Inorganica Chimica Acta, 33 (1979) L149–L150
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Macrocycle Synthesis. CR-Type Complexes Displaying Pendant Ligation and N_3S Coordination

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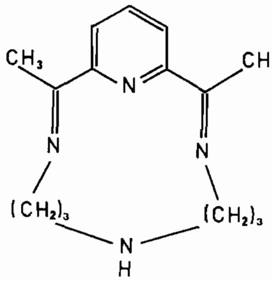
Received January 2, 1979

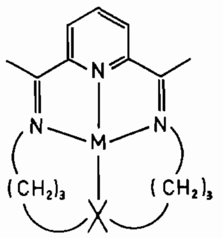
A quadridentate, macrocyclic ligand such as CR (*I*) may be modified by alterations in (i) its degree of unsaturation [1], (ii) the size of the chelate rings [2], (iii) the donor atoms (by modification [3] or replacement [4]), and (iv) by attachment of pendant coordinating groups. Such changes will be reflected in the properties of enclosed metal ions, and may be of interest in studies relating to macrocyclic coenzymes [5]. For example, square-planar ligands with an attached fifth coordinating group have been the subject of synthetic work aimed at improved analogues of the cobalamins [6].

Complexes of the CR type may be prepared by metal-template condensation of 2,6-diacetylpyridine (DAP) with the appropriate diamino ligand. Use of triamines leads to N_4-coordination of the enclosed metal ion [1, 2], while the diaminophosphine *IIa* gives an N_3P donor set [4] (*IIIa*). We have employed the 'tripod' tetramine 3,3′,3″-triaminotripropylamine (*tpt, IV*) to synthesise complexes of the quinquedentate ligand *V* [which we designate [2] 3,3(3)-CR], and the diaminosulphide *IIb* to form a complex of the N_3S macrocycle *IIIb* [CR(S)].

Tpt was prepared by a modification of the procedure of Mann and Pope [7]. 3,3′-iminobispropylamine was fused with phthallic anhydride at 180 °C giving the di-N-phthaloyl derivative, fusion of which with N-(3-bromopropyl)phthalimide at 150 °C gave 3,3′,3″-triphthalimidotripropylamine hydrobromide. Acid hydrolysis of this compound yielded *tpt*·4HCl from which the tetraperchlorate may be readily prepared [8]. The diaminosulphide (*IIb*) was made by Lehmann's method [9], involving reaction of N-(3-bromopropyl)phthalimide with sodium hydrosulphide and acid hydrolysis of the product. The nickel(II) and copper(II) complexes of 3,3(3)-CR were crystallised as diperchlorate salts from 1 m*M* solutions of DAP, metal perchlorate and *tpt*·$4HClO_4$ refluxed in aqueous ethanol for 8 hours. The Cu(II) complex of CR(S) was prepared in an analogous manner.



I



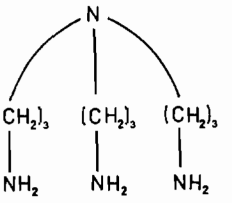
III

$H_2N—(CH_2)_3—X—(CH_2)_3—NH_2$

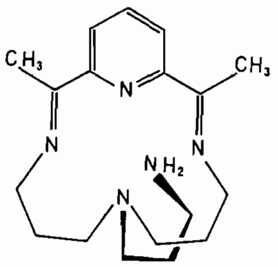
II

IIIa X = PC_6H_5
IIIb X = S

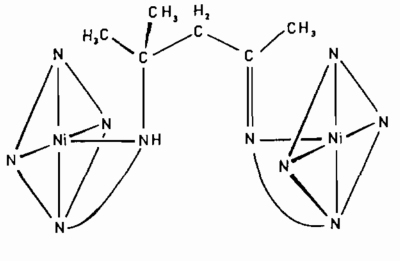
IIa X = PC_6H_5
IIb X = S



IV



V



VI

With each of the three primary amino groups of *tpt* able to form Schiff-base linkages it is surprising that the template syntheses proceeded in 65–80% yield with no indication of polymeric products. The pH of the reaction mixture was in each case adjusted to that at which, from stability constant measurements [10], the concentration of the binary complex of tetramine and metal ion was expected to be close to a maximum (Ni, 8.7; Cu, 9.0). Departure from these pH values was found to markedly decrease the efficiency of the template reaction, lending support to the idea that the integrity of the ternary complex of metal ion, polyamine and DAP is crucial to the success of such condensations [2, 11].

