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Metal Complexes of Schiff Base Macrocycles Having Present Pendant Arms Bearing Ligating Groups

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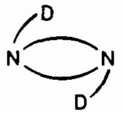
There has been considerable recent interest in the synthesis of metal complexes of macrocycles having present pendant arms bearing additional ligating groups [1]. One potential of this area is the concept that by having two such pendant arms attached at appropriate positions on the macrocyclic framework an 'opened cyptand' would result, thus leading to modified complexation properties over the corresponding clathrochelates or simple macrocyclic precursors:

(a)

(a) cryptand

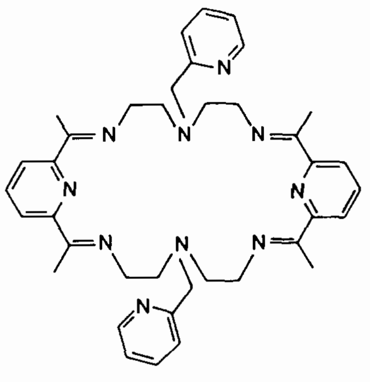


(b)

(b) 'opened' cryptand

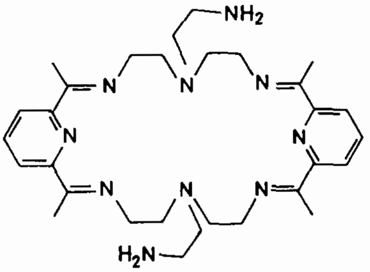
The facile synthesis of '2 + 2' Schiff base macrocycles from heterocyclic dicarbonyl derivatives and α,ω-alkanediamines through use of template techniques has given many novel metal complexes [2–4]. We have extended this technique to include functionalised diamines in order to prepare macrocycles containing pendant arms and here present a preliminary account.

The reaction of 2,6-diacetylpyridine with N-2-aminoethyl-N-2-pyridylmethyl-1,2-diaminoethane in the presence of barium salts leads to the formation of mononuclear barium complexes of (I). For example use of $Ba(NCS)_2$ as the templating device gives (I), $Ba(NCS)_2$, H_2O (*Anal.*, Found: C, 52.3; H, 5.0; N, 18.2%. Calcd. for $C_{40}H_{48}N_{12}OS_2Ba$, C, 52.5; H, 5.3; N, 18.3%). The m.s., determined using f.a.b. shows peaks at 838, 780 and 643 amu corresponding to $[Ba(I)NCS]^+$, $[Ba(I)]^+$ and $[(I)]^+$ respectively. The IR shows bands at 3400 cm^{-1} (broad, H_2O); 1620 cm^{-1} ($\nu_{C=N}$) and 2050 cm^{-1} (ν_{NCS}) – no bands are detected for free carbonyl or free amine functions.



I

Complexes of macrocycle (II) derived from the reaction of 2,6-diacetylpyridine with N,N-bis(2-aminoethyl)-1,2-ethanediamine in the presence of barium salts were similarly obtained. Using $Ba(ClO_4)_2$ as the templating device (II), $Ba(ClO_4)_2$, H_2O is recovered (*Anal.*, Found: C, 39.9; H, 5.2; N, 15.3; Cl, 8.0%. Calcd. for $C_{30}H_{48}N_{10}Cl_2O_9Ba$, C, 40.0; H, 5.3; N, 15.5; Cl, 7.8%). The IR spectrum shows bands at 3300 and 3280 cm^{-1} (ν_{NH_2}), 1620 cm^{-1} ($\nu_{C=N}$) and 1090 and 620 cm^{-1} (ν_{ClO_4}).



II

The ^1H NMR spectrum of (I), $Ba(NCS)_2$, H_2 recorded at 400 MHz in CD_3OD solution showed at room temperature only resolved signals attributable to the aromatic components of the macrocycle. The aliphatic signals were detected only as broad lines. At low temperature (213 °K) the spectrum was fully resolved showing seven signals for the pyridinyl protons, two methyl resonances and complex multiplets for the remaining aliphatic protons. This suggests that the barium is not centrally coordinated within the macrocycle but it has not been possible to corroborate this as we have so far been unable to grow crystals suitable for X-ray crystallographic study. The NMR observations indicated that some fluxional behaviour is present

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in the system as has been noted before for Ba^{++} complexes of tetraimine Schiff base macrocycles [5]. It is not yet possible to define precisely the nature of the fluxionality and further work is in progress.

Transmetallation reactions using copper(II) have been effected to yield homodinuclear copper(II) complexes. The reactions are best carried out with constant anion presence. **(II)**, Ba(ClO$_4$)$_2$, H$_2$O reacts with Cu(ClO$_4$)$_2$ to give **(II)**, Cu$_2$(ClO$_4$)$_4$, 4H$_2$O (*Anal.*, Found, C, 31.4; H, 4.4; N, 11.9; Cl, 11.9; Cl, 11.8%. Calcd. for $C_{30}H_{54}N_{10}Cl_4O_{20}Cu_2$, C, 31.5; H, 4.7; N, 12.2; Cl, 12.4%). If the transmetallating species have a different anion to that in the macrocyclic complex then a mixed anion species results as in the reaction of Cu(ClO$_4$)$_2$ with **(I)**, Ba(NCS)$_2$, H$_2$ where **(I)**, Cu$_2$(NCS)(ClO$_4$)$_3$, H$_2$ is the product (*Anal.*, Found, C, 40.3; H, 3.9; N, 14.1; S, 3.0%. Calcd. for $C_{39}H_{48}N_{11}Cl_3O_{13}SCu_2$, C, 40.6; H, 4.8; N, 13.3; S, 3.2%). The IR of this complex shows two bands in the C=N region, 1645 and 1620 cm^{-1} suggesting a non-symmetric copper(II) coordination. The thiocyanato C=N stretch has shifted to 2120 cm^{-1} indicating a more ionic environment than in the Ba^{++}-macrocycle and the ClO$_4^-$ bands are present at 1090 and 620 cm^{-1}, again consistent with free anions. Preliminary magnetic moment studies show no coupling between the two copper(II) atoms, indicating the absence of an exchange pathway in contrast to the behaviour found in related dicopper(II) complexes derived from non-functionalised tetraimine Schiff base macrocycles [6].

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