CRYSTAL STRUCTURES OF *N,N'*-BIS(1-NAPHTHYLMETHYL)-1,4,10,13-TETRAOXA-7,16-DIAZACYCLOOCTADECANE COMPLEXED WITH POTASSIUM AND BARIUM THIOCYANATES

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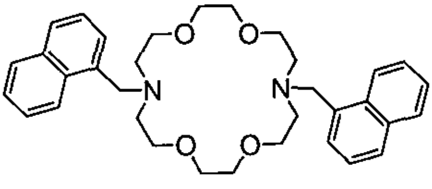
Abstract—The crystal structures of *N,N'*-bis(1-naphthylmethyl)-4,13-diaza-18-crown-6 (**1**)-KNCS and **1**-$Ba(NCS)_2$-H_2O complexes were analyzed by X-Ray crystallography. The structure of the **1**-$Ba(NCS)_2$-H_2O complex differs significantly from that of the **1**-KNCS complex. The K^+ cation is sevenfold, Ba^{2+} cation ninefold coordinated. The two naphthalene rings adopt an *anti* conformation for **1**-KNCS and *syn* conformation for **1**-$Ba(NCS)_2$-H_2O with the crown ether ring.

As an approach to the manipulation of an intramolecular electron transfer dynamics, photoresponsive supramolecular systems are of great significance particularly for their potential application to environmental and biological analytical reagent.[1] There are extensive investigations toward the characterization of photoinduced electron transfer (PET) fluoroionophores such as a donor-spacer-acceptor system.[2,3] Recently, it was found that the diazacrown ethers having two fluorescent pendants showed a strong tendency to form an inter- and intramolecular exciplex and displayed fluorescence with a low quantum yield.[4] The addition of metal cation enhanced the fluorescence emission intensity of *N,N'*-bis(1-naphthylmethyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (**1**) increased by a factor of 2.8 for KNCS and 41 for $Ba(NCS)_2$.[5] ^1H and ^{13}C NMR analyses of this 1:1 complexation behavior revealed that Ba^{2+} strongly coordinates with the azacrown nitrogen to cause a dramatic decrease in an intramolecular charge-transfer character. In addition, it was suggested that the exchange rate between the free host (**1**) and its complex with metal ions played a role in controlling the extent of the emission-intensity enhancement that was observed in the presence of a given metal ion. In this paper, we report the preparation and the crystal structure of **1**-KNCS and **1**-$Ba(NCS)_2$.



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The single crystals of **1**-KNCS[6] and **1**-$Ba(NCS)_2$-H_2O[7] were obtained from mixtures with 1:1 stoichiometry between a methanol solution of metal thiocyante and a $CHCl_3$ solution of **1**. The molecular structure of **1**-KNCS is shown in Figure 1. The complex has the stoichiometry as **1**-KNCS. An ORTEP diagram show that the two naphthalene rings adopt an *anti* conformation with respect to one another across the crown ether ring. The two naphthalene groups are far from each other and do not interact with the K^+ directly.

The selected bond lengths, bond angles, and torsion angles are given in Table 1. The K^+ ion sits roughly at the centre of the hexagon of ligating donor atoms. The six ligating donor atoms are alternately 0.06–0.63 Å above and below their mean plane. The four oxygen and two nitrogen atoms are endodentate. The four K(01)–O distances are not equal (2.684—2.837 Å, average 2.74 Å) (that is, the hexagon is slightly deformed) and shorter than the sum of the corresponding ionic radii (2.86 Å =1.46 + 1.40 Å)[8,9] and those (2.805 Å) of 18-crown-6-KNCS complex.[10] The K(01)–N distances (3.074 and 3.115 Å, average 3.09 Å) are shorter than that of the sum of the corresponding ionic radii (3.17 Å =1.46 +

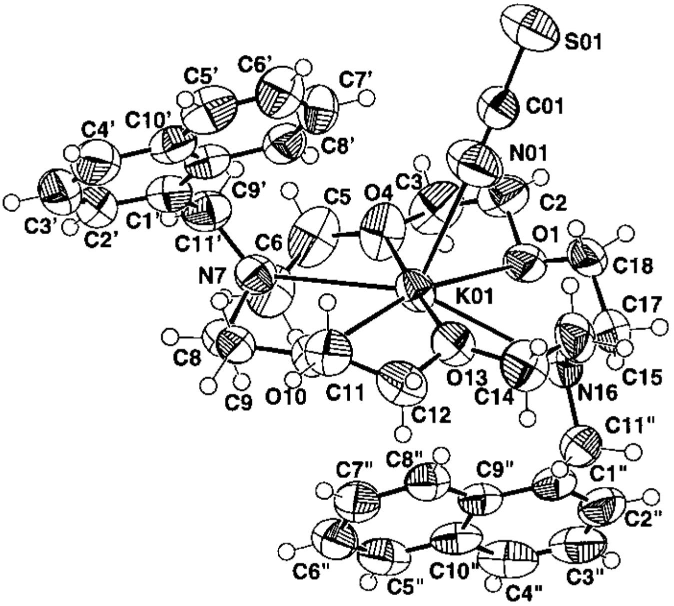

Figure 1. An ORTEP drawing of **1**·KNCS with thermal ellipsoids to enclose 50% probability. Hydrogen atoms are shown as spheres with their arbitary radii of 0.15Å.

