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Metal Complexes from Polyoxa-polyaza-macrocycles

By Francesco De Sarlo,* Antonio Guarna, and Gian Paolo Speroni†

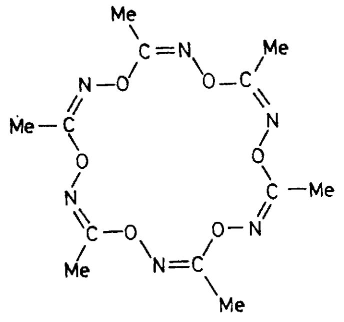
(*C.N.R., Centro di studio sulla chimica e la struttura dei composti eterociclici e loro applicazioni, Istituto di Chimica organica, and †Istituto di Chimica generale ed inorganica, Università di Firenze, Firenze, Italy*)

Summary Evidence for the existence of complexes of alkali metals and barium with heteromacrocyclic oligomers of acetonitrile oxide is presented; complexes of the hexamer (**1**) and the heptamer with potassium have been isolated.

CYCLIC polyethers have been reported as reagents for the synthesis of metal complexes, particularly suitable for alkaline cations.[1] The structural analogy of polyethers with some new heteromacrocycles, recently prepared by nucleophilic polymerisation of acetonitrile oxide,[2] suggested an investigation on the capability of these compounds to trap metal ions.

The hexamer (**1**), the heptamer, and the octamer of acetonitrile oxide, all having analogous structures, were treated in chloroform with solid picrates of several cations (Na^+, K^+, Rb^+, Cs^+, NH_4^+, Ba^{2+}, Co^{2+}, and Ni^{2+}).[3] In all experiments the picrate ion coloured the solution, thus indicating that some co-ordination had occurred (in each case, a blank check was negative).‡ Some of these solutions were examined by atomic absorption spectrometry, in comparison with blank studies; significant amounts of metal were detected in solutions of the hexamer with sodium or potassium picrate and of the heptamer or the octamer with potassium picrate, whereas the amount of metal was negligible in solutions of the same ligands with cobalt or nickel picrate.

Similarly, the same polymer solutions were treated with thiocyanates [NaCNS, KCNS, NH_4CNS, and $Ba(CNS)_2$][5] and i.r. spectra were recorded; a band at 2070 cm^{-1}, indicating dissolution of salt, was observed for the hexamer only with KCNS, for the heptamer with either KCNS or NH_4CNS, and for the octamer with all the thiocyanates mentioned (this test is less sensitive than the previous one).



(1)

The complex between the hexamer (**1**) and KCNS, ratio 2:1, has been isolated by refluxing the materials (excess of the salt) in chloroform, and cooling to give needles, m.p. 242—245 °C (decomp.). [Found: C, 36·4; H, 4·7; N, 22·7; K, 4·2; CNS, 6·1%; *M*, 403 in $CHCl_3$. $(MeCNO)_{12}\cdot KCNS$ requires: C, 38·4; H, 4·6; N, 23·3; K, 5·0; CNS, 7·4%; *M*, 781·8]. The found molecular weight, about one half of the expected value, indicates that the ligand and the salt possibly give a 1:1 complex in solution which crystallizes with the ligand to give a 2:1 ratio in the solid. A 1:1 complex between the heptamer and KCNS has been prepared by slow concentration of a solution of the reagents in methanol: m.p. 198—200 °C (decomp.). [Found: C,

‡ 3,6-diaryl-1,4,2,5-dioxadiazines, dimers of aromatic nitrile oxides analogous to the above polymers (ref. 4), do not complex with the same picrates.

36·5; H, 4·3; N, 22·7; K, 6·4; CNS 10·0%; *M*, 499 in $CHCl_3$. $(MeCNO)_7 \cdot KCNS$ requires: C, 36·3; H, 4·3; N, 22·6; K, 7·9; CNS, 11·7%; *M*, 496·2]. The i.r. spectra ($CHCl_3$) of both the above complexes show, besides ν(C≡N) at 2070 cm^{-1} two equal intensity bands at 1660—1680 cm^{-1}, assigned to ν(C=N) (the 1660 cm^{-1} absorption is stronger in the pure ligand). The so-called 'insoluble polymer' of acetonitrile oxide was believed to have a linear structure of the type: · · · –C(Me)=N–O–C(Me)=N–O– · · · ;[2] however a macrocyclic structure similar to that of the hexamer (**1**), but with much higher molecular weight, cannot be excluded. This compound has been dissolved in methanol containing KCNS; a solid separates on partial concentration, m.p. 133—135 °C (decomp.) (a mixture of polymer and KCNS decomposes above 165 °C); i.r. (KBr): ν(C≡N) 2070 cm^{-1}; the absorptions of the polymer exhibit a major modification at *ca.* 1300 cm^{-1}, where the lower frequency shoulder of the strong band at 1310 cm^{-1} appears as a well defined band at 1290 cm^{-1}; n.m.r. (CD_3OD): br s at δ 2·12, close to the values reported for the other polymers.[2] The pure insoluble polymer was recovered from the complex by refluxing in water.

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