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

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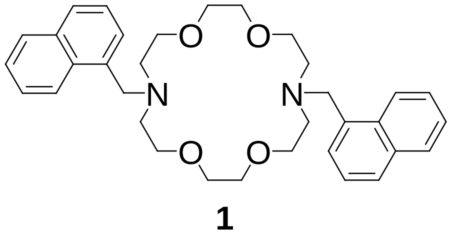
Abstract – The crystal structures of *N,N'*-bis(1-naphthylmethyl)-4,13-diaza-18-crown-6 (**1**) complexed with LiNCS and $Zn(NCS)_2$ were analyzed by X-Ray crystallography. Diazacrown (**1**) formed a unique 1:2 complex with LiNCS, while $Zn(NCS)_2$ complex of **1** consisted of an ion pair with $[Zn(NCS)_4]^{2-}$ and $\mathbf{1}\cdot 2H^+$. The two naphthalene rings in the crystals adopt an *anti* conformation with respect to each other.

Photo-responsive supramolecular systems are of great significance particularly for their potential application to nanoscale devices for cation sensor and switch.[1,2] There are extensive investigations toward the characterization of photoinduced electron transfer (PET) fluoroionophores which is known as one of the typical electron donor-spacer-electron acceptor systems. Recently, it was found that the azacrown ethers having two fluorescent pendants show a strong tendency to form inter- and intramolecular exciplexes and display fluorescence in low quantum yields.[3] The addition of metal cation enhanced the fluorescence intensity of *N,N'*-bis(1-naphthylmethyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (**1**) by a factor of 1.1-41. Moreover, the crystal structures of **1**, **1**·KNCS and **1**·$Ba(NCS)_2\cdot H_2O$ were elucidated by



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[†] Dedicated to Professor Steven M. Weinreb on the occasion of his 65th birthday.

X-Ray crystallographic analysis. The K$^+$ and Ba^{2+} cations were surrounded by the diazacrown nitrogen atoms to form 1:1 complexes with the host crown ether (**1**). The diazacrown ether (**1**) showed the following cation selectivity: Mg^{2+} > K$^+$ > NH$_4^+$ > Ba^{2+} > Rb$^+$ > Zn^{2+} > Na$^+$ > Cs$^+$ > Ca^{2+} > Li$^+$. However, the crystal structure of complex formed between **1** and metal cation having low association ability for this host molecule has not been elucidated. We now report the crystal structures of **1**·LiNCS and **1**·Zn(NCS)$_2$, aiming at contribution to a deeper understanding of PET systems.

The single crystals of **1**·2LiNCS and (H$_2$·**1**)[Zn(NCS)$_4$] were obtained from the MeOH-CHCl$_3$ mixtures containing **1** and a large excess of metal thiocyanate. The molecular structure of **1**·2LiNCS[4] is shown in Figure 1. Diazacrown ether (**1**) formed a unique 1:2 complex with LiNCS. The complex (**1**·2LiNCS) is centrosymmetric and the two naphthalene rings adopt an *anti* conformation with respect to one another across the diazacrown ether ring. The Li1 coordinates to the O1, O2^i (symmetry code: (i) 1-x, -y, 1-z), N1, and N2 atoms in a distorted tetrahedral mode. The six legating donor atoms (O1, O2, N1, O1^i, O2^i, N1^i) of diazacrown ether deviate from their mean plane by 0.11-0.16 Å. The Li1-O distance is close to the sum of the corresponding ionic radii (Li-O: 2.13 Å = 0.73 + 1.40 Å) and that (1.93 Å) of the 1,5,9-trioxacyclododecane-LiNCS complex.[5] The Li1-N distance is shorter than the sum of the corresponding ionic radii (Li-N: 2.44 Å = 0.73 + 1.71 Å).[6] The thiocyanate anion sits on the Li1 and displace 61° from the diazacrown-ring mean plane (defined by the N1, O1, and O2^i atom) and is existed by near the naphthalene ring (the N2-C10 distance: 3.470 Å).