Table 1. Bond lengths (Å), bond angles (°), and torsion angles (°) of **1**·KNCS

K(01)–O(1)	2.837 (3)	N(01)–K(01)–N(16)	89.87 (12)
K(01)–O(4)	2.684 (3)	O(1)–K(01)–N(16)	60.50 (9)
K(01)–N(7)	3.074 (3)	N(7)–K(01)–N(16)	156.78 (9)
K(01)–O(10)	2.749 (3)	C(01)–N(01)–K(01)	165.7 (4)
K(01)–O(13)	2.695 (3)	N(01)–C(01)–S(01)	179.0 (4)
K(01)–N(16)	3.115 (3)	C(11')–N(7)–K(01)	130.4 (2)
K(01)–N(01)	2.785 (5)	C(11")–N(16)–K(01)	128.8 (2)
N(01)–C(01)	1.130 (5)	N(7)–K(01)–N(01)–C(01)	-72.4 (18)
C(01)–S(01)	1.605 (5)	N(16)–K(01)–N(01)–C(01)	105.4 (17)
O(10)–K(01)–O(13)	61.29 (8)	O(1)–C(2)–C(3)–O(4)	62.6 (5)
O(4)–K(01)–N(01)	93.80 (14)	O(4)–C(5)–C(6)–N(7)	62.2 (6)
O(13)–K(01)–N(01)	83.46 (13)	N(7)–C(8)–C(9)–O(10)	-65.1 (4)
O(10)–K(01)–N(01)	116.67 (11)	O(10)–C(11)–C(12)–O(13)	59.5 (5)
O(4)–K(01)–O(1)	59.82 (9)	O(13)–C(14)–C(15)–N(16)	-64.8 (5)
N(01)–K(01)–O(1)	78.61 (11)	N(16)–C(17)–C(18)–O(1)	-70.5 (5)
O(4)–K(01)–N(7)	60.80 (9)	C(6)–N(7)–C(11')–C(1')	165.8 (4)
O(10)–K(01)–N(7)	60.80 (8)	C(8)–N(7)–C(11')–C(1')	45.8 (5)
N(01)–K(01)–N(7)	113.26 (13)	C(15)–N(16)–C(11")–C(1")	166.2 (4)
O(13)–K(01)–N(16)	61.39 (9)	C(17)–N(16)–C(11")–C(1")	-73.0 (5)

1.71 Å).[8,9] The thiocyanate anion sit on K(01) and displace 5° from perpendicular position to the crown ring mean plane. The K–N (thiocyanate anion) distance is 2.785 Å. Thus, K(01) is surrounded by six donor atoms and thiocyanate anion in a hexagonal pyramidal coordination.

An ORTEP view of compound **1**-Ba(NCS)$_2$-H$_2$O is illustrated in Figure 2 and the selected bond lengths, bond angles, and torsion angles are listed in Table 2.

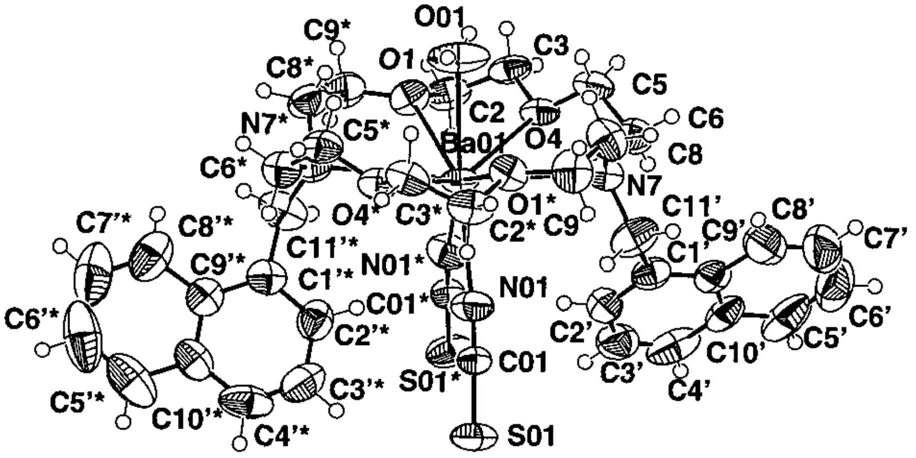

Figure 2. An ORTEP drawing of **1**·Ba(NCS)$_2$·H$_2$O with thermal ellipsoids to enclose 50% probability. Symmetry codes: (*) 1/2 - x, y, 1-z

