Crystal Structure and Fluorescence Behavior of \(N,N'-\text{Bis} (1\text{-naphthylmethyl})\)-diaza-18-crown-6 Diisothiocyanate

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Abstract: \(N,N'-\text{bis} (1\text{-naphthylmethyl})\)-diaza-18-crown-6 (1) showed weak emissions, suggesting that photoinduced electron transfer (PET) from the amine group to the excited naphthalene occurs. The PET fluoroionophore (1) was found to display unique photophysical properties in the presence of a guest cation. Single crystals of the HNCS salt of 1 were grown from 1 and NH\(_4\)SCN. The crystal structure of the HNCS salt of 1 was elucidated by X-ray crystallographic analysis. The HNCS salt of 1 consists of a 1\(\cdot\)2H\(^+\) and 2NCS\(^-\) ion pair. The 1\(\cdot\)2HNCS salt gave an emission band at 332 nm. Complexation of 1 with HNCS increased the fluorescence intensity of the host by a factor of 29. The emission enhancement of 1 with HNCS was caused by the proton which dissociates from HNCS.

Key words: photoinduced electron transfer, fluoroionophore, diaza-18-crown-6, isothiocyanate, crystal structure

1 INTRODUCTION

Photo-responsive supramolecular systems are of great significance particularly because of their potential applications as environmental and biological analytical reagents\(^1\)\(^-\)\(^6\). Extensive attempts to characterize photoinduced electron transfer (PET) fluoroionophores such as donor-spacer-acceptor systems have been carried out. De Silva et al.\(^4\)\(^,\)\(^5\) have synthesized an azacrown ether with a 9-anthrylmethyl group as a PET fluoroionophore. Recently, it was found that diazacrown ethers with two fluorescent pendant groups showed a strong tendency to form inter- and intramolecular exciplexes and displayed fluorescence with low quantum yield\(^7\)\(^-\)\(^12\). The addition of guest cation enhanced the fluorescence emission intensity of \(N,N'-\text{bis} (1\text{-naphthylmethyl})\)-diaza-18-crown-6 (1) by a factor of 1.2\(\cdot\)41. The intensity ratio decreased in the following order: Ba\(^{2+}\) (41) > Ca\(^{2+}\) (15) > Zn\(^{2+}\) (5.4) > NH\(_4\)\(^+\) (4.9) > Mg\(^{2+}\) (3.5) > K\(^+\) (2.8) > Na\(^+\) (2.2) > Rb\(^+\) (1.5) > Li\(^+\) (1.3) > Cs\(^+\) (1.2). The crystal structures of 1\(^0\) and its lithium thiocyanate complex (1\(\cdot\)2LiNCS)\(^13\)\(^,\)\(^14\), potassium thiocyanate complex (1\(\cdot\)KNC(S)\(^15\), barium thiocyanate complex (1\(\cdot\)Ba(NCS)\(_2\) \(\cdot\) H\(_2\)O)\(^14\) and zinc thiocyanate complex (H\(_2\)\(\cdot\)1 [Zn(NCS)\(_4\)])\(^15\) were elucidated by X-ray crystallographic analyses. The K\(^+\) and Ba\(^{2+}\) cations were surrounded by the diazacrown nitrogen and oxygen atoms to form 1:1 complexes with the host crown ether (1). Diazacrown (1) forms a unique 1:2 complex with LiNCS; the Zn(NCS)\(_2\) complex of 1 consisted of a [Zn(NCS)\(_4\)]\(^2+\) and 1\(\cdot\)2H\(^+\) ion pair. In this paper, we report the crystal structure and fluorescence behavior of the HNCS salt of \(N,N'-\text{bis} (1\text{-naphthylmethyl})\)-diaza-18-crown-6 (1).
2 EXPERIMENTAL

