Syntheses of Photoresponsive Cyclobutane-1,2-dicarbonyl-capped 2·n Diazacrown Ethers by Intramolecular [2 + 2]Photocycloaddition and the Structures of their Lithium and Mercury(II) Complexes
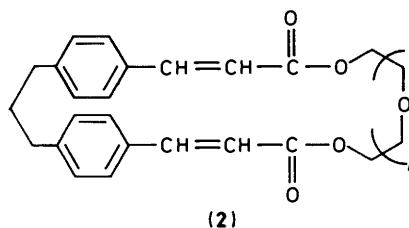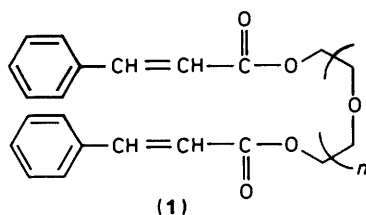
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Photoresponsive cyclobutane-1,2-dicarbonyl-capped 2·n diazacrown ethers (7) have been prepared by intramolecular [2 + 2]photocycloaddition of p,p'-trimethylenedicinnamoyl-capped 2·n diazacrown ethers (5); the cyclobutane-1,2-dicarbonyl-capped 2.1 diazacrown ether (7a) showed a highly selective complexing ability for the lithium cation, although (5) did not show any complexing abilities for alkali, alkaline-earth, and other metal ions. The crystal structures of (5a), the 1:1 lithium and mercury(II) thiocyanate complexes (8) and (9) of (7a) have been determined by X-ray analyses. The structures of (8) and (9) revealed that the configuration of the cyclobutane ring is in the β-form and slightly distorted. Complex (8) consists of dimeric molecules in which the lithium atom is directly bonded to the two oxygen atoms of the amido groups and the two nitrogen atoms of the thiocyanate group of the counter anion and adjacent complex in a slightly distorted tetrahedral configuration. The Hg atom in (9) is also bonded directly to the two oxygen atoms of the amido groups, the two sulphur atoms of the thiocyanate groups, and the simple nitrogen atom of the counter anion of the adjacent complex in a distorted trigonal bipyramidal configuration.

Since 1973 many crown ethers have been synthesized which exhibit selective complexing abilities towards alkali, alkaline-earth, and other metal and/or ammonium ions.[1] Recently, many kinds of photoresponsive crown ethers have been investigated by several research groups with the aim of controlling the extraction ability of crown ethers by light or thermal means.[2] For example, the alkali cation binding abilities of benzocrown ethers containing the azo group were enhanced by photo-irradiation. Cyclobutanocrown ethers formed by intramolecular [2 + 2]photocycloaddition have received attention from the viewpoint of crown ether synthesis in this respect.[3] However, these reports did not describe the possibility of a photoreversible cleavage of the cyclobutanocrown ethers in order to control the complexing ability. Egerton et al.[4] reported that irradiation of cinnamic acid with >300 nm u.v. light gave a dimer by means of intramolecular [2 + 2]photocycloaddition, while irradiation of the dimer with 200 nm u.v. light gave, in contrast, the corresponding starting monomer. In concert with these findings, we have reported the syntheses of cyclobutanocrown ethers by the intramolecular [2 + 2]photocycloaddition of α,ω-dicinnamoyl polyethylene glycol derivatives (1) and (2), and

extraction abilities toward alkali and alkaline-earth metal ions due to the presence of the ester groups in the crown ether moiety, although its structure takes the β-form.[6] As a consequence of this reaction, we have studied the syntheses of photoresponsive cyclobutane-1,2-dicarbonyl-capped 2·n diazacrown ethers (7) by the intramolecular [2 + 2]photocycloaddition of p,p'-trimethylene dicinnamoyl-capped 2·n diazacrown ethers (5) in order to improve the complexing ability of the photoresponsive cyclobutanocrown ethers with alkali metal ions.[7]

Results and Discussion

Synthesis of p,p'-*Trimethylenedicinnamoyl-capped* 2·n *Diazacrown Ethers* (5).—Condensation of (3) with (4a) in benzene in the presence of triethylamine gave (5a) in a 28% yield, together with its dimer (6a) in a 7.7% yield. Also (5b) and (6b) were obtained in 14 and 9.1% yields respectively by the same method. The structures of these products were established by their elemental analyses and ^{1}H n.m.r. mass spectral data and/or gel-permeation chromatography. The ^{1}H n.m.r. spectrum of (5b) showed the signals of the trimethylene protons at δ 2.40—

(1)

(2)

their photoreversible reactions.[5,6] The extraction of abilities of the cyclobutanocrown ethers derived from (1) toward alkali metal cations were found to be very low or negligible as a result of the structures being in the δ form, containing ester groups in the macrocycle, a disadvantageous feature for complexation.[5] Also the cyclobutano crown ether derived from (2) showed low

2.06 (m, 2 H) and 2.90—2.52 (m, 4 H), and the signals of the p-phenylene protons at δ 7.16—6.57 (m, A_2B_2 pattern, 8 H) together with the signals of olefinic protons as a pair of A_2B_2 patterns at δ 7.47 (2 H, d, *J* 15.4 Hz) and 6.66 (2 H, d, *J* 15.4 Hz). However, the signals of the p-phenylene protons of the dimers (6a) and (6b) were shifted downfield (ca. 0.40 p.p.m.) compared
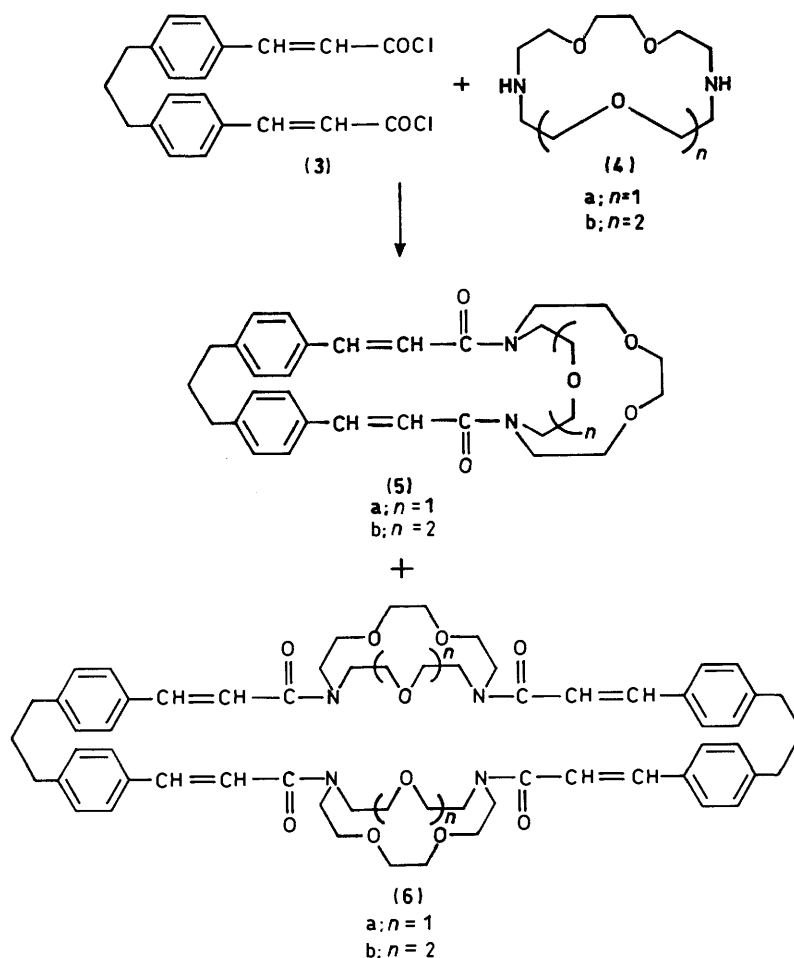
with those of their respective monomers as a result of decreases in the anisotropic effect[8] caused by the aromatic rings being placed opposite. Furthermore, the parent peaks M^+ of the dimers in the mass spectra could not be obtained, although the M^+ values of the corresponding monomers agreed well with the calculated values. We then examined the behaviour of (6a) and (6b) on gel-permeation chromatography. Compounds (6a) and (6b) had longer retention times than the corresponding monomers (5a) and (5b). The molecular weights of (6a) and (6b), which were calculated from the retention times using the calibration curves, were nearly all consistent with the expected values of the dimers.

