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STRUCTURAL, THERMAL AND MICROSCOPIC STUDIES OF POTASSIUM CRYPTATE K(222)NCS · H_2O *

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ABSTRACT

The crystals of the title compound are isomorphous with the Rb and Cs analogues and have cell constants $a = 14.365(3)$, $b = 8.310(2)$, $c = 22.251(5)$, $\alpha = 107.45(5)°$, space group $P2/a$ and $Z = 4$. The potassium ion is coordinated by the two nitrogen atoms and the six oxygen atoms of the ligand. Structural analysis indicates that the cryptate conformation is very similar to that of the Rb compound, but differs from that of the KI complex. The thermal behaviour of K(222)NCS·H_2O crystalline powder was investigated by DSC. After dehydration, the anhydrous material undergoes two reversible phase transitions before melting at 428 K. These findings were confirmed by microscopic observation of single crystals between crossed polarizers. Enthalpic and entropic changes are reported, and comparison between the entropies of fusion of the ligand and the complex is discussed in terms of ligand rigidity.

INTRODUCTION

The cryptand 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane, known as kryptofix or (222), forms cage complexes with a number of cations. Those with alkaline metals have received particular attention. Changes in cryptand conformation have been observed and connected with the dimensions of the encaged ion. For most of the (222) complexes studied, however, there appears to be no special interaction with the anion [1].

As the potassium complex with (222) is very stable in aqueous solution (log $K = 5.4$ [2]), investigation of the thermal behaviour of its crystals to check their stability appeared worthwhile.

In the present paper, we describe the thermal behaviour and the crystal structure of the title compound; the thermal findings were also checked by hot-stage optical microscopy of single crystals between crossed nicols.

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EXPERIMENTAL

The complex K(222)NCS · H_2O was prepared by mixing equimolar amounts of KNCS and (222) in boiling acetone. The solution was allowed to cool and the complex precipitated by adding ethyl ether. Single crystals were obtained by redissolving the precipitate in acetone to which some water had been added, and allowing the solution to evaporate very slowly. Elemental analysis of the complex $C_{19}H_{38}N_3O_7SK$ (M.W. = 491.68) gave: C = 46.44; N = 8.56; H = 7.83, compared with the calculated values: C = 46.41; N = 8.54; H = 7.80.

The crystals of this compound are isomorphous with the Rb and Cs analogues [3] and their cell constants are: $a = 14.365(3)$, $b = 8.310(2)$, $c = 22.251(5)$ Å, $\beta = 107.45(5)°$, space group $P2/a$ and $Z = 4$. 3439 independent reflections (1979 greater than $3\sigma(I)$) measured on a Nonius CAD 4 diffractometer were used for structure solution and refinement. The structure was solved by Patterson and Fourier techniques, and refined by anisotropic least-squares methods (unit weights) to an R factor of 0.073.

The thermal behaviour of crystalline powders of the title compound was investigated with a Perkin–Elmer DSC-2C differential scanning calorimeter, using either sealed or crimped standard aluminium sample pans. The runs were preferentially performed at a scan rate of 5 K min^{-1}, the sensitivity being adjusted according to the sample mass (2–10 mg). Dry nitrogen was allowed to flow in the sample cell of the thermal apparatus at ca. 10 ml min^{-1}. Occasionally, thermal curves were recorded under the same conditions with a Mettler TA 2000 thermal analyser.

The thermal results were also checked by optical microscopy, using a Reichert Zetopan apparatus equipped with hot stage, polarizers and an Olympus OM2 camera.

RESULTS AND DISCUSSION

The structure of the compound consists of $(KC_{18}H_{36}N_2O_6)^+$ cations, thiocyanate anions and water molecules. Atomic coordinates for the non-hydrogen atoms are collected in Table 1. In the complex cations, the K^+ ions are eight-coordinated by the two N and the six O atoms of the ligand (Fig. 1a), forming a distorted, bi-capped trigonal prism of approximate D_3 symmetry (Fig. 1b). The distances between the K and the N and O atoms of the ligand and the angles of the chelate rings are shown in Table 2. The K ions lie on the two-fold axis. The N...N distances, the O...O edge of the triangular faces and the α angle, which give good indications of the dimensions of the K^+-containing cavity [1], are: 5.93(1), 4.31(1) (average) Å and 15.9(1) deg. (average), respectively.