2.1 X-ray crystallographic analysis of 1·2HNCS

Compound (1) was synthesized using a method similar to a previously reported method\(^{39}\). Single crystals of 1·2HNCS for X-ray analysis were grown in a chloroform and methanol solution (1:1 v/v) at room temperature. A colorless plate crystal of C\(_{12}\)H\(_{24}\)O\(_7\)N\(_8\)S\(_2\) of approximate dimensions of 0.17 \(\times\) 0.14 \(\times\) 0.03 mm was mounted on a glass fiber. All measurements were made on a Rigaku Raxis-Rapid imaging plate with graphite monochromated Cu K\(\alpha\) radiation (\(\lambda = 1.54187\) Å). The data collection and cell refinement: Rigaku Raxis-Rapid. Data reduction: Crystal Structure 3.8.\(^{39}\) Refinement: SHELXL97\(^{46}\). Molecular graphics: ORTEP-III and Mercury 1.4.2\(^{47}\). All H atoms were fixed to 1.2U eq of the parent atoms. Cambridge Crystallographic Data Centre (CCDC) 780163 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Crystal data for 1·2HNCS: C\(_{12}\)H\(_{24}\)O\(_7\)N\(_8\)S\(_2\) monoclinic, \(\overline{P}_{\text{I}}\), \(a = 8.808(4)\) Å, \(b = 13.934(7)\) Å, \(c = 15.114(7)\) Å, \(\alpha = 104.49(3)\)°, \(\beta = 101.37(3)\)°, \(\gamma = 105.76(3)\)°, \(V = 1657.1(14)\) Å\(^3\), \(Z = 2\), \(M_\text{r} = 660.89\), \(D_\text{c} = 1.324\) mg m\(^{-3}\), \(\mu = 18.242\) cm\(^{-1}\), \(T = 297(1)\) K, refinement on \(F^2\) (SHELXL97), \(R[F>2\sigma(F)] = 0.0668\), \(wR(F^2) = 0.1334\), and \(S = 0.825\).

2.2 Fluorescence spectral measurements of 1 and 1·2HNCS

Fluorescence spectra were measured with a JASCO Model FP-6500 spectrofluorimeter (JASCO, Easton, MD, USA). Fluorescence spectra of 1 (2.0 \(\times\) 10\(^{-5}\) M, 1 M = 1 mol dm\(^{-3}\)), 1-methylnaphthalene (1MN, 4.0 \(\times\) 10\(^{-5}\) M), and 1·2HNCS (2.0 \(\times\) 10\(^{-5}\) M) excited at 280 nm were measured in methanol under nitrogen at room temperature.

3 RESULTS AND DISCUSSION

The naphthalene-functionalized diaza-18-crown-6 (1) was prepared by N-alkylation of diaza-18-crown-6 with 1-chloro-3-methylnaphthalene in toluene-triethylamine using a previously reported method\(^{39}\). Single crystals of 1·2HNCS were grown from 1 and NH\(_4\)SCN in a mixture of methanol-chloroform (1:1 v/v). The structure of 1·2HNCS was confirmed by X-ray crystallographic analysis. The crystal structure and selected geometric parameters of 1·2HNCS are shown in Fig. 1 and Table 1.

The HNCS salt of 1 consists of a 1·2H\(\ddagger\) and 2NCS\(\ddagger\) ion pair. The distances between the ammonium H atom and the isothiocyanate anion are 1.84(4) Å for H43···N3 and 1.88(5) Å for H44···N4; these lengths are shorter than the sum(2.5 Å)\(^{18}\) of their van der Waals radii. The N-C-S angles are 178.7(3)° for N3-C35-S1 and 178.8(4)° for N4-C35-S2. The two NCS\(\ddagger\) anions (N3-C35-S1 and N4-C35-S2) make angles of 39.49(3)° and 51.15(3)° with the diaza-18-crown-6 ring (defined by C23-C34/01-04/N1/N2).

The two naphthalene rings have an anti conformation with respect to one another across the diaza-18-crown-6 ring (Fig. 1). The conformations of 1·2HNCS is similar to that of 1\(^\ddagger\), 1·KCNSe\(^{44}\), and H\(_2\)·1·[2Zn(NCS)\(_{\ddagger}\)]\(^{19}\). The angle of the intersection between the least-squares plane of naphthalene ring A, defined by C11-C10, and ring B, defined by C12-C21, and the diaza-18-crown-6 ring are 115.0(1)° and 114.2(1)°, respectively. Selected bond distances and torsion angles are shown in Table 1. The conformations of the diazacrown ether rings are N1-C23 (10.14°), N2-C24 (0.27°), O1-C25 (13.51°), O2-C26 (0.88°), C27-C28 (12.38°), C30-C31 (12.65°), C32-C33 (12.35°), C34-C35 (15.08°), C35-S1 (178.8°) and 178.8° for N3-C35-S1 and 178.8° for N4-C35-S2.

Intermolecular \(\pi\)–\(\pi\) interactions between the naphthalene planes are observed (Fig. 2). The distances between the intermolecular naphthalene planes are 3.529(5) Å for C12···C18 [symmetry code: (i) 2-x, 2-y, 1-z] and 3.616 (5) Å for C9···C10 [symmetry code: (ii) 1-x, 1-y, 1-z], which are within the range associated with \(\pi\)–\(\pi\) interactions [3.3–3.8 Å]\(^{19,21}\). There are some intermolecular C···H-O interactions, as shown in Fig. 2 and Table 2. The H42···O4[ (iii) 1+x, y, z, (iv) x-1, y, z] distances are similar to those of 7,16-bis(1-pyrenylmethyl)-1,4,10,13-tetraoxa-7,16-diazacyclopentadecane (2.85 Å)\(^{22}\) and N\(_2\)N′-di(tronon-2-yl)piperazine (2.50–2.64 Å)\(^{23}\).