Intramolecular [2 + 2]Photocycloaddition of (5) and Its Photoreversible Reactions.—Irradiation of (5a) and (5b) in acetonitrile for 1.5 h under a nitrogen atmosphere at ambient temperature (Pyrex filter with a 450 W high-pressure mercury lamp) in the absence of any sensitizer gave (7a) and (7b) in 91.7
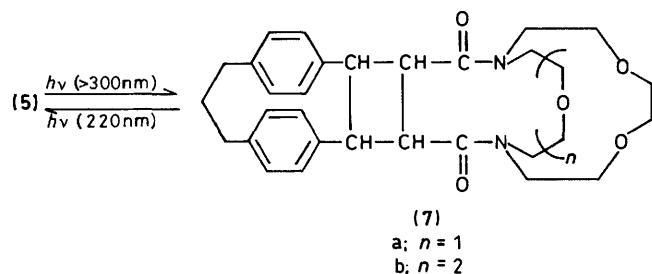
and 31.6% yields, respectively. X-Ray analysis of (5a) shows that the two carbon–carbon double bonds lie in the same direction and that the distance between the two double bonds is ca. 4.7—4.8 Å as described below. This distance is much longer than that observed for olefinic compounds (4.0 Å)[9] in which inter-molecular [2 + 2]photocycloaddition can occur in the crystalline state. Indeed, the attempted intramolecular [2 + 2]photocycloaddition of (5) in the solid state failed. Many research groups[9] reported that the *trans-cis* isomerization of the carbon–carbon double bond in ethyl cinnamate generally competes with the photodimerization. In the above photoreaction, however, the main product was the β-isomer, although very small amounts of side-reaction products were observed by means of t.l.c. Therefore, the intramolecular [2 + 2]photocycloaddition of (5) must have occurred after the two double bonds approached within 4.0 Å of each other, made possible by the molecular flexibility of (5) in solution before *trans-cis* isomerization of the two carbon–carbon double bonds could occur. The respective configuration of (7a) and (7b) were elucidated by comparison of their n.m.r. spectra with those of the corresponding starting materials and a 2D COSY n.m.r. study of (7b). Since in compounds (7a) and (7b) the bridge chain is too short to allow the formation of a δ-isomer, these intramolecular [2 + 2]photocycloadducts should be the β-isomer. Indeed, this was substantiated by the fact that, in the n.m.r. spectra, the aromatic protons absorb at a higher field where they are deshielded by the opposite aromatic groups, thus producing spectra differing from those of the starting materials (5a) and (5b). The results are also confirmed by X-ray analyses of the 1:1 complexes, (8) and (9), of (7a) with lithium
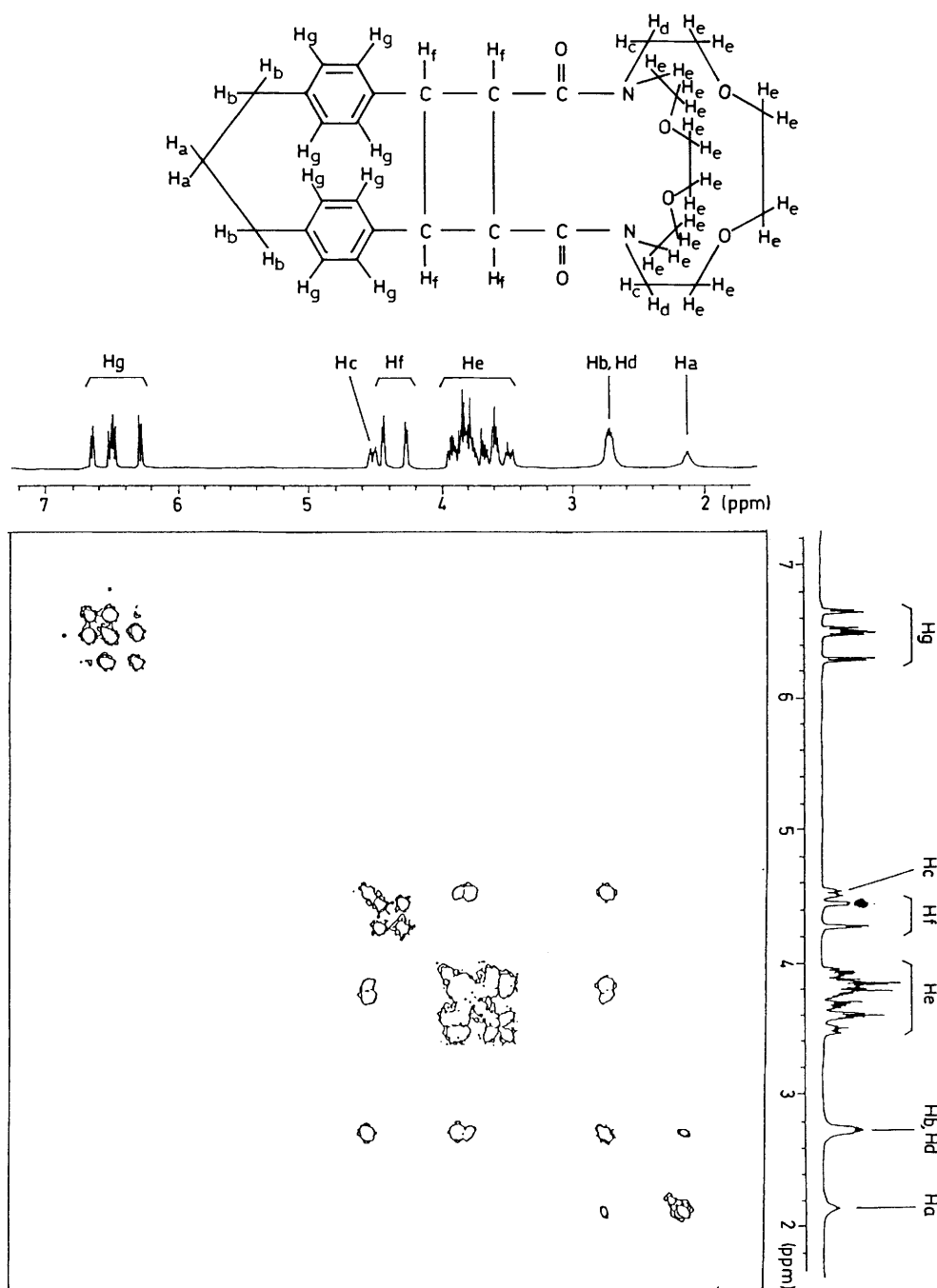
Figure 1. The 2D ^{1}H COSY spectrum of (7a) in CDCl$_3$ at room temperature