TABLE 1

Positional parameters ($\times 10^4$) with estimated standard deviations in parentheses for $C_{19}H_{38}N_3O_7SK$

Atom	*x/a*	*y/b*	*z/c*
K1	2500	626(4)	5000
N1	2434(7)	637(13)	3656(5)
C2	1387(10)	778(18)	3261(6)
C3	864(9)	2162(17)	3463(6)
04	783(5)	1782(10)	4085(4)
C5	286(8)	3053(15)	4301(6)
C6	143(8)	2550(16)	4913(6)
07	1088(6)	2412(11)	5275(4)
C8	972(10)	2105(18)	5984(6)
C9	1994(10)	2016(18)	6463(6)
C19	2833(10)	−887(18)	3505(6)
C20	2431(10)	−2376(17)	3733(7)
021	2719(5)	−2334(9)	4421(4)
C22	2315(11)	−3719(16)	4645(6)
K2	2500	−745(5)	0000
N21	7561(8)	762(13)	1351(5)
C22	8601(10)	965(18)	1753(6)
C23	9129(10)	2329(18)	1535(6)
024	9217(6)	1883(10)	917(4)
C25	9743(9)	3111(15)	701(6)
C26	9876(8)	2591(16)	87(6)
027	6058(6)	2501(11)	376(4)
C28	5939(10)	2167(18)	990(6)
C29	6956(10)	2116(17)	1466(6)
C210	7179(10)	−794(17)	1499(6)
0211	7700(6)	−2202(9)	−586(4)
C212	7314(11)	−3579(14)	−360(6)
N	8551(9)	4658(16)	2710(7)
C	9110(9)	5505(16)	2647(6)
S	4945(3)	3207(5)	2563(3)
O(H_2O)	8507(7)	−4283(12)	−2207(5)

As in the Rb and Cs isomorphs, the thiocyanate ions and the water molecules form zigzag chains held together by H bonds (S...O = 3.315 Å and N...O = 2.964 Å).

These findings are in closer agreement with the data reported for the Rb(222)NCS · H_2O [3] than with those of the K(222)I complex [1]. This is rather surprising, as it is known [1] that in these cases the anions show no special interaction with the cations, while the ligand modifies its conformation to adjust its cavity to the dimensions of the metal cation [3]. In the present case, conformation of the ligand appears to be more affected by the presence of the NCS–H_2O chains than by the dimensions of the complexed cation.

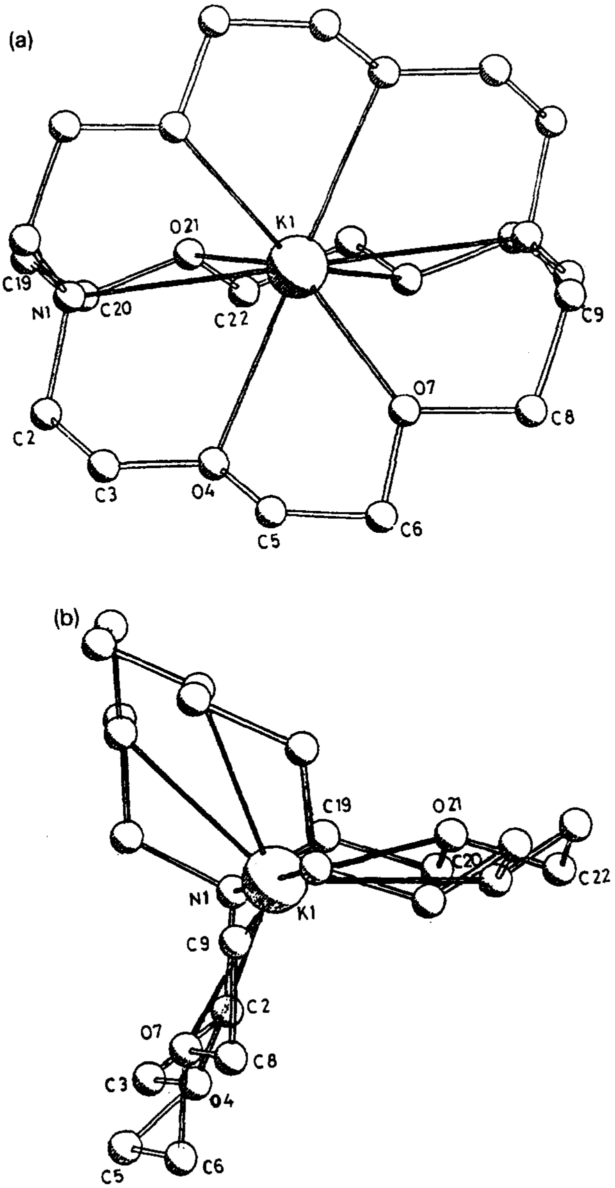

Fig. 1. Perspective view of the complex cation, showing (a) the coordination of the potassium ion and (b) the approximate D_3 symmetry.

