The Crystal Structure of a Rubidium "Cryptate" $[RbC_{18}H_{36}N_2O_6]SCN\cdot H_2O$

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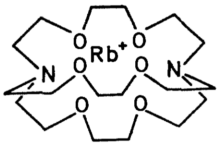
Summary The crystal structure of the rubidium "cryptate" $[RbC_{18}H_{36}N_2O_6]SCN\cdot H_2O$ is reported and the Rb^+ cation is shown to be located in the cavity of the macrobicyclic system.

B. DIETRICH, J. M. LEHN, AND J. P. SAUVAGE recently reported the synthesis of several diazapolyoxa-macrobicyclic compounds.[1] These molecules have a strong tendency to form complexes or inclusion compounds with alkali cations.[2] The determination of the structure of several of these complexes, named cryptates,[2] has been undertaken in order to show that the cation is located in the cavity of the macrobicyclic system, and to study the conformation of the ligand.

We report the results of the study of the rubidium thiocyanate derivative:



$SCN^-\cdot H_2O$

(I)

Crystals were grown by slow evaporation of a dilute solution of (I) in acetone. Reciprocal lattice symmetry is C_{2h}. The unit cell dimensions are: $a = 22\cdot655 \pm 0\cdot022$, $b = 8\cdot311 \pm 0\cdot008$, $c = 14\cdot409 \pm 0\cdot015$ Å, $\beta = 109\cdot75 \pm 0\cdot25°$, $D_m = 1\cdot33$, $D_c = 1\cdot351$g cm^{-3}.

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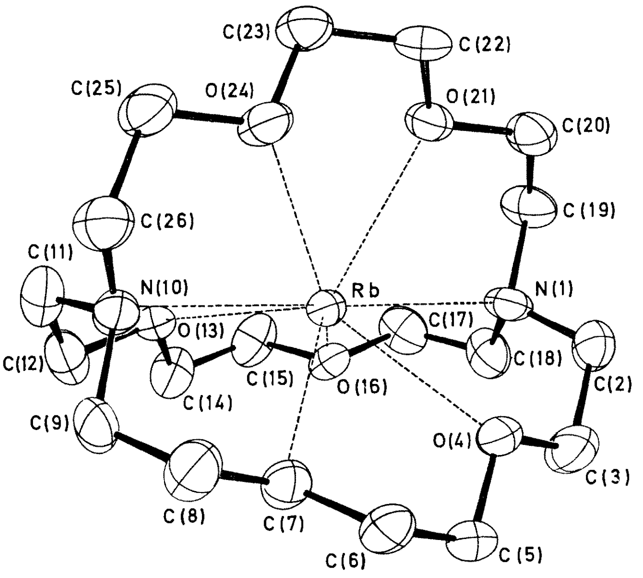
The intensities of 3823 independent reflections (1802 with $\sigma I/I < 0{\cdot}2$) were collected on a Pailred diffractometer using Cu-K_α radiation on a cylindrical crystal. The intensities of *hkl* reflections with $h = 2n + 1$ are weak, only 240 independent reflections of this type being above background. Absorption corrections have been applied ($\mu R = 0{\cdot}62$).



FIGURE

The structure has been determined by Patterson and electron-density Fourier methods. The packing of the complex cations $(RbC_{18}H_{36}N_2O_6)^+$ presents a periodicity of $a/2$ in the [100] direction. A two-fold crystallographic symmetry is thus imposed on these units, and only the thiocyanate group and the water molecule participate in reflections with $h = 2n + 1$.

Full-matrix anisotropic least-squares refinement[3] on all non-hydrogen atoms led to the discrepancy factors:

$$R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0{\cdot}087$$

$$R_2 = [\Sigma\omega(|F_o| - |F_c|)^2/\Sigma\omega|F_o|^2]^{1/2} = 0{\cdot}103.$$

The overall structure of the complex cation $(RbC_{18}H_{36}N_2O_6)^+$ is shown in the Figure.[4] The Rb^+ cation, located in the cavity of the macrocyclic system is directly surrounded by the two nitrogen and the six oxygen atoms present in $C_{18}H_{36}N_2O_6$.

The existence of three conformations of the ligand (*exo–exo*, *endo–endo*, and *exo–endo*) has been considered for these compounds.[2] In the cryptate under study, the conformation is found to be *endo–endo*; thus the two nitrogen atoms participate with the six oxygen atoms in the bonding with Rb^+. The polyhedron defined by these atoms is approximately a bicapped trigonal prism of D_3 symmetry. The symmetry of the complete cation is also D_3.

The distances between Rb^+ and the nitrogen and oxygen atoms of the ligand are: $Rb^+ \cdots N = 3{\cdot}004(6)$, $Rb^+ \cdots O(1) = 2{\cdot}905(7)$, $Rb^+ \cdots O(2) = 2{\cdot}897(7)$, and $Rb^+ \cdots O(3) = 2{\cdot}894(6)$ Å. These distances are in fair agreement with the sum of the ionic radius of Rb^+ (1·48) and the van der Waals' radii of nitrogen (1·50) or oxygen (1·40 Å).[5]

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[1] B. Dietrich, J. M. Lehn, and J. P. Sauvage, *Tetrahedron Letters*, 1969, 2885.

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[4] C. K. Johnson, ORTEP, ORNL, 3794, 1965.

[5] L. Pauling, "Nature of the Chemical Bond," 3rd edn., Cornell University Press, Ithaca, New York, 1960.