Table 1. Extraction of metal picrates* from the aqueous phase † to the organic phase (%)

Compd	Li$^+$	Na$^+$	K$^+$	Rb$^+$	Cs$^+$	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Ag$^+$
(5a)	1	1	1	1	0	1	0	0	0	0	1	0	2
(7a)	39	24	27	25	33	8	10	10	11	19	19	25	39
(5b)	0	0	1	1	1	0	0	0	1	0	0	0	5
(7b)	1	1	1	1	1	1	0	1	0	1	0	1	4

* Azacrown ether = 7.0 × 10^{-4} M, picric acid = 7.0 × 10^{-5} M, and metal nitrate = 0.1 M. † Solvent: Water and dichloromethane (equal volumes).

thiocyanate and mercury (II) thiocyanate as described below. Compound (7b) is sterically very crowded and shows interesting properties: for example, in the 2D COSY ^{1}H n.m.r. spectrum of (7b) as shown in Figure 1, the chemical shift of one proton of the

methylene group adjacent to the nitrogen atom is ca. 0.8 p.p.m. further downfield than that of the starting material (5b), whereas the other proton on the same carbon atom is generally found upfield (ca. 1.00 p.p.m.) from that of (5b). As expected from the
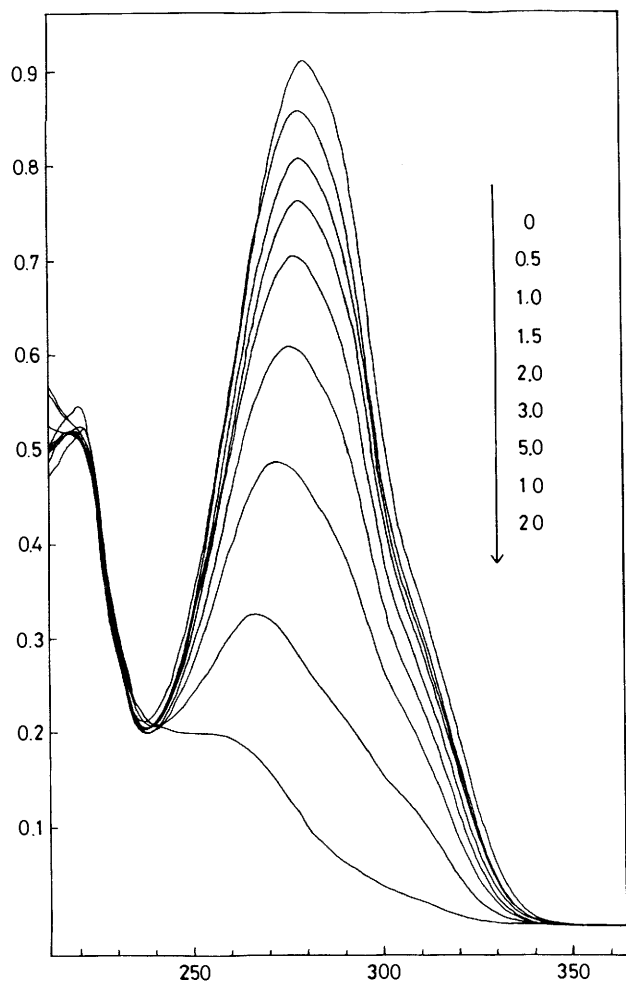
Figure 2. Spectral changes of (5a) to (7a) in acetonitrile (2.00 × 10⁻⁴ mol/l). The numbers beside the arrow are the elapsed irradiation times (min)
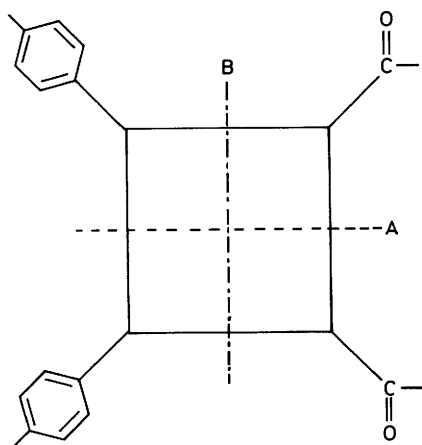

Figure 3.

Corey-Pauling-Koltum (CPK) model, the upfield and downfield shifts of the methylene protons can be attributed to steric compression[10] between the carbonyl group and the methylene protons adjacent to the nitrogen atom.

Photoreversible Reaction between (5) *and* (7).—An acetonitrile solution of the pure (5a) was irradiated with 220 nm u.v. light using a grating monochrometer with a 500 W xenon lamp. As is shown in Figure 2, the absorption band at 275 nm increased with u.v. irradiation of the solution, and a steady state was
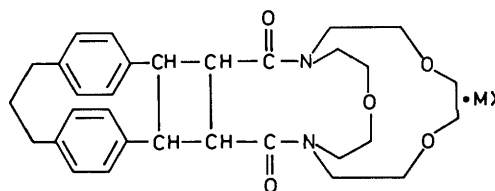
(8) M=Li, X=SCN
(9) M=Hg,X=(SCN)₂

attained after 3 h. The structure of the irradiated products were confirmed by direct comparison of the R_F values from t.l.c. and the spectral data with those of authentic samples. Irradiation of pure (5b) was also carried out by the same method. The photoreversible cleavages of (7a) and (7b) gave (5a) and (5b) in 44.8 and 39.1% yields, respectively, calculated from the intensity of the absorption bands at 275 nm in the steady state. T.l.c. of the irradiated solution of (7) shows also the presence of two other reaction products, although the structures of the products were not confirmed because the yields of the side reaction products were very low. The results suggest that, in the photoreversible reaction of (7)—(5), the cleavage (fashion A) of the C–C single bonds in the cyclobutane ring occurred together with the cleavage (fashion B) of the C–C bonds,[4] as is shown in Figure 3, although another cleavage cannot be ruled out. However, the photoreversible reaction between (5) and (7) suggests the possibility of its use controlling the extraction ability of the metal ions by those crown ethers, although the yields of the reversible reactions are relatively low because of the side reactions.

