

The Synthesis of a Novel Schiff Base Bis(Crown Ether) Ligand containing Recognition Sites for Alkali and Transition Metal Guest Cations

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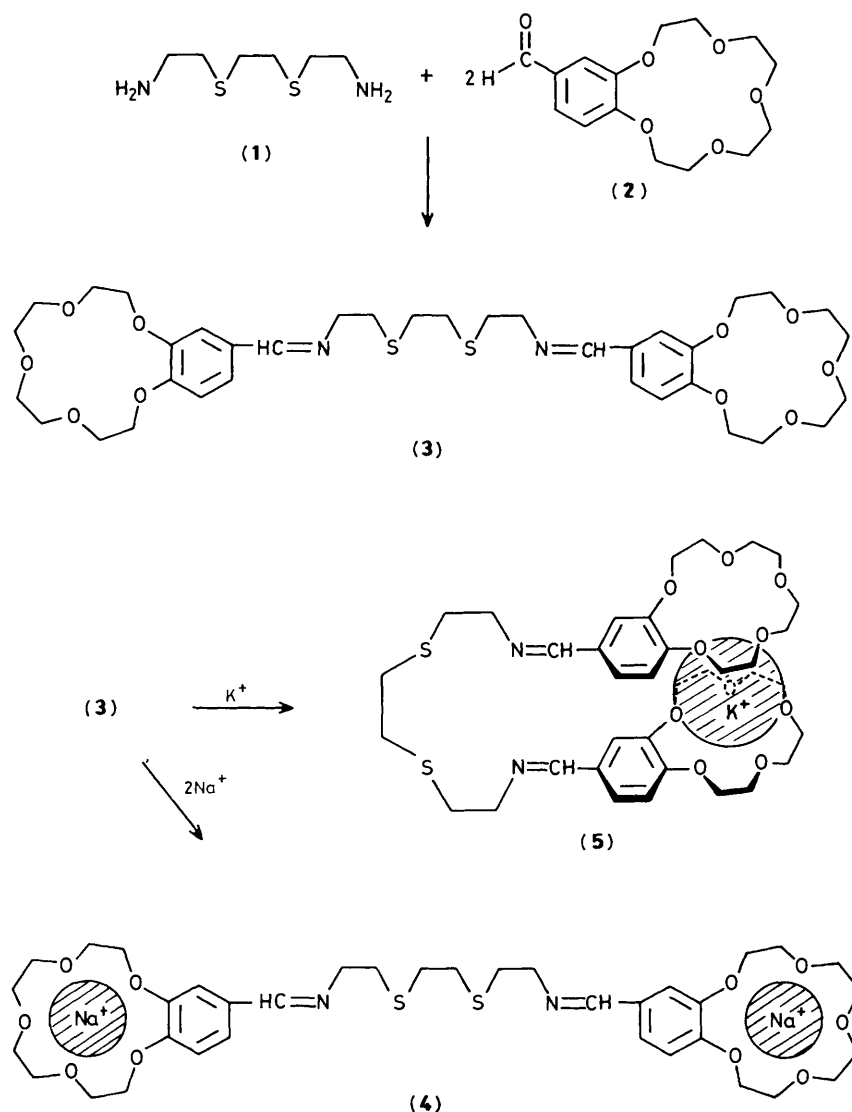
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A novel Schiff base bis(crown ether) ligand containing recognition sites for alkali and transition metal guest cations has been prepared; preliminary complexation studies reveal that the stoichiometry of Schiff base bis(crown ether) ligand to potassium guest cations is dependent upon the stereochemical requirements of co-bound silver(I) or copper(II) guest cations.

The design and synthesis of macropolycyclic molecules containing more than one recognition site for binding several guest species is of considerable current interest in the chemical literature.¹ These multisite receptors may exhibit allosteric properties² by binding sequentially two or more guest metal cations in close proximity to one another. The resulting polynuclear complexes may facilitate electron transfer studies and serve as models of relevance to biological redox processes. This communication reports the preparation of a novel Schiff base bis(crown ether) ligand (**3**) containing recognition sites for alkali and transition metal ions.

