Ditopic Ligands. Synthesis and Complexation Properties of a Pyridine-containing Macrocyclic Hexa-amine, 'Pyridine[24]-N_6O_2'

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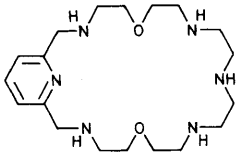
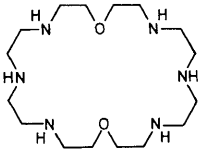
The synthesis of a 'pyridine[24]-N_6O_2' macrocycle (**1**) is described; it forms 1 : 1 complexes with zinc, cobalt, and nickel and dinuclear complexes with platinum, palladium, and rhodium.

Ditopic macrocycles which incorporate two chelating subunits facilitate the assembling of two cations held in proximity.[1—5] The binding properties of the symmetric hexa-aza-macrocycle, (**8**), incorporating two bis(diethylenetriamine) sub-units have been previously reported.[1,2,5,6] The synthesis and complexation properties of the related pyridine-containing macrocyclic hexa-amine, (**1**), is described. Since (**1**) contains two slightly dissimilar binding units, it should be able to form homo- or hetero-dinuclear macrocyclic complexes in which the ions are closely bound. The interest in such complexes lies in the unusual physical properties they may possess, in their potential chemical reactivity as dinuclear catalysts,[4,5] and in their significance as models of biological dimetallic sites.[6,7]

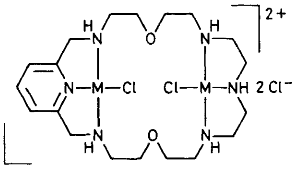
Reaction of diethylenetriamine tris(toluene-*p*-sulphonate) (**2**),[8] with 2-(2-chloroethoxy)ethanol and base (K_2CO_3) afforded the diol (**3a**) (m.p. 96—97 °C, 94%) which was treated with toluene-*p*-sulphonyl chloride in pyridine to give the di(toluene-*p*-sulphonate) (**3b**) (oil, 92%).[6] Successive treatment of (**3b**) with potassium phthalimide in dimethylformamide (DMF), hydrazine in refluxing ethanol, 3 M hydrochloric acid, and an excess of toluene-*p*-sulphonyl chloride and triethylamine in tetrahydrofuran afforded the amino(toluene-*p*-sulphonate) (**3c**) (glass, 75%). Reaction of its disodium salt (Na–MeOH), (**3d**), with 2,6-di(bromomethyl)pyridine, (**4**), in DMF at 75 ° C gave the macrocycle (**5**) as a colourless solid (m.p. 92—93 °C, 63%). Removal of the protecting tosyl groups was effected with HBr in acetic acid in the presence of



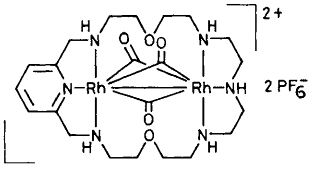
(1)



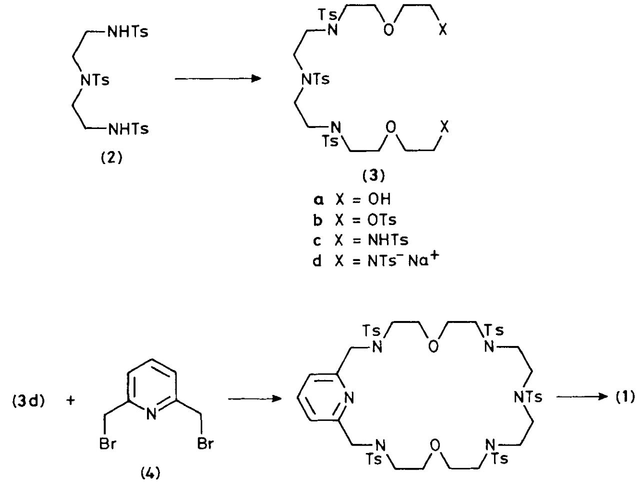
(8)



(6); a M = Pd
b M = Pt



(7)



Ts = tosyl = p-$MeC_6H_4SO_2$–

Scheme 1

phenol at 120 °C. Passage of an aqueous solution of the hydrobromide salt down an anion exchange resin gave (**1**) as a colourless oil (90%) *m/z* 381 (M^+ + 1), 380 (M^+), 293, 269, 243, 231; δ_H (DCl, D_2O) (py = pyridyl) 7.96 (1H, t, *J* 7.8 Hz), 7.49 (2H, d), 4.53 (4H, s, CH_2py), 3.96 (4H, t, *J* 5.0 Hz, CH_2O), 3.91 (4H, t, *J* 4.9 Hz, CH_2O), 3.61 (8H, s, CH_2N), 3.51 (4H, t, *J* 5.0 Hz, CH_2N), and 3.42 (4H, t, *J* 4.9 Hz, CH_2N); δ_C (DCl, D_2O) 150.5, 139.4, 123.2 (py); 65.5, 65.3 (CH_2O); 50.6 (CH_2); 47.9, 47.5 (CH_2N); and 44.2, 43.6 (CH_2N). The synthetic sequence is summarised in Scheme 1,† producing (**1**) in 37% overall yield from (**2**).