Complexing Ability of (5) *and* (7) *with Metal Ions.*—The complexing ability of the crown ether with metal cations depends on several factors.[11] These include cavity size of the ligands, cation diameter, spatial distribution of the ring binding sides, and the character of the heteroatoms, etc. Also the study of *n·n·n* cryptands[12] has shown that a three-dimensional arrangement of binding sites leads to very stable inclusion complexes (cryptates) with many cations. For example, the stability constant for K⁺ is five orders of magnitude higher with the 2.2.2 cryptand than the 2.2 cryptand. Therefore, in order to compare the complexing ability of (7) with that of the corresponding starting crown ether (5), the extraction abilities of (5) and (7) for a variety of metal cations were measured by the method described by Pedersen[13] and the results are summarized in Table 1. It was found that (7a) extracts Li⁺ most efficiently among the alkali metal ions, although (5a), (5b), and (7b) did not show any extraction ability toward them. The extraction ability of (5a) was found to be: Li⁺ > Cs⁺ > K⁺ > Rb⁺ > Na⁺. Furthermore, (5a) showed a high extraction ability toward the silver(I) cation. These findings are in contrast to the results obtained by Vogtle *et al.*[14] That is, they suggest the complexing ability of the *p*-xylyl-capped 2.2 diazacrown ethers for alkali metal ions is selective towards the sodium ion. Also *N,N′*-dimethyl-2.1-diazacrown ether shows higher extraction abilities toward Ca²⁺, Sr²⁺, and Ba²⁺ compared with alkali metal cations.[15] In the case of alkali metal cations, the extraction ability of the diazacrown ethers show very low complexing ability, especially toward Li⁺ cation. The cavity sizes of (5a), (5b), (7a), and (7b) estimated from CPK molecular models are *ca.* 0.5—1.5, 1.5—3.0, 0.8—1.5, and 1.7—2.5 Å, respectively. The cavity sizes of (5a), (5b), and (7b) are sufficiently compatible with the diameter of Rb⁺ cation to allow complexing. However, (5a), (5b), and (7b) did not show any extraction abilities toward alkali and other metal cations as described above. The reasons for the low complexing ability of

Table 2. Fractional atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses for compound (5a)

Atom	x	y	z
C(1)	8 346(2)	2 412(4)	8 572(3)
N(2)	7 936(2)	3 433(3)	8 130(2)
C(3)	7 975(2)	3 719(4)	7 216(3)
C(4)	7 239(2)	3 735(5)	6 493(3)
O(5)	6 809(1)	2 643(3)	6 407(2)
C(6)	6 107(2)	2 644(5)	5 705(3)
C(7)	5 623(2)	1 582(5)	5 725(3)
O(8)	5 459(2)	1 415(4)	6 476(2)
C(9)	4 992(2)	329(5)	6 528(3)
C(10)	4 663(2)	597(4)	7 271(3)
N(11)	5 223(2)	608(3)	8 187(2)
C(12)	5 554(2)	1 869(4)	8 569(3)
C(13)	6 384(2)	1 949(4)	8 622(3)
O(14)	6 677(1)	3 169(2)	9 051(2)
C(15)	6 754(2)	4 186(4)	8 465(3)
C(16)	7 576(2)	4 411(4)	8 547(3)
C(17)	5 386(2)	−523(4)	8 638(3)
C(18)	5 913(2)	−508(4)	9 601(3)
C(19)	6 335(2)	−1 518(4)	9 951(3)
C(20)	6 866(2)	−1 610(4)	10 888(3)
C(21)	6 758(2)	−908(4)	11 600(3)
C(22)	7 274(2)	−1 009(4)	12 478(3)
C(23)	7 916(2)	−1 805(4)	12 674(3)
C(24)	8 027(2)	−2 486(4)	11 963(3)
C(25)	7 504(2)	−2 420(4)	11 081(3)
C(26)	8 467(2)	−1 959(4)	13 637(3)
C(27)	8 823(2)	−701(4)	14 057(3)
C(28)	9 485(2)	−243(4)	13 776(3)
C(29)	9 293(2)	121(4)	12 772(3)
C(30)	9 706(2)	−400(4)	12 258(3)
C(31)	9 556(2)	−16(4)	11 365(3)
C(32)	8 978(2)	870(3)	10 952(2)
C(33)	8 550(2)	1 380(4)	11 470(3)
C(34)	8 714(2)	1 002(4)	12 375(3)
C(35)	8 856(2)	1 281(4)	10 003(3)
C(36)	8 378(2)	2 174(4)	9 536(3)
O(37)	8 683(2)	1 686(3)	8 194(2)
O(38)	5 111(2)	−1 536(3)	8 260(2)

Table 3. Fractional atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses for compound (8)

Atom	x	y	z
C(1)	5 435(9)	2 309(9)	5 872(16)
N(2)	5 196(7)	1 790(7)	6 574(12)
C(3)	4 530(11)	2 163(11)	6 977(19)
C(4)	4 781(14)	2 125(10)	8 181(22)
O(5)	5 560(10)	2 633(8)	8 837(17)
C(6)	5 566(18)	3 353(19)	9 083(32)
C(7)	6 371(13)	3 821(10)	9 793(17)
O(8)	7 080(7)	3 652(7)	9 447(10)
C(9)	7 030(13)	4 184(10)	8 539(14)
C(10)	7 806(12)	3 964(12)	8 209(16)
N(11)	7 709(6)	3 176(8)	7 500(10)
C(12)	8 258(9)	2 393(11)	8 077(14)
C(13)	7 793(12)	1 753(11)	9 591(15)
O(14)	7 071(7)	1 376(6)	7 669(10)
C(15)	6 401(11)	976(10)	7 996(15)
C(16)	5 577(10)	911(9)	7 015(16)
C(17)	7 170(7)	3 246(9)	6 466(11)
C(18)	7 003(8)	2 441(9)	5 685(12)
C(19)	6 701(8)	2 666(9)	4 437(13)
C(20)	7 326(8)	2 338(8)	3 828(13)
C(21)	7 988(9)	1 719(9)	4 247(13)
C(22)	8 276(8)	1 240(10)	3 532(13)
C(23)	7 892(8)	1 365(9)	2 402(13)
C(24)	7 323(10)	2 072(9)	1 975(16)
C(25)	7 041(9)	2 555(8)	2 701(13)
C(26)	8 022(12)	678(11)	1 580(17)
C(27)	7 201(18)	198(19)	763(24)
C(27')	7 608(18)	−97(17)	1 525(22)
C(28)	6 608(13)	−287(11)	1 162(18)
C(29)	6 205(9)	147(9)	1 942(15)
C(30)	5 542(10)	812(10)	1 510(13)
C(31)	5 365(8)	1 368(9)	2 281(13)
C(32)	5 809(7)	1 300(9)	3 391(11)
C(33)	6 375(9)	557(9)	3 830(16)
C(34)	6 571(9)	10(8)	3 077(14)
C(35)	5 847(8)	2 100(9)	4 155(12)
C(36)	6 110(8)	1 937(8)	5 406(11)
C(37)	5 119(7)	3 047(6)	5 574(10)
O(38)	6 768(6)	3 969(6)	6 070(9)
Li(39)	5 546(18)	4 230(13)	5 453(22)
S(40)	4 357(3)	4 004(3)	1 814(4)
C(41)	4 890(9)	4 431(8)	2 986(12)
N(42)	4 927(9)	4 730(7)	3 821(10)

(5a), (5b), and (7b) is attributed to a special distribution of ring binding sites and the character of the heteroatom of the diazacrown ether moiety. For example, in (5a) there are three oxygen atoms and two nitrogen atoms which may take part in co-ordination. However, the co-ordinating ability of the nitrogen atom is decreased by the electron attracting properties of the substituent carbonyl group. Furthermore, the direction of the lone pair electrons of the nitrogen atoms toward the incorporated cation is lower down the axis of the other oxygen atom due to the rigidity of the bridged molecular structure. Therefore, only three oxygen atoms of the five heteroatoms in the diazacrown ether moiety of (5a) can contribute to the complexing ability. Also, the negligible extraction ability of (5b) and (7b) can be ascribed to the same reason, although (5b) and (7b) have four oxygen atoms and two nitrogen atoms which may take part in co-ordination.