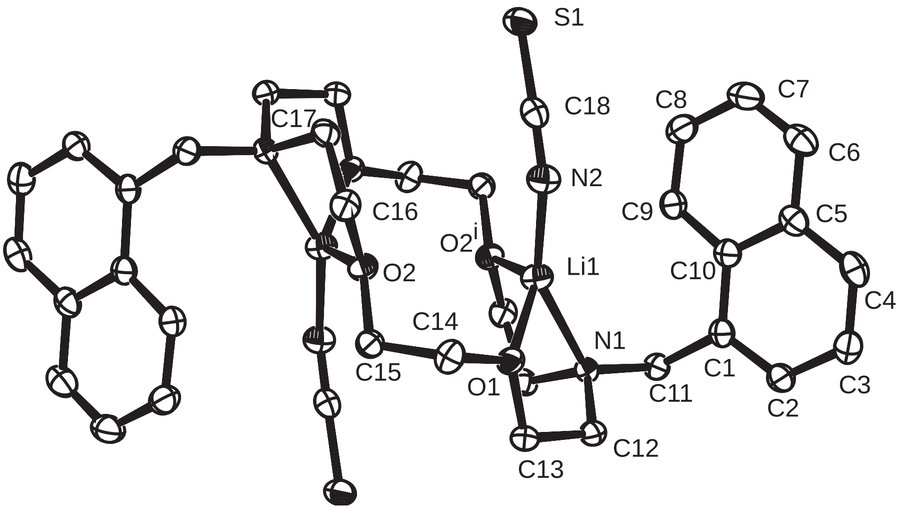

Figure 1. An ORTEP drawing of **1**·2LiNCS showing 50% probability displacement ellipsoids. H atoms are omitted.

Table 1. Bond lengths (Å), bond angles (°), and torsion angles (°) of **1**·2LiNCS

S1-C18	1.636(2)	C11-N1-Li1	126.01 (13)	N1-Li1-N2	152.23 (17)
N2-C18	1.171(2)	C18-N2-Li1	141.13 (18)	Li1-N2-C18-S1	12 (3)
S1-C18	1.6362 (18)	S1-C18-N2	177.38 (17)	C12-N1-C11-C1	-75.44 (17)
O1-Li1	1.975 (3)	O1-Li1-O2^i	128.25 (16)	C17^i-N1-C11-C1	163.58 (14)
O2-Li1^i	2.032 (3)	O1-Li1-N1	82.66 (12)	N1-C12-C13-O1	-46.96 (19)
N1-C17^i	1.483 (2)	O1-Li1-N2	107.67 (16)	O1-C14-C15-O2	-70.14 (17)
N1-Li1	2.179 (3)	O2^i-Li1-N1	82.50 (12)	O2-C16-C17-N1^i	-52.58 (17)
N2-Li1	1.963 (3)	O2^i-Li1-N2	108.27 (16)		

symmetry code: (i) 1-x, -y, 1-z

This means that photoinduced electron transfer from thiocyanate anion to the naphthalene chromophore could occur easily. The Li-N distance of the thiocyanate anion is 1.963 Å, which is nearly equal to that (1.958 Å) of the 1,5,9-trioxacyclododecane-LiNCS complex.[5] To our knowledge, this is the first case of two Li^+ cation coordination to 4,13-diaza-18-crown-6 ether.

Zinc thiocyanate complex of **1** consists of an ion pair with $[Zn(NCS)_4]^{2-}$ and $\mathbf{1}\cdot 2H^+$, as shown in Figure 2.