These considerations stem from comparison of the present findings with those in ref. 1 (Tables 8.31 and 8.32). Support is expected to come from an attempt to determine the structure of the anhydrous form. Indirect evidence was also sought by optical examination of single crystals submitted to increasing temperatures in the hot stage of the microscope. Some information might have been obtained had either nucleation or growth of the

TABLE 2

Selected bond distances (Å) and angles (deg) for the $[K(C_{18}H_{36}N_2O_6)]^+$ cation represented in Fig. 1

Distances	
N1–K1	2.964(10)
O4–K1	2.853(8)
O21–K1	2.838(8)
O7–K1	2.727(8)
Angles	
O4–K1–N1	61.3(2)
O21–K1–N1	61.2(2)
O21–K1–O21′	59.8(2)
O7′–K1–N1	60.7(3)
O7–K1–O4	55.6(2)

dehydrated material taken place in preferred directions. However, the experiments did not live up to our expectations (see Fig. 2b, in which random dehydration is observed to take place).

Following the results obtained for crystalline powders with thermal methods (see below), optical-microscopic determinations on single crystals were extended to temperatures higher than those necessary for dehydration. Micrographs taken during a complete experiment are collected in Fig. 2, where micrograph a shows the crystals at room temperature between crossed nicols. Beyond dehydration (Fig. 2b, at about 353 K), a phase transition is observed (Fig. 2c, at about 403 K), followed by another (Fig. 2d, at about 418 K) and by the beginning of melting (Fig. 2e, at about 427 K). The melt was subsequently allowed to crystallise (at about 421 K, Fig. 2f) by lowering the temperature. Further lowering of the temperature caused the crystal to undergo the high-temperature phase transition (Fig. 2g, at about 393 K). The reversibility of the transition was then checked by increasing the temperature (Fig. 2h, at about 417 K). The cooling conditions needed to detect the low-temperature phase transition could not be obtained, however.

Thermal analysis of the potassium compound was performed in a sealed sample pan. In the first run, a broad endotherm that peaked at about 358 K was attributed to removal of the water molecule. On cooling the sample and repeating the heating run we noticed a series of peaks coupled with a substantial intensity decrease of the 358 K peak. Repetition produced the same peaks, but at different heights, pointing to the presence of aqueous vapour in the pan in equilibrium with a partially dehydrated compound. Provision of a small hole in the pan cover allows this vapour to escape, giving the increasing-temperature thermogram shown in Fig. 3. This has three peaks that are also present at lower temperatures in the cooling curve. These curves are reproducible in successive cooling-heating cycles. It is to be