Isolation of the Complexes (8) *and* (9).—Lithium thiocyanate reacted in acetonitrile with (7) to precipitate a 1:1 complex (8) as colourless needles in 65% yield. When mercury(II) thiocyanate was treated similarly, a 1:1 complex (9) was isolated as colourless needles in 31% yield. In the ^{1}H n.m.r. spectrum of (8), one proton of the methylene protons adjacent to the nitrogen atom, which overlapped with the benzyl protons in (7a), were shifted downfield *ca.* 0.27 p.p.m. Also the protons of the cyclobutane ring were shifted downfield *ca.* 0.22—0.31
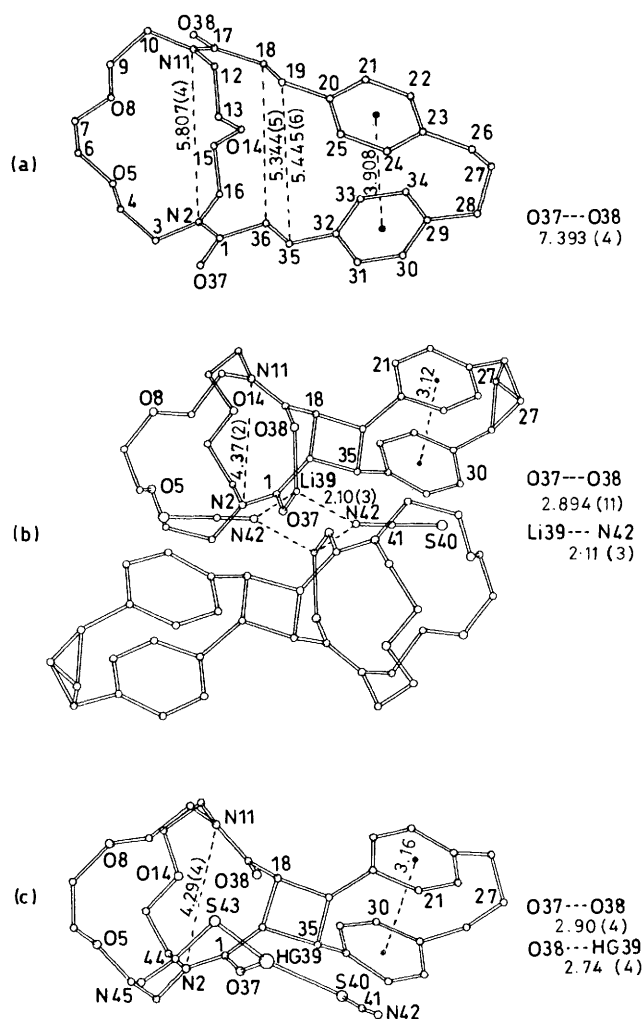
p.p.m. compared with those of (7a). However in complex (9), the methylene protons described above were shifted downfield less (*ca.* 0.04—0.07 p.p.m.) than those in (7a). Although none of the other protons showed noteworthy n.m.r. shifts, in the i.r. spectra of complexes (8) and (9), the stretching bands of the C=O and C≡N bonds did show marked shifts. For example, the γ(C=O) of (7a) appeared at 1 628 cm^{-1}, although that of (8) shifted to 1 610 cm^{-1}. However that of (9) shifted only slightly to 1 630 and 1 623 cm^{-1}. The γ(C≡N) band of (8) shifted to 2 040 cm^{-1} and that of (9) shifted and separated to 2 075, 2 105, and 2 130 cm^{-1}, respectively, compared with that (2 100 cm^{-1}) of LiSCN and/or Hg(SCN)$_2$. The above results imply that the guest molecule (LiSCN and/or Hg(SCN)$_2$) was not incorporated into the cavity of the diazacrown ether moiety of (7) and the oxygen atoms of the two amido groups co-ordinated to the metal ions. Furthermore, the separation of the γ(C≡N) band in the i.r. spectrum of (9) to 2 075, 2 105, and 2 130 cm^{-1} means there are three kinds of SCN bonds in (9) as described below, although such separation of the γ(C≡N) band could not be observed in (8).

X-Ray analysis of (5a), (8), *and* (9). In order to investigate the structures in more detail, the X-ray analysis of (8) and (9) was

Table 4. Fractional atomic co-ordinates ($\times 10^4$) *parameters* (A^2), with estimated standard deviations in parentheses for compound (9)

Atom	x	y	z
C(1)	9 055(7)	−81(28)	7 619(32)
N(2)	9 289(6)	−229(31)	8 671(22)
C(3)	9 669(10)	−565(40)	8 437(30)
C(4)	9 909(10)	634(53)	7 738(32)
O(5)	9 961(6)	1 941(29)	8 612(24)
C(6)	10 172(13)	3 126(59)	7 957(55)
C(7)	10 057(14)	4 535(66)	7 957(63)
O(8)	9 612(8)	5 043(31)	8 098(29)
C(9)	9 414(16)	5 011(53)	6 867(41)
C(10)	8 974(12)	5 282(50)	6 996(42)
N(11)	8 747(8)	4 200(32)	7 503(31)
C(12)	8 661(10)	4 655(44)	8 674(45)
C(13)	8 934(10)	4 054(52)	9 746(43)
O(14)	8 930(7)	2 426(28)	9 740(23)
C(15)	9 244(9)	1 596(55)	10 359(35)
C(16)	9 234(9)	1(28)	9 933(26)
C(17)	8 684(8)	2 809(35)	6 841(31)
C(18)	8 430(7)	1 633(44)	7 495(28)
C(19)	8 181(9)	641(41)	6 429(31)
C(20)	7 732(9)	697(39)	6 533(34)
C(21)	7 541(9)	−259(56)	5 610(33)
C(22)	7 151(9)	−749(39)	5 859(28)
C(23)	6 973(9)	−120(41)	6 744(31)
C(24)	7 149(9)	1 018(43)	7 511(38)
C(25)	7 522(9)	1 421(40)	7 305(35)
C(26)	6 609(9)	−980(50)	7 155(37)
C(27)	6 617(11)	−2 752(42)	7 528(39)
C(28)	6 875(10)	−3 332(54)	8 616(34)
C(29)	7 322(10)	−2 977(43)	8 459(29)
C(30)	7 534(11)	−1 925(48)	9 126(33)
C(31)	7 877(13)	−1 357(44)	8 842(29)
C(32)	8 033(8)	−1 926(41)	7 885(26)
C(33)	7 852(11)	−3 282(43)	7 286(33)
C(34)	7 487(9)	−3 702(45)	7 673(35)
C(35)	8 322(10)	−1 009(37)	7 200(30)
C(36)	8 631(11)	65(29)	8 036(28)
O(37)	9 128(5)	−374(31)	6 544(25)
O(38)	8 782(7)	2 699(29)	5 861(16)
HG(39)	9 118(1)	284(2)	4 671(2)
S(40)	8 662(3)	−1 820(14)	4 220(12)
C(41)	8 736(12)	−1 956(41)	2 597(36)
N(42)	8 750(8)	−2 038(47)	1 677(30)
S(43)	9 484(3)	2 544(15)	4 153(12)
C(44)	9 886(8)	1 865(59)	4 395(40)
N(45)	10 208(7)	1 642(38)	4 739(28)

