the macrocyclic ligands (IIa—d) by the reaction of the dialdehyde (I) with anhydrous nickel(II) acetate in anhydrous methanol, followed by the addition of the appropriate diamine and tetraethylammonium iodide. The dialdehyde (I) can be formed by the reaction[1] of 2-aminobenzaldehyde with malondialdehyde tetramethyl acetal in aqueous acid, followed by neutralization of the resulting salt. The fifteen-membered ligands (IIa and b) and their sixteen-membered analogue (IId) possess a fused dibenzocorrin chromophore, but have none of the substituents of corrin (III). The tribenzo-ligand (IIc) is fully conjugated.

Modifications of the above synthetic procedure have led to the preparation of the copper(II) mono-perchlorate complex and bis-thiocyanatocobalt(III) complex of the ligand 'dibenzocorromin' (IIa). All the complexes have been characterised by analytical and spectral data. They are dark green solids, the nickel(II) and cobalt(III) complexes being green in solution and the copper(II) complex


(I)


(II)


(III)

a; R = $-CH_2{\cdot}CH_2-$
b; R = $-CH(Me){\cdot}CH_2-$
c; R = *o*-phenylene
d; R = $-CH_2{\cdot}CH_2{\cdot}CH_2-$

yellow. Unlike simple β-iminoamino complexes[1,2] they are relatively stable to hydrolysis. Their u.v. spectra have similarities to those of the related corrin complexes,[3] but absorb light of higher wavelength by virtue of their more extended chromophore. The nickel(II) complexes are planar and diamagnetic.

Although corrin metal complexes have been synthesised by several elegant procedures,[3,4] there is much interest in simple and readily available model compounds. Most interest has centred on the complexes of dimethylglyoxime,[5] but the ligands 1,3-bis(biacetylmonoximeimino)propane[6] and 11,13-dimethyl-1,4,7,10-tetra-azacyclotrideca-10,12-diene,[7] have also been advanced as models because of their monobasic character. However, the ligands described in this communication are more faithful structural models for corrins, as they contain only slightly modified versions of the corrin chromophore.

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