Intermolecular C-H···\(\pi\), C-H···N, and C-H···S interactions between 1 and NCS\(\ddagger\) are observed in the crystal structure of 1·2HNCS, as shown in Fig. 3 and Table 2. The H···N distances are similar to those of 5-benzyl-1,3,5-tri(methyl)pyrimidine-2,4,6-(1H,3H,5H)-trithione (2.85 and 2.95 Å)\(^{24}\). The H···C distance for C-H···\(\pi\) interactions are within the range of typical C-H···\(\pi\) interactions (C-H···\(\pi\) = 2.8–3.1 Å)\(^{25,26}\). The H···N distances (2.642 and 2.665 Å) are shorter than those of 2,2'-bi-2-imidazoline (2.91 and 2.97 Å)\(^{28}\). The combinations of intermolecular C-H···\(\pi\), C-H···O, C-H···N and C-H···S interactions in 1·2HNCS...
build up a three-dimensional network.

3.1 Fluorescence spectral behavior of 1·2HNCS

Figure 4 show the fluorescence spectra of 1 (2.0 × 10^{-5} M), 1-methylnaphthalene (1MN, 4.0 × 10^{-5} M), and 1·2HNCS (2.0 × 10^{-5} M) excited at 280 nm and measured in methanol under nitrogen at room temperature.

As reported before, 1 gave a broad emission band with a maximum at 472 nm in addition to emission band at 332 nm. The formation of a intramolecular exciplex should be

| N1-C11 | 1.518(4) | N1-C23 | 1.507(5) |
| N1-C34 | 1.512(5) | N2-C22 | 1.522(4) |
| N2-C28 | 1.508(5) | N2-C29 | 1.522(6) |
| N3-C35 | 1.161(6) | N4-C36 | 1.154(6) |
| S1-C35 | 1.631(5) | S2-C36 | 1.632(5) |
| S1-C35-N3 | 178.7(3) | S2-C36-N4 | 178.8(4) |

Table 1 Selected geometric parameters (Å, °) of 1·2HNCS

Fig. 2 Intermolecular π···π and C-H···O interactions of 1·2HNCS. symmetry codes: (i) 2-x, 2-y, 1-z, (ii) 1-x, -y, -z, (iii) 1 + x, y, z, (iv) x-1, y, z.

Table 2 Hydrogen-bond geometry (Å , °) of 1·2HNCS

Fig. 3 Intermolecular C-H···π, C-H···N, and C-H···S interactions between 1 and NCS⁻. Symmetry code: (v) x, 1+y, z, (vi) 1+x, y, z, (vii) 1+x, 1+y, z, (viii) 1-x, 1-y, 1-z, (ix) x-1, y, z, (x) x, y-1, z, (xi) 1-x, 1-y, -z.
emission enhancement of a stronger emission band at 332 nm than that of NH₄SCN also may be due to the proton dissociates from NH₄SCN. PET fluoroionophore quantum yield of fluorescence recovery ment is due to protonation to the two nitrogen atoms of the excited naphthalene chromophore by the diazacrown unit. The latter emission-band intensity of 1·2HNCS was higher than that of 1·2HNCS salt showed fluorescence intensity ratio (I₁·2HNCS/I₁MN) was 29. The fluorescence enhancement is due to protonation to the two nitrogen atoms of the diazacrown ring. A measure of the guest induced fluorescence recovery (I₁·2HNCS/I₁MN) would also be important parameter instead of fluorescence quantum yield to evaluate PET fluoroionophore. The fluorescence intensity ratio (I₁·2HNCS/I₁MN) was 0.23, indicating that the fluorescence quantum yield of 1·2HNCS is smaller than that of 1MN (Φᵢ = 0.21).

4 CONCLUSION

In conclusion, the crystal structure of 1·2HNCS, which obtained from 1 and NH₄SCN, was elucidated by X-ray crystallographic analysis. The HNCS salt of 1 consists of an ion pair with 1·2H⁺ and 2NCS⁻. The 1·2HNCS salt showed a stronger emission band at 332 nm than that of 1. The emission enhancement of 1·2HNCS occurred by the proton of HNCS. Therefore the emission enhancement of 1 with NH₄SCN also may be due to the proton dissociates from NH₄SCN. PET fluoroionophore (1) could be used as a pH fluorescent sensor.

References

Fig. 4 Fluorescence spectra of 1 (2.0 × 10⁻⁵ M), 1-methylnaphthalene (1MN, 4.0 × 10⁻⁵ M), and 1·2HNCS (2.0 × 10⁻⁵ M) in methanol, excited at 280 nm.
N,N'-Bis(1-naphthylmethyl)-diazonia-18-crown-6 Diisothiocyanate


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