2,2′-Bipyridyl 'Crown Ethers.' Synthesis and *X*-Ray Crystal Structure of a Cobalt(II) Complex

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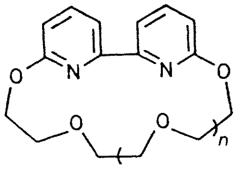
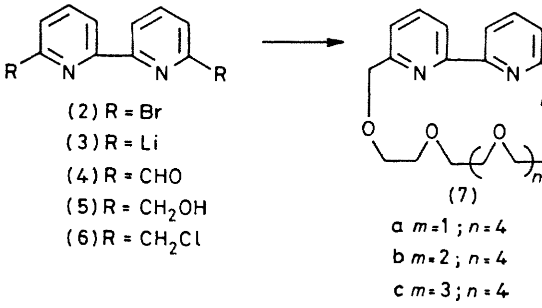
Summary A newly-synthesized bipyridyl hexaethyleneglycol crown ether reacts with $CoCl_2$ to form a pentacoordinate complex containing a novel Co^{II}–O(ether) bond.

Although 2,2′-bipyridyl has been used as a classic bidentate ligand for over 90 years,[1] only recently has this molecule been incorporated into a macrocyclic framework.[2] Our early synthetic[3] and theoretical[4] studies with (**1**) suggested that heteroatoms adjacent to the pyridine nucleus retarded metal ion complexation because of steric problems caused by the preferred conformation of the integrated imidate units[5] and the reduced *N*-electron densities.[6] We herein report our initial successful attempts to circumvent these structural obstacles.



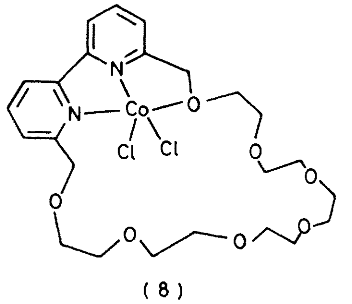
(1)

Treatment of 6,6′-dibromo-2,2′-bipyridyl (**2**)[2,7,8] with 3·2-equiv. of n-butyl-lithium (2·23 M in hexane) in tetrahydrofuran (THF) at −90 °C generated the dilithio intermediate (**3**), which upon addition of *NN*-dimethylformamide gave (55%) the dialdehyde (**4**): m.p. 236—237 °C. Reduction of (**3**) with sodium borohydride in absolute methanol yielded (99%) the diol (**5**)† (m.p. 146—147 °C), which was subjected to excess thionyl chloride to give (73%) the dichloride (**6**):† m.p. 157—158 °C; ^{1}H n.m.r. ($CDCl_3$) δ 4·79 (s, 4H), 7·55 (dd, 2H, *J* 7·8 and 1·2 Hz), 7·91 (t, 2H, *J* 7·8 Hz), and 8·49 (dd, 2H, *J* 7·8 and 1·2 Hz). Reaction of (**6**) with the disodium salt of hexaethyleneglycol afforded the 1:1 macrocycle (**7a**)† in 21% isolated yield, as a colourless oil: ^{1}H n.m.r. ($CDCl_3$) δ 3·29 (s, 4H), 3·43 (m, 8H), 3·75 (m, 8H), 4·82 (s, 4H), 7·50 (dd, 2H, *J* 7·8 and 1·2 Hz), 7·89 (t, 2H, *J* 7·8 Hz), 8·40 (dd, 2H, *J* 7·8 and 1·2 Hz); i.r. (neat) 1150 (C–O) cm^{-1}. The 2:2- and 3:3-macrocycles (**7b,c**)† (10 and 3%, respectively) as well as other members of the oligomeric series were also isolated and characterized.



SCHEME

When (**7a**) was treated in boiling absolute methanol with an equimolar amount of $CoCl_2 \cdot 6H_2O$, followed by addition of ethyl acetate, the blue crystalline complex (**8**)† was obtained (80%): m.p. 142—143 °C; i.r. (KBr) 2860, 1595, 1570, 1435, 1380, and 1100 cm^{-1}. Complex (**8**) could be recrystallized from ethyl acetate; however, chloroform or benzene as solvents gave crystals suitable for *X*-ray analysis.



(8)

Crystal data: $CoCl_2C_{24}H_{34}N_2O_7$, M.W. = 592·4, monoclinic space group $P2_1/c$, $a = 9{\cdot}692(4)$, $b = 28{\cdot}692(10)$, $c = 9{\cdot}835(3)$ Å, $\beta = 97{\cdot}89(3)°$, $Z = 4$, $D_c = 1{\cdot}452$ g cm^{-3}, $R = 0{\cdot}064$ for 1674 observed reflections measured by an automated diffractometer.

