Transition Metal Cryptates: the Crystal and Molecular Structure of a Cobalt(II) Cryptate, $[Co(C_{16}H_{32}N_2O_5)][Co(SCN)_4]$

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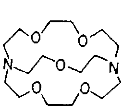
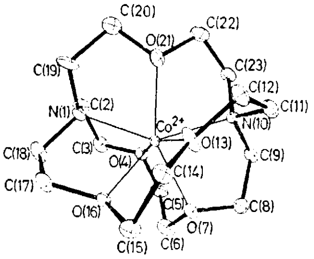
Summary A heptaco-ordinate cobalt(II) atom completely enclosed in the macrobicyclic polyether ligand, $C_{16}H_{32}N_2O_5$ is present in the [2] cryptate $[Co(C_{16}H_{32}N_2O_5)][Co(SCN)_4]$.

In continuation of our studies on macrocyclic metal complexes[1] we now report the structure of a [2] cryptate[2] in which a cobalt(II) cation is completely enclosed within the molecular cavity of ligand (L).



(L)



Several transition metal cryptates or clathro-chelates obtained *in situ* by encapsulation reactions have already been reported with ligands containing more specific co-ordination sites than the diamino-polyether ligands.[3]

The [2] cryptate, $[Co(L)][Co(SCN)_4]$ denoted by (A) was obtained by mixing ligand (L) and cobalt (II) thiocyanide in the ratio 1 : 1 in chloroform. Suitable crystals for *X*-ray studies were obtained by recrystallizing (A) in a mixture of acetone and acetonitrile.

(A) crystallizes in the space group *Pbca* with $a = 22{\cdot}661(20)$, $b = 16{\cdot}092(16)$, $c = 15{\cdot}797(16)$ Å, $D_m = 1{\cdot}60$, $D_c = 1{\cdot}57$ g cm^{-3}, $Z = 8$, 3247 above background diffractometer observations with Mo-K_α radiation.

The structure was solved by Patterson and Fourier techniques and least squares methods with anisotropic thermal parameters for all non-hydrogen atoms. Current R value is 0·033.

The crystal structure of (A) consists of $[Co(L)]^{2+}$ cations and $[Co(SCN)_4]^{2-}$ anions. As is shown by the Figure, the metal atom in the cation is completely enclosed within ligand (L) and is bonded to the seven heteroatoms. The co-ordination polyhedron of the cobalt is most conveniently described as a distorted pentagonal bipyramid with N(1), N(10), O(7), O(16), and O(21) in the equatorial positions and O(4) and O(13) in the axial positions.

The Co–N(1) and Co–N(10) bond distances have values of 2·201(5) and 2·243(5) Å respectively. The Co–O(4), –O(7), –O(13), –O(16), and –O(21) bond lengths are respectively 2·183(4), 2·207(4), 2·096(4), 2·219(4), and 2·181(4) Å.

The values of the C–C torsion angles which range from 36 to 52° indicate the presence of strain within the ligand, probably due to the small size of the metal cation with respect to the size of the molecular cavity in the macrobicyclic ligand. The C–C, C–O, and C–N bonds within ligand (L) have the normal expected values.

The co-ordination around the cobalt atom in the $Co(SCN)_4^{2-}$ anion is tetrahedral with N-bonded linear SCN groups. The mean value of the Co–N bond distances is 1·952(5) Å.

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