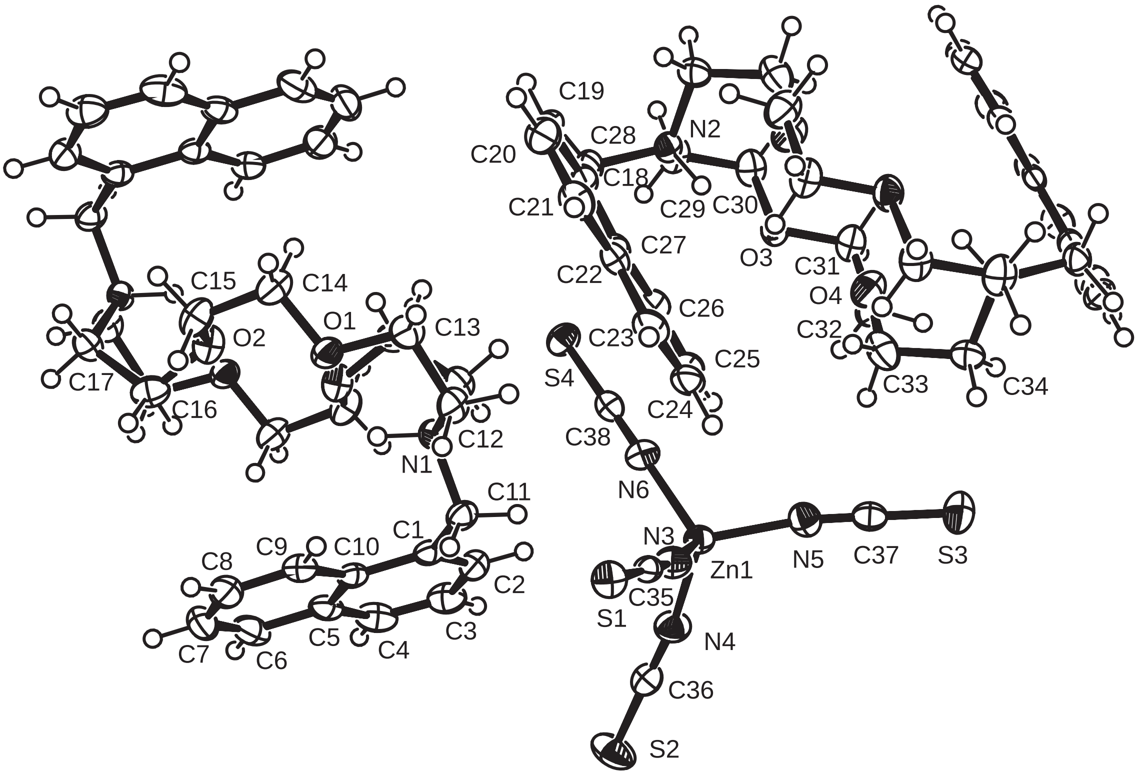

Figure 2. An ORTEP drawing of $(H_2\cdot\mathbf{1})[Zn(NCS)_4]$ showing 50% probability displacement ellipsoids.

Table 2. Bond lengths (Å), bond angles (˚), and torsion angles (˚) of $(H_2\cdot\mathbf{1})[Zn(NCS)_4]$

Zn1-N3	1.9599(17)	N5-C37	1.170(3)	Zn1-N6-C38	178.68(19)
Zn1-N4	1.958(2)	N6-C38	1.163(2)	Zn1-N3-C35-S1	55(9)
Zn1-N5	1.950(2)	N3-Zn1-N4	106.24(8)	Zn1-N4-C36-S2	-173(7)
Zn1-N6	1.9628(19)	N3-Zn1-N5	110.57(7)	Zn1-N5-C37-S3	60(18)
S1-C35	1.617(2)	N3-Zn1-N6	110.30(8)	Zn1-N6-C38-S4	117(17)
S2-C36	1.604(2)	N4-Zn1-N5	110.36(10)	N1-C12-C13-O1	54.1(2)
S3-C37	1.608(2)	N4-Zn1-N6	109.21(8)	O1-C14-C15-O2	-64.5(2)
S4-C38	1.623(2)	N5-Zn1-N6	110.09(8)	O2-C16-C17-N1^{ii}	56.8(2)
N2-C34^{i}	1.508(3)	Zn1-N3-C35	170.32(19)	N2-C29-C30-O3	52.0(2)
N3-C35	1.162(2)	Zn1-N4-C36	166.2(2)	O3-C31-C32-O4	-67.4(2)
N4-C36	1.166(3)	Zn1-N5-C37	171.26(17)	O4-C33-C34-N2^{i}	55.2(2)

