

π -Acceptor Macrocycles: New Crown Ethers containing Isocyanide Groups

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The synthesis and preliminary complexation properties of a novel series of crown ethers containing a single aryl isocyanide unit are presented; i.r. and u.v.-visible spectra and stability constant data confirm that the isocyanide group participates in metal binding.

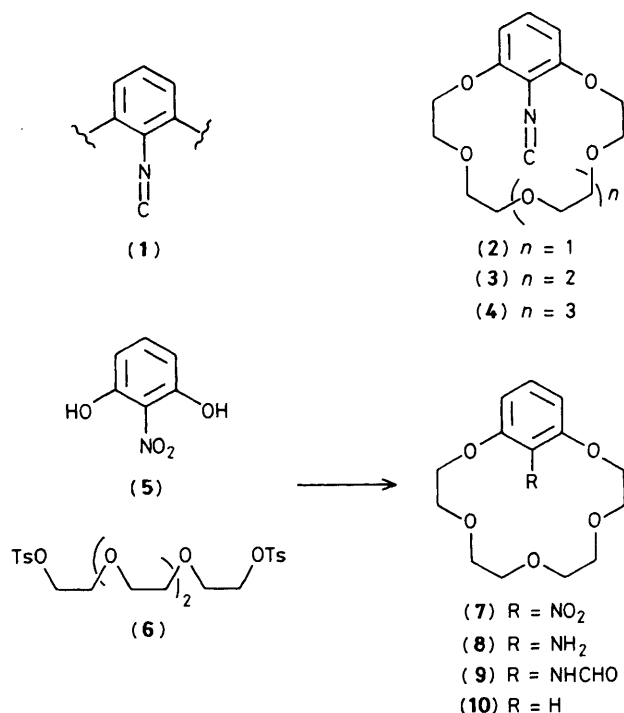
The recognition that cyclic ligands have enhanced metal binding properties compared to their open-chain analogues has generated intense interest in macropolycyclic multidentate ligands.¹ A wide variety of crown ethers, cryptands, and spherands have been prepared and their metal complexes studied.² Most of these ligands contain strongly σ -donating donor atoms (*e.g.* O, N, S) and the main interaction between metal and ligand is thought to be ion/dipole-electrostatic in nature; with the result that metals in their higher oxidation states are most strongly bound.³ In contrast there are few examples of cyclic ligands containing π -acceptor groups,⁴ which should define more electron deficient cavities, and complex metals in lower oxidation states. 2,6-Disubstituted aryl isocyanides (**1**) are attractive candidates for incorporation into cyclic ligands as they show both strong σ -donor and π -acceptor bonding to metals which can be finely tuned by varying the 4-substituent.⁵ We have initiated research aimed at the preparation of polyisocyanide macrocycles as ligands for low and zerovalent metal species. We report here the synthesis and preliminary metal complexation properties of the first members of this family; crown ethers containing a single aryl isocyanide unit (**2**)—(**4**).⁶

The cyclic isocyanides (**2**)—(**4**) were prepared in four steps. For example, the reaction of 2-nitroresorcinol (**5**) and tetraethylene glycol bis(toluene-*p*-sulphonate) (**6**) in dry dimethylformamide (DMF) with Cs_2CO_3 as base gave, after alumina chromatography and crystallization from hexane, nitro crown ether (**7**)[†] (19%; m.p. 125–126°C). The nitro group was reduced using TiCl_3 to cyclic aniline (**8**)[†] (100%; m.p. 119–120°C) and converted with formic acetic anhydride into formamide (**9**)[†] (95%; m.p. 98–101°C). Dehydration of (**9**) with trichloromethyl chloroformate provided, after alumina chromatography and crystallization from hexane, isocyanide crown ether (**2**)[†] (83%; m.p. 107–108°C). Larger ring isocyanides (**3**) and (**4**) were prepared by a related route with similar yields.

Inspection of Corey–Pauling–Koltun (CPK) molecular models suggests the isocyanide group and non-phenolic oxygens in the ring can co-ordinate a metal ion. In the smaller

ligands this requires a ‘perching’ conformation with binding occurring above the plane of the oxygens. With the larger rings the isocyanide and bound metal should move into the cavity of the macrocycle.

All three rings (**2**)—(**4**) form complexes with transition metals. For example, reaction of (**2**) in toluene with AgClO_4 results in a white crystalline complex, $(\text{2})\cdot\text{AgClO}_4^\dagger$ (98%; m.p. 185–186°C). Similar complexes were obtained with (**3**) and (**4**). Table 1 lists the isocyanide stretching frequencies for the complexes. In each case there is an increase of 50–55 cm^{-1} compared to uncomplexed ligand, confirming that the isocyanide group is participating in metal binding. These shifts are smaller than those in Ag^+ complexes of simple isocyanides (*e.g.* 2,6-dimethylphenylisocyanide· Ag^+ 2225 cm^{-1}) perhaps owing to the electron donating effect of the co-ordinating ring



[†] All new compounds gave satisfactory spectroscopic and combustion analysis data.

Table 1. I.r. data and stability constants for crown ether-metal complexes.

Complex	$\nu_{N=C}$ (cm ⁻¹ ; smear)	K_s in MeOH
(2)·AgClO ₄	2190	8.10×10^4
(3)·AgClO ₄	2188	5.86×10^5
(4)·AgClO ₄	2185	9.70×10^5
(10)·AgClO ₄	—	1.2×10^4
(2)	2135	—

ether oxygens. In addition, the two λ_{max} values in the u.v.-visible spectra change from 274 and 283 nm in (2)—(4) to 279 and 289 nm in (2)·AgClO₄, (3)·AgClO₄, and (4)·AgClO₄; plots of ϵ_{app} vs. macrocycle: silver ion ratio agree with a 1:1 stoichiometry for the complexes.

Further evidence for isocyanide-metal interactions is provided by stability constant values (K_s) for the complexes, which were also obtained by the above u.v.-visible method⁷ (see Table 1). Rings (2), (3), and (4) show a ca. 1 to 2 order of magnitude increase in stability compared to the resorcinol-derived crown ether (10)[‡] which lacks the -N=C group. Furthermore, the stability of the complex increases ca. 2–5 fold with each additional ethyleneoxy unit in the ring. This is consistent with the Ag⁺-CN-unit moving closer to the plane of the ether oxygens as the size of the ring increases.

These results establish that crown ethers containing inward turning isocyanide groups can bind transition metal ions *via* a direct isocyanide-metal interaction.§ This key observation

[‡] These were prepared from resorcinol and the appropriate bis(toluene-*p*-sulphonate) in DMF with Cs₂CO₃ as base, ref. 8.

§ Similar effects have been seen with alkali metals and crown ethers containing convergent methoxyaryl and phenolic groups, ref. 9.

opens the way to a series of new macrocyclic ligands containing multiple converging isocyanide groups. Increasing the number of isocyanides in the ring should enhance the π -acceptor properties of these systems and extend the range of transition metals and oxidation states that can be complexed.

We thank Research Corporation for partial financial support of this work.

Received, 8th May 1985; Com. 618

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