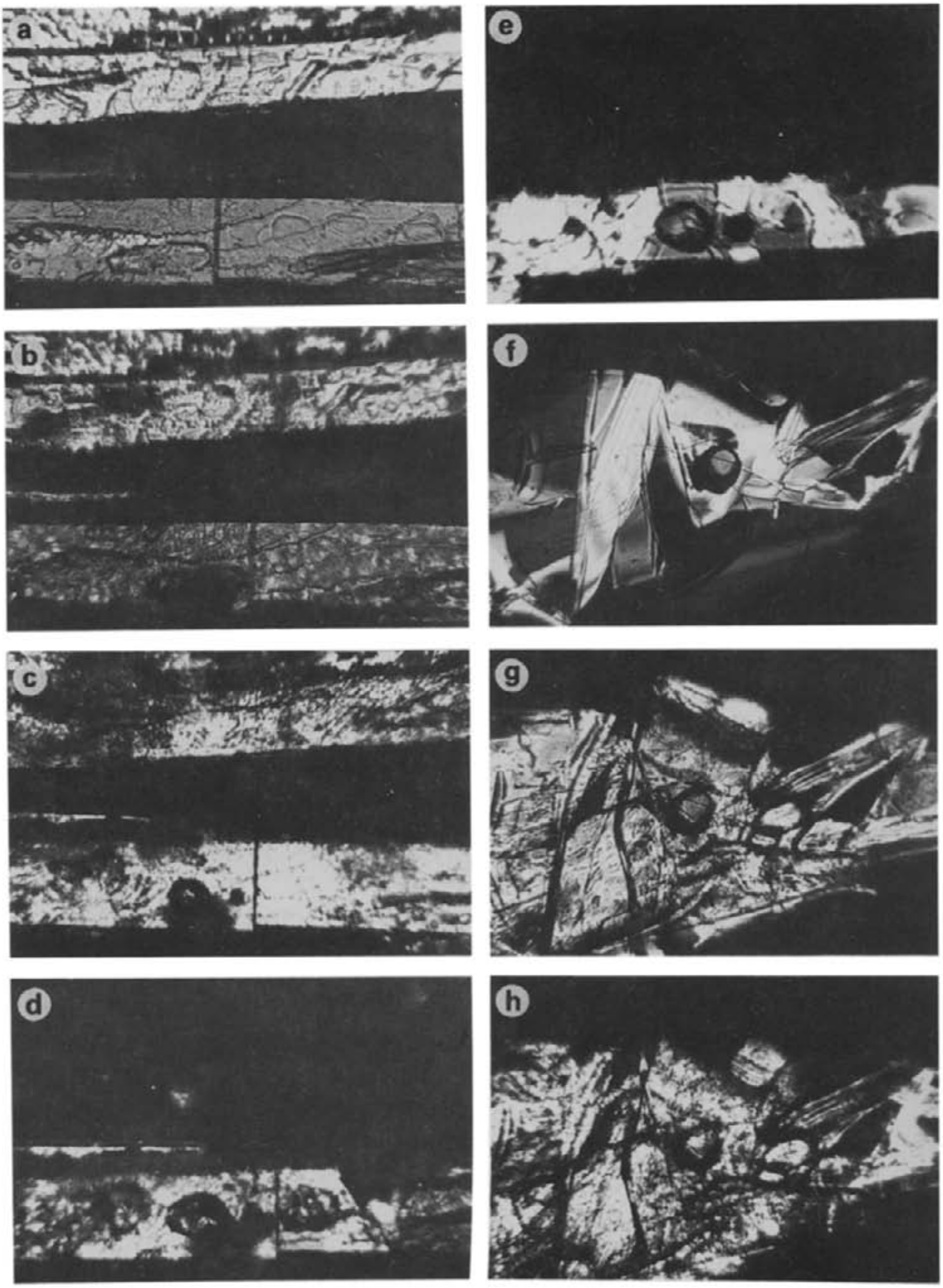

Fig. 2. Micrographs of a complete heating run of single crystals of K(222)NCS$\cdot$$H_2O$. Magnification ×58. The top crystal jumped out of the camera field during the higher temperature phase transition (see text).

noted that the low-temperature transformation is only found in cooling curves at scan speeds lower than 5 K min^{-1}. When the thermal runs are performed in crimped sample pans, the heat of dehydration is evaluated as

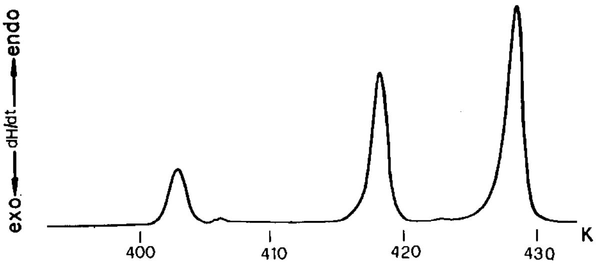

Fig. 3. Increasing temperature thermogram of K(222)NCS.

TABLE 3

Thermal data determined by differential scanning calorimetry

Thermodynamic quantity	[222]	K[222]NCS [a]
T^{f}_{fus} (K)	343.1 ± 0.6	428.0 ± 0.5
$\Delta_{fus}H$ (kJ mol^{-1})	40.0 ± 0.7	23.03 ± 0.04
$\Delta_{fus}S$ (J mol^{-1} K^{-1})	116.5 ± 2.0	53.8 ± 0.1
$\Delta^{402}_{trs}H$ (kJ mol^{-1})	–	4.30 ± 0.01
$\Delta^{417}_{trs}H$ (kJ mol^{-1})	–	11.13 ± 0.03

[a] Obtained by dehydration of the parent monohydrate in the thermal apparatus.

57.7 kJ mol^{-1}, corresponding to the loss of a single water molecule. This is in good agreement with previous findings on crystals hydrates [4].

The main thermal results are collected in Table 3. It may be observed that comparison with previously reported data on the KNCS/dibenzo-18-crown-6 system [5] indicates that complexation with KNCS greatly reduces the entropy of fusion with respect to that of the pure ligands. This was attributed to a stiffening of the ligand when complexed [5]. The entropic data show that this stiffening is rather higher than in ref. 5 and can perhaps be traced to the fact that the present ligand is anchored on 8 positions, whereas that in ref. 5 was anchored on 6.

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