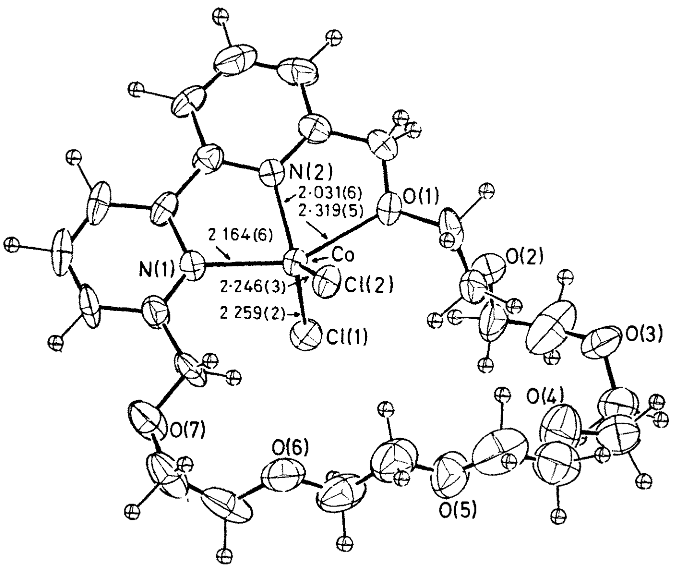


FIGURE. The molecular structure of (**8**) showing selected bond lengths (Å). Selected angles within the co-ordination sphere are: Cl(1)–Co–Cl(2) = 121·7(1); Cl(1)–Co–N(1) = 102·1(2); Cl(1)–Co–N(2) = 120·8(2); Cl(1)–Co–O(1) = 92·6(2); Cl(2)–Co–N(1) = 98·6(2); Cl(2)–Co–N(2) = 116·4(2); Cl(2)–Co–O(1) = 94·5(2); Cl(2)–Co–N(2) = 79·0(3); N(1)–Co–O(1) = 151·0(3); N(2)–Co–O(1) = 72·0(3)°.

The molecule (Figure) contains pentaco-ordinate Co^{II}; one of the co-ordination sites is occupied by an ether oxygen atom O(1). The geometry of the inner co-ordination sphere is given by the selected bond distances and angles in the Figure. It has neither square pyramidal nor ideal trigonal bipyramidal geometry, but, perhaps, is best considered to be a distorted form of the latter, since three of the donor atoms [Cl(1), Cl(2), and N(2)] very closely lie in a trigonal plane.‡

Co-ordination of the ether oxygen to Co^{II} is highly unusual. Macrocyclic ether complexes of group IA and IIA metals ions[9] as well as lanthanides[10] and actinides[11] in high oxidation states are known. Some ether complexes of early transition metals in high oxidation states are known.[12] However, ether complexes of the later transition metals are not expected to be particularly stable, especially in the +2 oxidation state. The ether co-ordination demonstrated here is assumed to be weak, based upon the long Co–O distance of 2·319(5) Å. This value is considerably longer than typical Co^{II}–O distances, such as 1·93 Å in $CoCl_2 \cdot 2H_2O$.[13]

It is somewhat surprising that this complex has the pentaco-ordinate geometry rather than the customary tetrahedral geometry, or a six co-ordinate structure in which both O(2) and O(7) bind the metal. Initially Co^{II} was chosen because this d^7 ion can conform to several geometries; thus (**7a**) can impose one of several geometries or co-ordination numbers on the metal without substantial

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† All new compounds have been fully characterized by elemental and spectral analyses.

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

loss in crystal field stabilisation energy (CFSE) Since tetrahedral and five-co-ordinate geometries are energetically similar and since the ether oxygen atom may co-ordinate without loss of other ligands, Co–O complexation is apparently stabilized by the chelate effect Although a hexaco-ordinate structure can be envisaged, the resultant highly distorted octahedron would cause substantial losses in CFSE

The nearest structural analogue to (**8**) found in the literature[14] appears to be the terpyridine complex of CoCl$_2$ The co-ordination geometry of [Co(terpy)Cl$_2$] is quite similar, however, the uniqueness of the present complex is not its geometry but rather the co-ordination of the ether oxygens[15]

We thank N S F, Dow U S A, and the A P Sloan Foundation to the S R E B (travel grant) for support and Dr J L Atwood for assistance with the acquisition of the *X*-ray data

(*Received*, 18*th July* 1979, *Com* 773)

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