Table 2. Bond lengths (Å), bond angles (°), and torsion angles (°) of **1**·Ba(NCS)$_2$·H$_2$O

Ba(01)–O(01)	2.759 (6)		O(01)–Ba(01)–O(1)	68.86 (9)
Ba(01)–O(1)	2.767 (4)		N(01)–Ba(01)–N(01)	75.8 (2)
Ba(01)–O(4)	2.853 (4)		O(01)–Ba(01)–O(4)	75.46 (7)
Ba(01)–N(7)	3.127 (5)		O(1)–Ba(01)–O(4)	59.39 (13)
Ba(01)–N(01)	2.790 (5)		O(01)–Ba(01)–N(7)	85.84 (8)
S(01)–C(01)	1.616 (5)		O(1)^{i}–Ba(01)–N(7)	60.04 (12)
C(01)–N(01)	1.151 (7)		N(01)–Ba(01)–N(7)	102.6 (2)
N(7)–C(11')	1.486 (7)		N(01)^{i}–Ba(01)–N(7)	84.1 (2)
N(7)–Ba(01)–N(01)–C(01)		75.0 (17)	O(4)–Ba(01)–N(7)	58.20 (12)
N(7)^{i}–Ba(01)–N(01)–C(01)		-110.1 (17)	O(01)–Ba(01)–N(7)^{i}	85.84 (8)
O(1)–C(2)–C(3)–O(4)		60.9 (6)	N(7)–Ba(01)–N(7)^{i}	171.7 (2)
O(4)–C(5)–C(6)–N(7)		-60.5 (7)	N(01)–C(01)–S(01)	177.9 (6)
N(7)–C(8)–C(9)–O(1)^{i}		-65.0 (8)	C(11')–N(7)–Ba(01)	114.4 (4)
C(8)–N(7)–C(11')–C(1')		-165.4 (6)		
C(6)–N(7)–C(11')–C(1')		-44.0 (9)		

Symmetry codes: (i) 1/2 - x, y, 1-z

The structure of the **1**-Ba(NCS)$_2$-H$_2$O complex differs significantly from that of the **1**-KNCS complex. The two naphthalene rings of **1**-Ba(NCS)$_2$-H$_2$O adopt a *syn* conformation with respect to each other. The Ba^{2+} ion is coordinated by the six donor atoms (four oxgen and two nitrogen atoms) of the diazacrown ether, the two nitrogen atoms of the thiocyanate anions on one side (near naphthalene ring) and the oxygen atom of water molecule on the opposite side. The Ba^{2+} ion is displaced 0.17 Å from the mean plane of the azacrown. As shown in Table 2, the Ba(01)-O and Ba(01)–N(7) distances of the diazacrown are shorter than the sum of the corresponding ionic radii (Ba–O: 2.87 Å = 1.47 + 1.40 Å, Ba–N: 3.18 Å = 1.47 + 1.71 Å).[8,9] The coordinated structure of **1**-Ba(NCS)$_2$-H$_2$O is similar to that of Ba(NCS)$_2$-18-crown-6-H$_2$O.[11] In conclusion, the coordinated structure also is responsible for a large difference in the relative emission-intensity enhancement that was observed in the presence of guest cation.

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6. Crystal data of **1**-KNCS. mp 162—163 °C (Recrystallization from chloroform : methanol (1:1 *v/v*)), KNCS·$C_{34}H_{42}N_2O_4$, M_r=639.89, orthorhombic, $P2_12_12_1$, a=10.818(2), b=36.962(5), c=8.383(2) Å, V=3352.0(11) Å^3, Z=4, D_x=1.268 gcm^{-3}, refinement on F^2 (*SHELXL93*)[12], $wR(F^2)$=0.1441, $R[F^2>2s(F^2)]$=0.0501.
7. Crystal data of **1**-Ba(NCS)$_2$-H$_2$O. mp 291—292 °C (Recrystallization from chloroform : methanol (1:1 *v/v*)), Ba(NCS)$_2$·$C_{34}H_{42}N_2O_4$·H_2O, M_r=814.23, monoclinic, $I2/a$, a=16.910(7), b=9.417(5), c=23.637(7) Å, β=101.70(4)°, V=3686(3) Å^3, Z=4, D_x=1.467 gcm^{-3}, refinement on F^2 (*SHELXL93*)[12], $wR(F^2)$=0.1188, $R[F^2>2s(F^2)]$=0.0473.
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