Figure 4. The molecular structures of (a) (**5a**), (b) (**8**), and (c) (**9**) with selected interatomic distances (Å) and the atom numbering scheme. A filled circle denotes the centroids of the phenyl rings

carried out. The final atomic parameters for (**5a**), (**8**), and (**9**) are listed in Tables 2, 3, and 4 and the molecular structures are illustrated in Figure 4. As is shown in Figure 4a, the two double bonds in (**5a**) are *trans* and situated in such positions relative to each other as to make the ring closure possible. Also the alkene–alkene distances [C(19)···C(35) and C(18)···C(36)] are 5.445(6) and 5.344(5) Å, respectively. The distance between the centroids of the two phenyl groups and the dihedral angle between the two phenyl groups are 3.908 Å and 28.2(1)°, respectively, and the intramolecular distances between the N(2)···N(11) atoms, and O(37)···O(38) are 5.807 and 7.393(4) Å, respectively. In (**8**) no special disorder was observed for guest molecule or the host molecule except for the trimethylene group. Trimethylene groups are notoriously difficult to refine owing to their potential for disorder. As shown in Figure 4b, the configuration of the cyclobutane ring moiety is a slightly distorted β-form and the dihedral angle between the planes of C(18)–C(19)–C(35) and C(19)–C(18)–C(36) is 6.0(16)°. The distance (3.12 Å) between the centroids of the two phenyl groups and the dihedral angle [8.4(6)°] of the two

phenyl groups are smaller than those in (**5a**) due to intra-molecular [2 + 2]photocyclization of (**5a**). Furthermore, the intramolecular distances between O(37) and O(38) of the amido groups, and N(2) and N(11) are 2.894 and 4.37(2) Å, respectively. The complexing manner differs completely from that of the complexes of crown and azacrown ethers with metal ions in which the metal ions are incorporated into the cavity of the macrocyclic moiety of the host molecule. Complex (**8**) consists of dimeric molecules in which the lithium ion is bridged by the nitrogen atom of the thiocyanate group of the counter anion. The bridging Li_2N_2 unit is constrained to be planar by the presence of the crystallographic inversion centre in the middle of the dimer, and the lithium ions are complexed by co-ordination to the two oxygen atoms of the two amido groups and two nitrogen atoms of the thiocyanate groups of the counter anion with slightly distorted tetrahedral configuration. The bond distances of Li–O(37), Li–O(38), Li–N(42), and Li–N(42′)(1 − x, 1 − y, 1 − z) are 1.93(2), 1.90(2), 2.10(3), and 2.11(3) Å, respectively. The bond angles around the Li atom range from 93.3(13) to 122.2(8)° with an average value of 109.7°. The values of bond lengths and bond angles indicate that the Li atom is bonded with nearly the same strength to the O(37) and O(38) atoms, although the bond angle of O(38)–Li–N(42)

[122.2(8)°] is slightly larger than that of O(37)–Li–N(42) [110.6(8)°].

As is shown in Figure 4c, the structure of the organic moiety in (9) is very similar to that of the complex (8). For example, the distance between the centroids of the two phenyl groups and the dihedral angle of the two phenyl groups are 3.16 Å and 7.9(10)°, respectively, and the intramolecular distances between N(2)⋯N(11) and O(37)⋯O(38) atoms are 4.28(3) and 2.84(3) Å, respectively. The cyclobutane ring is slightly distorted and the dihedral angle between the planes of C(18)–C(19)–C(35) and C(19)–C(18)–C(36) is 17(3)°. The Hg atom is complexed by the two oxygen atoms, two sulphur atoms, and one nitrogen atom of the counter anion of the neighbouring complex. The bond distances of Hg(39)–O(37), Hg(39)–O(38), Hg(39)–S(40), and Hg(39)–S(42) are 2.18(3), 2.74(2), 2.389(13), and 2.375(13) Å , respectively. Also the intermolecular atomic distance between Hg(39) and N(45′)(2 − x, −y, 1 − z) is 2.87(3) Å. The values of Hg(39)–O(37), Hg(39)–S(40), and Hg(39)–S(43) are almost comparable to the sums (2.10 and 2.48 Å) of the covalent radii between Hg and S.[16] However, the distances of Hg(39)–O(38) and Hg(39)–N(45′) are slightly longer than the sum of the ionic radius of a mercury(II) ion (1.10 Å) and the van der Walls radius of a oxygen atom (1.40 Å) or N(1.50 Å). The bond angles of O(37)–Hg(39)–S(43), O(37)–Hg(39)–S(40), and S(40)–Hg(39)–S(43) are 118.5(8), 88.5(8), and 152.8(5)°, respectively, and the sum of these bond angles is 360°. The bond angles between S(40)–Hg(39)–N(45′), O(38)–Hg(39)–S(40), O(37)– Hg(39)–O(38), and S(43)–Hg(39)–N(45′) are also 99.2(7), 109.3(6), 71.1(9), and 92.7(7)°, respectively. These results revealed that the O(37), Hg(39), S(40), and S(43) atoms take a slightly distorted trigonal planar configuration and the O(38) and O(45′) atoms are bonded axially from above and below the plane containing O(37), Hg(39), S(40), and S(43). These results are in accord with the finding of the splitting and shift of the γ(C≡N) absorption of the i.r. spectrum in (9) as described above. The weak interaction between Hg(39) and N(45′) suggests dimer formation in complex (9) in the crystal. Therefore, the total co-ordination sphere of the Hg atom can be described as a trigonal bipyramidal configuration with the N(45′) atom of the adjacent in the apex. Another finding of interest in the complexing manner of (9) is the difference in the bond lengths between Hg(39)–O(37) and Hg(39)–O(38). The bond length [2.74(2) Å] of Hg(39)–O(38) is much longer than that [2.18(3) Å] of Hg(39)–O(37), although in complex (8), the two oxygen atoms of the amido groups are co-ordinated to the Li atom with nearly the same bond distances. This result is attributed to the difference in the way in which the O(37) and O(38) atoms are co-ordinated to the Hg(39) atom as described above.

Experimental

All m.p.s. are uncorrected. The i.r. spectra were measured on a JASCO IRA-2 diffraction grating infrared spectrometer. U.v. spectra were obtained on a Hitachi 330 spectrometer and ^{1}H n.m.r. spectra were obtained on a JEOL GX400 and JEOL FX-90Q spectrometers with SiMe$_4$ as an internal standard. For irradiation of (4) on a preparative scale, the solution was internally irradiated with an USHIO high-pressure mercury lamp (HPL)(UM-452). Also, photocleavage of (6) to (4) was carried out by means of a 220 nm u.v. light using a grating monochromator (Model JASCO CT-10), with a 500W xenon lamp (JASCO PS-X500) and a band width of 0.5 nm. Gel-permeation chromatography was carried out on a Hitachi 635 high-pressure liquid chromatograph using a Hitachi Gelpack W-520 as the GLC column (10.7 × 30 mml). Chloroform was used as the eluting solvent. U.v. spectrum was determined at 254 nm.