Complexation of transition metal cations within the macrocycle may be conveniently monitored by fast atom bombardment mass spectrometry (f.a.b.m.s.) and u.v.–visible spectrophotometry.[9,10] Admixture of 1:2 aqueous glycerol solutions of nickel, cobalt, and zinc perchlorates and (**1**) followed by f.a.b.m.s. analysis revealed peaks due to 1:1 complexes at *m/z* 445 [(**1**) + Zn]$^{\cdot+}$ and *m/z* 440 [(**1**) + Co]$^{\cdot+}$ and [(**1**) + Ni]$^{\cdot+}$ which were distinguished by their characteristic isotope patterns. The zinc complex was isolated from MeOH as the ligand-protonated species [(**1**)·ZnH]$^{3+}3ClO_4^-$ and the cobalt complex showed $\lambda_{max.}(H_2O)$ at 461 nm. The u.v.–visible spectrum of the nickel complex in water was

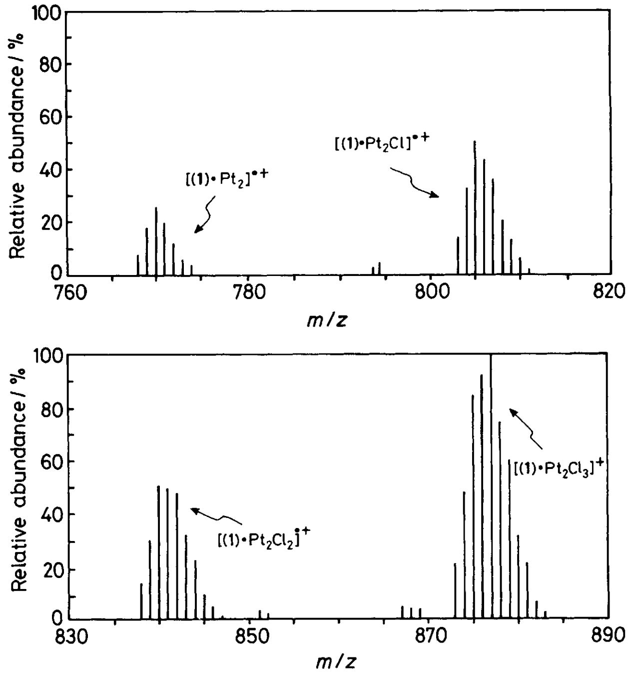


Figure 1. Fast atom bombardment mass spectrum of (**6b**) (thiodiglycol matrix, 8 keV, xenon atoms).

strikingly similar to those of the octahedral complexes, Ni(ethylenediamine)$_3^{2+}$ and Ni(diethylenetriamine)$_2^{2+}$, with weak $\lambda_{max.}$ at 330, 545, and 860 nm.[11] With cobalt and nickel the ligand presumably wraps around the cation to give an octahedral complex, as proposed for the 1:1 binding of (**8**).[2]

Reaction of (**1**) with $PtCl_2(Bu^tCN)_2$ in CH_2Cl_2 gave a pale cream solid which analysed as a diplatinum dichloride complex, (**6b**). Complex (**6b**) is soluble in water and a 1:2 electrolyte (Ω = 236 S cm^{-1}). F.a.b.m.s. analysis using a thiodiglycol matrix revealed a weak molecular ion at *m/z* 875 [(**1**)·Pt_2Cl_3]$^+$ with fragments at 840, 805, and 770 due to successive loss of chlorine (Figure 1). Similar behaviour was observed with the dipalladium complex (**6a**),[10] formed by reaction of $PdCl_2(MeCN)_2$ with (**1**) in refluxing CH_2Cl_2. Complexes (**6a**) and (**6b**) may exist in a 'chair' or 'boat' conformation in solution and ^1H n.m.r. spectroscopic analysis of (**6a**) revealed two triplets for the *para* pyridine ring proton at δ 8.11 and 8.03, in ratio 4:1, consistent with this interpretation. Treatment of (**1**) with an equimolar amount of $Rh_2Cl_2(CO)_4$ in MeOH at 0 °C gave an orange solution, with evolution of one equivalent of CO from which a pale yellow solid was isolated following addition of an excess of NH_4PF_6 in MeOH. The i.r. spectrum revealed three bands at 1804, 1812, and 1824 cm^{-1}, typical of bridging carbonyls[5] and analytical data suggest that the complex is a dirhodium tricarbonyl complex (**7**). This necessarily exists in the 'boat' form analogous to the dirhodium tricarbonyl complex of (**8**) which has been characterised by *X*-ray crystallography.[5]

In conclusion (**1**) is a versatile cation receptor capable of forming both 1:1 and 2:1 complexes, with the latter preferred for square planar d^8 ions such as Rh^I, Pt^{II}, and Pd^{II}. Further experiments are necessary to define the heterodinuclear complexation chemistry of (**1**). For example, co-complexation of copper and zinc (in which the copper may preferentially bind to the pyridine site) in the presence of bridging imidazole and azide ligands is being studied in order to model closely the dimetallic site in the enzyme superoxide dismutase.[1,7]

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† New compounds and complexes gave satisfactory analytical and spectroscopic data consistent with their structures.

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