Condensation of 1,8-diamino-3,6-dithiooctane (**1**)³ with two moles of 4-formylbenzo-15-crown-5 (**2**)⁴ gave the Schiff base bis(crown ether) (**3**) in excellent yield (90%, m.p. 98–99 °C). Its structure was verified by elemental analysis, mass spectrometry, and ¹H and ¹³C n.m.r. spectroscopy.

Three recognition sites are present, the Schiff base-dithia function for binding a transition metal ion and two crown ether subunits for binding alkali metal guest ions. ¹³C N.m.r. spectroscopy was used initially to investigate the complexation of (**3**) with alkali metal cations, potassium and sodium. The stepwise addition of the respective alkali metal nitrate salt to



an acetone (75%)–chloroform (25%) solution of (3) led to considerable shifts of the OCH₂ carbons of the benzo-15-crown-5 units.

Interestingly the stoichiometry of (3) to the guest alkali metal cation was found to be 1:2 for sodium and 1:1 for potassium.† This result suggests that in the former case the two benzo-15-crown-5 units of (3) are acting independently of one another and complexing two sodium cations (4). With potassium however the two benzo-15-crown-5 units are lying cofacial to one another and are acting co-operatively to form an intramolecular sandwich complex (5).

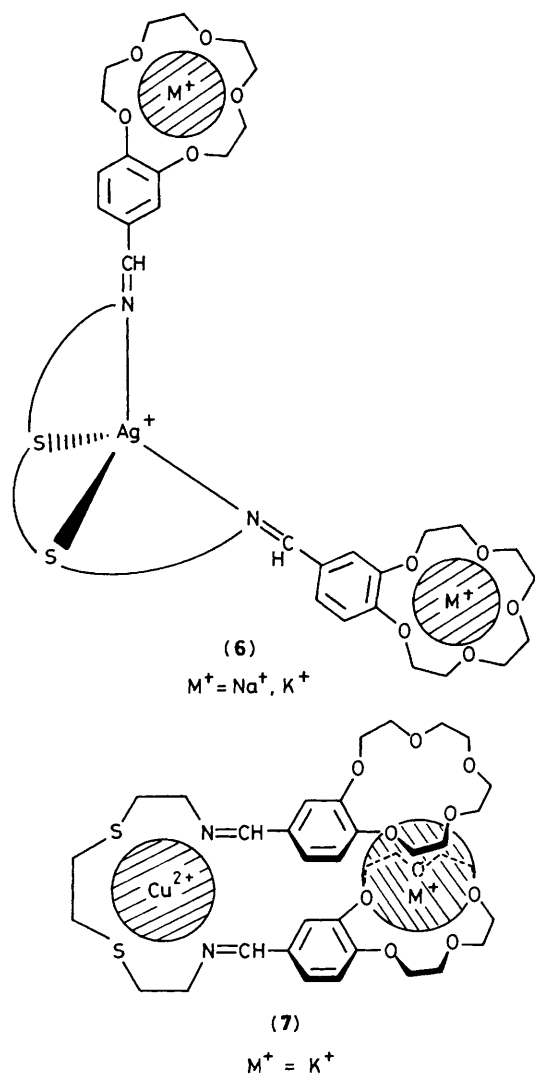
Since the binding properties of crown ethers are sensitive to changes in conformations⁶ or effective 'size' of the host cavity⁷ it was of interest to study the effect of chelation of a transition metal ion guest at the Schiff base-dithia recognition site. This was achieved by high field ¹³C n.m.r. spectroscopy using the diamagnetic silver(I) and paramagnetic copper(II) cations.