symmetry code: (i) 2-x,-y,2-z, (ii) 2-x,-y,1-z

The Zn^{2+} cation did not coordinate to the nitrogen atom of **1**. The zinc cation of $[Zn(NCS)_4]^{2-}$ has a tetrahedral coordination, and the Zn-N bond lengths is in the range of 1.95—1.96 Å, which is close to that of $(HTen)_2[Zn(NCS)_4]$[8] and (4,10-bis(tropon-2-yl)-4,10-diaza-1,7-dioxacyclododecane)-zinc *tetrakis*-(thiocyanato)zinc.[9] Both the two naphthalene rings and the two hydrogen atoms bonded to the ammonium nitrogen atoms of **1**·2H$^+$ adopt *anti* conformations with respect to one another across the diazacrown ether ring. The ion pair structure of (H$_2$·**1**)[Zn(NCS)$_4$] resembles that of *N,N,N',N'*-tetraethyl-9,10-anthracenedimethanamine dihydrogen tetrachlorozincate(II).[10] The nitrogen atoms of diazacrown did not coordinate to Zn^{2+}. This suggests that the emission intensity of **1** would be greatly enhanced by forming a complex with proton generated from the Zn(NCS)$_2$-water system.

Thus, the crystal structures of PET fluoroionophores-derived metal salt complexes would afford much useful information on the stoichiometry in these complex and the coordination structure.

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REFERENCES AND NOTES

1. H. G. Löhr and F. Vögtle, *Acc. Chem. Res.*, 1985, **18**, 65; A. W. Czarnik, *Acc. Chem. Res.*, 1994, **27**, 302; L. Fabrizzi and A. Poggi, *Chem. Soc. Rev.*, **1995**, 197; B. Valeur and I. Leray, *Coord. Chem. Rev.*, 2000, **205**, 3; A. P. de Silva, H. Q. N. Gunaratne, T. Gunnlaugsson, A. J. M. Huxley, C. P. McCoy, J. T. Rademacher, and T. E. Rice, *Chem. Rev.*, 1997, **97**, 1515; K. Kubo and T. Sakurai, *Heterocycles*, 2000, **52**, 945.
2. K. Kubo, *'Topics in Fluorescence Spectroscopy: Advanced Concepts in Fluorescence Sensing*,' Vol. 9, ed. by C. D. Geddes, J. R. Lakowicz, Springer, New York, 2005, pp. 219-247.
3. K. Kubo, R. Ishige, N. Kato, E. Yamamoto, and T. Sakurai, *Heterocycles*, 1997, **45**, 2365; K. Kubo, T. Sakurai, N. Kato, and A. Mori, *ibid.*, 1999, **51**, 1229.
4. Crystal data of **1**·2LiNCS, $C_{36}H_{40}Li_2N_4O_4S_2$, *Mr* = 670.74, Monoclinic, $P2_1/c$, a = 7.932 (2)Å, b = 18.261 (4)Å, c = 11.602 (3)Å, β = 92.681 (16)°, V = 1678.7 (7) Å^3, Z = 2, D_x = 1.327 Mg m^{-3}, refinement on F^2 (*SHELXL97*),[11] $wR(F^2)$ = 0.1081, $R(F)$ = 0.0387.
5. J. Dale, J. Eggestad, S. B. Fredriksen, and P. Groth, *Chem. Commun.*, **1987**, 1391.
6. R. D. Shannon and C. T. Prewitt, *Acta Crystallogr.*, 1969, **B25**, 925; R. D. Shannon, *ibid.*, 1976, **A32**, 751.
7. Crystal data of (H$_2$·**1**)[Zn(NCS)$_4$], $C_{38}H_{44}N_6O_4S_4Zn$, *Mr* = 842.42, Triclinic, $P\bar{1}$, a = 9.713(2) Å, b = 11.339(3) Å, c = 20.368(5) Å, α = 90.739(14) °, β = 101.951(14) °, γ= 113.263(13) °, V = 2005.0(8) Å^3, Z = 2, D_x = 1.395 Mg m^{-3}, refinement on F^2 (*SHELXL97*),[11] $wR(F^2)$ = 0.0873, $R(F)$ = 0.0338.
8. S. R. Petrusenko, V. N. Kokozay, and I. O. Fritsky, *Polyhedron*, 1997, **16**, 267.
9. E. Yamamoto, K. Kubo, and A. Mori, *Bull. Chem. Soc. Jpn.*, 2003, **76**, 627.
10. K. Kubo and A. Mori, *J. Mater. Chem.*, 2005, **15**, 2902.
11. G. M. Sheldrick, *SHELXL97*: Program for X-Ray crystal structure determination and refinement, Göttingen University, Germany, 1997.