1,3-Bis[p-(2-carboxyvinyl)phenyl]propane was prepared according to the literature.[6] Other reagents employed were either commercial or prepared by the usual method.

1,3-Bis[p-(2-chlorocarbonylvinyl)phenyl]propane (2).—A mixture of thionyl chloride (40 ml) and 1,3-bis[p-(2-carbonylvinyl)phenyl]propane (3.6 g, 10.8 mmol) was stirred for 2 h at 40—45 °C. The excess of thionyl chloride was removed under reduced pressure and the residual solid used for the next reaction without further purification.

Reaction of (3) *and* (4).—Under a nitrogen atmosphere and at room temperature during a 4 h period, compound (3) (3.40 g, 9.2 mmol) in benzene (200 ml) and (4a) (2.0 g, 9.2 mmol) in benzene (200 ml) were added at the same rate to a benzene solution (700 ml) containing triethylamine (4.6 g, 46 mmol); the mixture was then stirred for a further 2 h. The precipitate was filtered off, the filtrate concentrated under reduced pressure, and the residue extracted with chloroform (200 ml); the extract was then washed with 1M HCl (100 ml × 2). The combined extracts were dried (MgSO$_4$) and concentrated under reduced pressure and the residue was chromatographed on activated alumina using chloroform as an eluant. The first fraction was collected and concentrated. Recrystallization of the residual solid from benzene–hexane gave (5a) in a 28% yield, m.p. 228.5—230.0 °C (Found: C, 71.8; H, 7.25; N, 5.2. C$_{31}$H$_{38}$N$_2$O$_5$ requires C, 71.79; H, 7.39; N, 5.40%); m/z 518 (C$_{31}$H$_{38}$N$_2$O$_5$$^+$), 475(18), 246(20), 151(85), 129(42), 115(45), and 56(42); $\gamma_{max.}$(KBr) 1 650, 1 600, 1 120, and 980 cm^{-1}; $\lambda_{max.}$(MeCN) 278 (ε 43 000) and 219 nm (2 600); δ_H(CDCl$_3$; 90 MHz) 2.10—2.40 (2 H, m), 2.68—2.92 (4 H, m), 3.40—4.04 (20 H, m), 6.76 (2 H, d, J 15.6 Hz), 6.70—7.10 (8 H, m), 7.42 (2 H, d, J 15.6 Hz). Compound (6a) obtained from the second fraction was recrystallized from toluene in 7.7% yield, m.p. 156.5—158.0 °C (Found: C, 71.6; H, 7.3; N, 5.2. C$_{62}$H$_{76}$N$_4$O$_{10}$ requires C, 71.79; H, 7.39; N, 5.40%); $\gamma_{max.}$(KBr) 1 640, 1 600, 1 180, and 1 120 cm^{-1}; $\lambda_{max.}$(MeCN) 285 (ε 82 100), 221 (51 200), and 209 nm (54 100); δ_H(CDCl$_3$; 400 MHz) 1.90—2.01 (4 H, m), 2.63—2.72 (8 H, m), 3.55—3.92 (40 H, m), 7.04 (4 H, d, J 15.4 Hz), 7.11—7.50 (16 H, m), and 7.65 (4 H, d, J 15.4 Hz).

Compounds (5b) and (6b) were obtained in a manner similar to that described above: (5b) (14%), m.p. 202.0—203.5 °C (Found: C, 69.3; H, 7.5; N, 5.1. C$_{33}$H$_{42}$N$_2$O$_6$·$\frac{1}{2}$H$_2$O requires C, 69.33; H, 7.76; N, 4.90%); m/z 562 (C$_{33}$H$_{42}$N$_2$O$_6$$^+$), 500(26), 432(11), 246(11), 151(14), and 129(10); $\gamma_{max.}$(KBr) 1 640, 1 600, 1 180, and 1 115 cm^{-1}; $\lambda_{max.}$(MeCN) 276 (ε 42 700) and 222 nm (14 900); δ_H(CDCl$_3$; 90 NHz) 2.10—2.20 (2 H, m), 2.62—2.92 (4 H, m), 3.44—4.00 (24 H, m), 6.66 (2 H, d, J 15.4 Hz), 6.62—7.20 (8 H, m), 7.45 (2 H, d, J 15.4 Hz); (6b) (9.1%), m.p. 198.0—199.0 °C (Found: C, 70.1; H, 7.3; N, 4.75. C$_{66}$H$_{84}$N$_4$O$_{12}$ requires C, 70.44; H, 7.52; N, 4.98%); $\gamma_{max.}$(KBr) 1 640, 1 600, 1 180, and 1 115 cm^{-1}; $\lambda_{max.}$(MeCN) 285 (ε 81 600), 221 (47 500), and 208 (47 100); δ_H(CDCl$_3$; 400 MHz) 1.87—2.00 (4 H, m), 2.57—7.69 (8 H, m), 3.51—3.99 (48 H, m), 6.81—6.92 (4 H, m), 7.11—7.47 (16 H, m), and 7.61—7.69 (4 H, m).

Gel Permeation Chromatography.—Compounds (5a), (5b), (6a), and (6b) submitted to gel-permeation chromatography, showed retention times of 12.11, 11.98, 10.51, and 10.36 min, respectively. The molecular weights of (6a) and (6b) were obtained from the calibration curves of polyethylene glycols and epoxy resins of known molecular weights.

Irradiation of (5).—Under a nitrogen atmosphere, a solution of (5a) (20.5 mg, 4.11 × 10^{-2} mmol) in acetonitrile (1 000 ml) was irradiated internally with a high-pressure mercury lamp (450 W) through a Pyrex filter at ambient temperature for 20 min. The solvent was evaporated and the residue was

chromatographed on activated alumina using chloroform as an eluant. The first fraction was collected and concentrated under reduced pressure. The residue was recrystallized from benzene–hexane to give (**7a**) (60%), m.p. 261.0—263.0 °C (Found: C, 69.25; H, 7.45; N, 5.45. $C_{31}H_{38}N_2O_5 \cdot H_2O$ requires C, 69.38; H, 7.51; N, 5.22%); m/z 518($C_{31}H_{38}N_2O_5^+$), 500(8), 475(10), 456(8), 430(8), 115(8), and 56(8). $\gamma_{max.}$(KBr) 1 628, 1 180, and 1 130 cm^{-1}; $\lambda_{max.}$(MeCN) 216 nm (ϵ 22 800); δ_H(CD$_3$CN; 400 MHz) 2.08—2.17 (2 H, m), 2.62—2.75 (6 H, m), 3.05—4.17 (16 H, m), 4.49 (1 H, q, J 4.2 Hz), 4.53 (1 H, q, J 4.2 Hz), 4.23—4.27 (2 H, m), 4.43—4.46 (2 H, m), 6.29—6.57 (4 H, m), and 6.51—6.68 (4 H, m). Compound (**7b**) was also obtained by a method similar to that described above; yield 32%, m.p. 300.0—302.0 °C (Found: C, 69.65; H, 7.55; N, 4.85. $C_{33}H_{42}N_2O_6 \cdot \frac{1}{2}H_2O$ requires C, 69.33; H, 7.76; N, 4.90%); m/z 562($C_{33}H_{42}N_2O_6^+$), 500(26), 432(16), 316(11), 246(14), 151(27), 129(15), and 56(13); $\gamma_{max.}$(KBr) 1 630, 1 185, and 1 115 cm^{-1}; $\lambda_{max.}$(MeCN) 215 nm (ϵ 14 000); δ_H(CD$_3$CN; 400 MHz) 2.02—2.17 (2 H, m), 2.68—2.74 (6 H, m), 3.42—3.96 (20 H, m), 4.25—4.27 (2 H, m), 4.44—4.45 (2 H, m), 4.51 (1 H, q, J 3.5 Hz), 4.55 (1 H, q, J 3.5 Hz), 6.28—6.51 (4 H, m), and 6.52—6.57 (4 H, m).