The addition of a molar equivalent of silver nitrate to (3) led to shifts of the respective NCH₂, SCH₂, and HC=N carbons by up to 2 p.p.m. Little change in the positions of the OCH₂ carbon absorptions were evident. Subsequent titration with sodium cations gave (3):2Na⁺ stoichiometry. Analogous experiments with potassium cations *also* gave the same stoichiometry of (3):2K⁺.‡

Hence in the presence of Ag⁺ the complexation of (3) with potassium is no longer of the 1:1 intramolecular sandwich complex type. It is well known that the silver(I) cation prefers linear or tetrahedral co-ordination.⁸ With (3), ¹³C n.m.r. spectroscopic evidence suggests the formation of a four-coordinate complex since large Δδ shifts of *all* the Schiff base-dithia carbon resonances were observed. Thus with tetrahedral silver(I) bound at the Schiff base-dithia recognition site, the stereochemical requirements of the transition

† Deduced from respective Δδ p.p.m. vs. [alkali metal salt]/[(3)] titration curves (ref. 5) and elemental analyses of the respective isolated complexes.

‡ Elemental analyses of the respective isolated hexafluorophosphate complexes of (3) with silver(I) and the group 1A metal cations confirm these stoichiometric findings. For example (6) M⁺ = Na⁺3PF₆⁻ requires C 32.6%, H 3.9%, N 2.4%. Found C 32.8%, H 4.2%, N 2.4%.



metal prevents the formation of an intramolecular sandwich complex with potassium and complex (6) results.

To test this rationalisation further analogous experiments with copper(II) were undertaken. With sodium cations the stoichiometry was found to be (3):2Na⁺, however with potassium, (3):1K⁺ stoichiometry was observed. § Because the copper(II) cation prefers square planar or tetragonal co-ordination⁸ the stereochemical requirements of the co-bound transition metal ion guest allows the formation of the preferred 1:1 intramolecular sandwich type complex for the potassium cation (7).

The author thanks the S.E.R.C. for use of the high field n.m.r. service at the University of Warwick and Dr. A. S. Rothin for preparing (1).

Received, 21st April 1986; Com. 529

References

- 1 B. A. Boyce, A. Carroy, J. M. Lehn, and D. Parker, *J. Chem. Soc., Chem. Commun.*, 1984, 1546; J. Rebek, Jr., J. E. Trend, R. V. Wattlely, and S. Chakravorti, *J. Am. Chem. Soc.*, 1979, **101**, 4333; J. C. Chambron and J. P. Savage, *Tetrahedron Lett.*, 1986, **27**, 865; A. D. Hamilton and P. Kazanjian, *ibid.*, 1985, **26**, 5735.
- 2 J. Rebek, Jr., *Acc. Chem. Res.*, 1984, **17**, 258; I. Tabushi, S. Kugimiya, and T. Sasaki, *J. Am. Chem. Soc.*, 1985, **107**, 5159.
- 3 F. P. J. Dwyer and F. Lions, *J. Am. Chem. Soc.*, 1950, **72**, 1545.
- 4 E. M. Hyde, B. L. Shaw, and I. Shepherd, *J. Chem. Soc., Dalton Trans.*, 1978, 1696.
- 5 E. Amble and E. Amble, *Polyhedron*, 1983, **2**, 1063.
- 6 I. Goldberg in 'Inclusion Compounds,' vol. 2, eds. J. L. Atwood, J. E. Davies, and D. D. MacNicol, Academic Press, London 1984, ch. 9, p. 261.
- 7 E. Weber and F. Vogtle, *Top. Curr. Chem.*, 1981, **98**, 1; C. J. Pedersen, *J. Am. Chem. Soc.*, 1967, **89**, 7071.
- 8 N. N. Greenwood and A. Earnshaw, 'Chemistry of the Elements,' Pergamon Press, 1984, ch. 28, p. 1364.

§ These stoichiometric results are confirmed by elemental analyses of the respective isolated hexafluorophosphate complexes.