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TABLE I. Infra-Red Spectra.

Compound	$\nu_{N-H/O-H}$ (cm^{-1})	$\nu_{C=N}$ (cm^{-1})
Ni·3,3(3)-CR·2ClO$_4$[a]	3311 3271	1665 1624
Cu·3,3(3)-CR·2ClO$_4$·H$_2$O	3320 3260	1625
Cu·CR(S)·2ClO$_4$·2H$_2$O	3360 (b)	1609

[a] The PF$_6^-$ and B(C$_6$H$_5$)$_4^-$ salts exhibit similar spectral features.

TABLE II. Magnetic and Reflectance Data.

Compound	Magnetic Moment (B.M.)	Reflectance Maxima (kK)
Ni·3,3(3)-CR·2ClO$_4$	3.15	25 19 13 9.2
Cu·3,3(3)-CR·2ClO$_4$·H$_2$O	1.95	16.1
Cu·CR(S)·2ClO$_4$·2H$_2$O	1.90	17

Spectral and magnetic data for the complexes are presented in the Tables. The presence of $\nu_{C=N}$ bands (in addition to the pyridine $\nu_{C=N}$ at 1590 cm^{-1}) in the correct positions for Schiff-base linkages of this kind [2], and the absence of strong $\nu_{C=O}$ absorptions around 1700 cm^{-1}, indicate that the required macrocycles have indeed formed. Observation of a pair of sharp ν_{N-H} bands is as expected for a single primary amino group [12], and reaction of acetone with [Ni.3,3(3)-CR]$^{2+}$ gives an apparently dimeric complex (*VI*) [ν_{N-H}, 3290 cm^{-1}; $\nu_{C=N}$, 1675 (strong), 1635 cm^{-1}] in a process that is well-documented for such a function [13]. The magnetic moments of the Cu(II) complexes show them to be magnetically dilute, and the position of the reflectance maximum for [Cu.3,3(3)-CR]$^{2+}$ suggests a square-pyramidal coordination geometry [14]. The Ni(II) complex is high-spin, and the reflectance spectrum again indicates a square-pyramidal stereochemistry. The 13 kK band would imply a ligand field weaker than anticipated for these donors in an octahedral or tetragonal structure, and the 9.2 kK band would suggest a stronger ligand field than expected in the unlikely trigonal bipyramidal stereochemistry [15].

Titration of 5 m*M* aqueous solutions of the 3,3(3)-CR compounds (25.0 °C, 0.5 *M* NaNO$_3$) showed a principal transition corresponding to approximately one titrateable group per mol; pK's were 6.25 and 8.87 for the Ni(II) and Cu(II) complexes respectively. We assign this transition to protonation of the coordinated primary amino group of these compounds, and have isolated the protonated complex Ni·3,3(3)-HCR·3ClO$_4$·H$_2$O from the titration solution at low pH. A pK of 6.3 has recently been reported for a tertiary amino group in a similar situation of pendant coordination to Ni(II) [3a]. In the present case minor transitions were also observed; these we ascribe to deprotonation with pK 8.05 of one water molecule per two molecules of the Ni(II) complex and, with pK 6.5, one water per four molecules of the Cu(II) complex. Coordination to two metal centres may be expected to significantly lower the high pK previously observed for water in monomeric Ni(II) and Cu(II) complexes of CR [16].

Preliminary results indicate that both Co(II) and Zn(II) can be successfully inserted into the 3,3(3)-CR macrocycle by template syntheses. It is of interest that in these cases *tpt*·4HCl gives much better results than *tpt*·4HClO$_4$, an effect that may again be related to the structure of the ternary intermediate [11]. The synthesis of *tpt* outlined above is capable of producing other ligands from which various pendant groups, incorporating several chelate ring sizes, may be introduced into the CR macrocycle.

Acknowledgments

We gratefully acknowledge valuable discussions of the titration results with Dr. M. T. Wilson and the careful work of Miss. J. A. Armstead on the diaminosulphide synthesis [17].

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8 Satisfactory analyses (C, H, N, S) and, wherever possible, m.p.s and ^{1}H-n.m.r. spectra were obtained for all compounds described herein. *Organic perchlorates can be dangerously explosive and should be handled with due care.*
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