Photoreversible Cleavage of (**7**).—An acetonitrile solution of (**6**) (4.0 × 10^{-5}M) was placed in a quartz cell (1 × 1 × 4 cm) and irradiated at room temperature with a 220 nm u.v. light using a grating monochromator with a xenon lamp (500 W). The u.v. spectral changes were recorded during irradiation, and a steady state was attained within 3 h. The photoreversible yields of (**5a**) and (**5b**) were calculated from the intensity of the absorption band at 275 nm in the steady state. Yields of (**5a**) and (**5b**) were 45 and 39% yields, respectively.

Solvent Extraction.—Equal volumes (5 ml) of dichloromethane containing 7 × 10^{-4}M of crown ethers (**5**) and/or (**7**) and an aqueous solution containing 1 × 10^{-1}M of metal nitrate and 7 × 10^{-5}M picric acid were mixed and agitated. The solution was then separated by a centrifugal separater. The upper solution was withdrawn and its absorbance at 380 nm was measured. A similar extraction and measurement were performed with pure dichloromethane and an aqueous solution containing 1 × 10^{-1}M of metal nitrate and 7 × 10^{-5}M of picric acid. Extraction abilities were calculated by the following equation: extraction ability = $(A_0 - A)/A_0 \times 100$. A_0 Was the absorbance in the absence of cyclobutanocrown ether and A was the absorbance in the presence of cyclobutanocrown ether.

Complexes (**8**) *and* (**9**).—Lithium thiocyanate (6.0 mg, 9.25 × 10^{-6} mol) was dissolved in a solution of (**7a**) (4.8 mg, 9.25 × 10^{-6} mol) in acetonitrile (4 ml). The mixture was concentrated to *ca.* 2 ml and set aside overnight. Crystalline (**8**) was precipitated in 65% yield, m.p. 290.0—292.0 °C (Found: C, 65.65; H, 6.55; N, 7.5; S, 5.65. $C_{32}H_{38}LiN_3O_5S$ requires C, 65.85; H, 6.56; N, 7.20; S, 5.49%); $\gamma_{max.}$(KBr) 2 040, 1 610, 1 180, and 1 130 cm^{-1}; δ_H(CD$_3$CN; 400 MHz) 2.02—2.20 (2 H, m), 2.60—2.80 (4 H, m), 2.91—3.02 (2 H, m), 3.20—4.38 (16 H, m), 4.51 (1 H, q, J 3.1 Hz), 4.54 (1 H, q, J 3.1 Hz), 4.45—4.49 (2 H, m), 4.73—4.78 (2 H, m), 6.21—6.66 (4 H, m), and 6.49—6.73 (4 H, m). Complex (**9**) was obtained by a similar method to that described above; yield 31%, m.p. 222.0—224.0 °C (Found: C, 47.45; H, 4.65; N, 6.85. $C_{33}H_{38}HgN_4O_5S_2$ requires C, 47.45; H, 4.59; N, 6.71%); $\gamma_{max.}$(KBr) 2 130, 2 105, 2 075, 1 630, and 1 135 cm^{-1}; δ_H(CD$_3$CN; 400 MHz) 2.05—2.18 (2 H, m), 2.60—2.81 (6 H, m), 3.11—4.26 (16 H, m), 4.53 (1 H, q, J 3.1 Hz), 4.57 (1 H, q, J 3.1 Hz), 4.29—4.35 (2 H, m), 4.46—4.51 (2 H, m), 6.29—6.60 (4 H, m), and 6.51—6.70 (4 H, m).

Crystallographic Data.—Crystals of dimensions 0.3 × 0.3 × 0.2, 0.2 × 0.2 × 0.2, and 0.3 × 0.15 × 0.1 mm for (**5a**),

(**8**), and (**9**) were used for X-ray crystallography. For (**5a**): $C_{31}H_{38}N_2O_5$, $M = 518.6$, monoclinic, space group $P2_1/n$, $a = 18.359(1)$, $b = 10.391(3)$, $c = 15.477(1)$ Å, $\beta = 108.84(1)°$, $U = 2 794.2$ Å^3, $Z = 4$, $D_c = 1.23$ g cm^{-3}, μ(Cu-K_α) = 6.8 cm^{-1}.

For (**8**): $C_{32}H_{28}LiN_3O_5S$, $M = 583.7$, monoclinic, space group $P2_1/n$, $a = 16.442(15)$, $b = 14.949(12)$, $c = 12.841(11)$ Å, $\beta = 111.89(6)°$, $U = 2 928.6$ Å^3, $Z = 4$, $D_c = 1.30$ g cm^{-3}, μ(Cu-K_α) = 13.3 cm^{-1}.

For (**9**): $C_{33}H_{38}N_4O_5S_2Hg$, $M = 835.4$, monoclinic, space group $P2_1/a$, $a = 34.967(29)$, $b = 8.300(6)$, $c = 11.308(12)$ Å, $\beta = 95.33(8)°$, $U = 3 267.5$ Å^3, $Z = 4$, $D_c = 1.70$ g cm^{-3}, μ(Mo-K_α) = 50 cm^{-1}. Intensity data were recorded on a Rigaku AFC-5R diffractometer with graphite monochromatized Cu-K_α radiation (2$\theta \leq 128°$) for (**5a**) and (**8**), and graphite monochromatized Mo-K_α radiation (2$\theta \leq 50°$) for (**9**). Of 4 655, 4 825, and 5 932 independent reflections measured, only 3 384, 2 461, and 3 586 were considered as observed with $F_0 \geq 2\sigma(F_0)$ for (**5a**), (**8**), and (**9**), respectively. It would seem that the crystals of (**8**) and (**9**) are of poor quality judging from the large standard deviations of cell constants and the ratio between independent and observed reflections. All intensities were corrected for Lorentz and polarization effects but not for absorption. The structures were solved by direct methods using MULTAN84,[17] and refined by block diagonal least-squares methods. For (**8**) the central carbon atom of the trimethylene moiety is disordered over two sites, *ca.* 1 Å apart, and occupancies for the split atom [C(27) and C(27′)] were set at 0.5 and not varied. The positions of the hydrogen atoms were estimated using standard geometry, and the final refinements with anisotropic temperature factors for the non-hydrogen atoms and isotropic temperatures for the hydrogen atoms were lowered R values 0.085[$R_w = 0.047$, $w = 1/\sigma^2(F_0)$], 0.175[$R_w = 0.161$, $w = 1/\sigma^2(F_0)$], and 0.182[$R_w = 0.128$, $w = 1/\sigma(F_0)$] for (**5a**), (**8**), and (**9**), respectively.

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