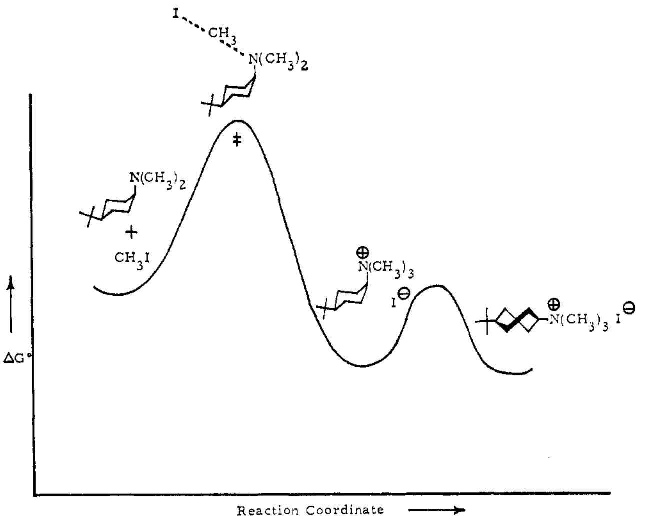

Figure 1.

form, such as *trans*-1,3-di-*tert*-butylcyclohexane, are found to have the ring largely in the boat conformation[21] and the methiodide of I should be also, although definite evidence on that point seems lacking.[23] The conclusions seem to be that the transition state is still chair, and near to starting material, and the reaction coordinate diagram must look approximately as summarized in Figure 1.

Experimental Section

***cis*-4-*tert*-Butylcyclohexanecarboxylic Acid.**—This compound was prepared according to a known procedure.[24] Chromatography of the ethyl ester (8 ft, 15% SE-30 Chromosorb W at 175° and 60 cc/min.) showed the ester to be at least 98% cis.

***cis*-4-*tert*-Butylcyclohexylamine.**—This compound was prepared from the acid according to the Schmidt method;[23] distillation yielded the amine, bp 91–92° (15 mm) [reported[23] 90° (15 mm)].

***cis*-4-*tert*-Butyl-*N*,*N*-dimethylcyclohexylamine (I).**—This compound was prepared essentially according to the method of Curtin,[23,25] bp 105–106° (25 mm). Chromatographic analysis (*vide supra*, 145° and 100 cc/min.) showed the amine to be at least 97.5% cis and the remainder an impurity which was not the trans isomer. *Anal.* Calcd for $C_{12}H_{25}N$: C, 78.62; H, 13.75. Found: C, 78.58; H, 13.66.

***trans*-4-*tert*-Butylcyclohexanecarboxylic Acid.**—The acid was prepared by known methods[11,23] and recrystallized from hexane, mp 172–174° (reported[24] 174–175°). Chromatography of the ethyl ester (*vide supra*) showed the acid to contain 98.4% of the trans isomer.

***trans*-4-*tert*-Butylcyclohexylamine.**—This compound was prepared from the acid by the same method as used for the cis amine, bp 92–93° (17 mm).[23,26]

***trans*-4-*tert*-Butyl-*N*,*N*-dimethylcyclohexylamine (II).**—This compound was prepared by a method identical with that used to prepare the cis amine I, bp 112–113° (28 mm). Chromatography (*vide supra*) showed that the amine was at least 99% trans. *Anal.* Calcd for $C_{12}H_{25}N$: C, 78.62; H, 13.75. Found: C, 78.86; H, 13.93.

Kinetic Measurements.—A solution of 100 mg ± 3.4 mg of amine was dissolved in 100 ml of acetonitrile (Matheson Coleman and Bell, AX 149, purified by distillation from magnesium sulfate under nitrogen) and stored under nitrogen. Resistance measurements were made on 10-ml aliquots of the standard amine solution to which was added 1.0 ml or 0.5 ml of methyl iodide (Matheson Coleman and Bell reagent grade IX 195) using an Industrial Instruments, Inc., conductivity bridge, Model No. RC16B2. The solution was kept under nitrogen during each kinetic run in a special cell designed to bubble nitrogen constantly through the solution.

Registry No.—I, 2523-69-5; II, 2523-68-4.

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[23] D. Y. Curtin, R. D. Stolow, and W. Maya, *J. Amer. Chem. Soc.*, **81**, 3330 (1959), have interpreted the reactions of the methiodide of I in terms of a chair form, and it seems that there must be at least a substantial amount of chair in equilibrium with the boat.

[24] H. H. Lau and H. Hart, *ibid.*, **81**, 4897 (1959).

[25] S. H. Pine, *J. Chem. Educ.*, 118 (1968).

[26] A value of 142–145° (17 mm) has been reported by D. V. Nightingale, J. D. Kerr, J. A. Gallagher, and M. Maienthal, *J. Org. Chem.*, **17**, 1017 (1952), but it appears that this value is incorrect.

Crystalline Complexes of Macrocyclic Polyethers with Thiourea and Related Compounds

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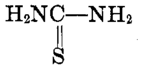
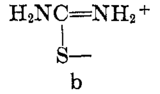
Crystalline complexes of macrocyclic polyethers with thiourea and with compounds related to thiourea have been prepared. Their stoichiometry lies between one molecule of polyether to one to six molecules of the other component, but no obvious rule for fixing the ratios has been discovered. The sizes of the molecules and the stoichiometry appear to eliminate the possibility that these are inclusion compounds and the exact nature of these complexes has yet to be determined.

The preparation and properties of a number of macrocyclic polyethers derived from aromatic vicinal diols have been previously reported.[1] It was shown that dibenzo-18-crown-6,[2] one of the polyethers, forms complexes with ammonium and monosubstituted ammonium salts which contain separate anions. It was considered possible that thiourea (a) will assume the tautomeric


$H_2NC(=S)-NH_2$

a


$H_2NC(-S^-)=NH_2^+$

b

zwitterion form (b) and complex with the cyclic polyether. There also was the possibility, however remote, for the formation of inclusion compounds of cyclic polyethers and their salt complexes when they are exposed to thiourea under suitable conditions. If such inclusion compounds did form, they would be, in the case of the salt complexes, doubly wrapped salts, first surrounded by the polyether and then by thiourea. A short study, therefore, was undertaken to test these intriguing possibilities. When thiourea was actually found to form complexes with several macrocyclic polyethers, the action of some compounds related to thiourea was also investigated.

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[1] C. J. Pedersen, *J. Amer. Chem. Soc.*, **89**, 7017 (1967).

[2] The abbreviated nomenclature for the cyclic polyethers is described in the first reference and will be used here without further explanation.

Results

In order to give greater significance to the melting points of the complexes, the melting points of the uncomplexed compounds are listed in Table I.

TABLE I

MELTING POINTS OF UNCOMPLEXED COMPOUNDS

Code no.	Compd	Mp, °C
XV	Dibenzo-14-crown-4	150–152
IV	Benzo-15-crown-5	79–79.5
XXV	Dibenzo-15-crown-5	113.5–115
XXI	Dibenzo-16-crown-5	117–118
X	Benzo-18-crown-6	43–44
XXVIII	Dibenzo-18-crown-6	164
XXIX	Bis(butylbenzo)-18-crown-6	135–137
LII	Benzocyclohexyl-18-crown-6	Below 26
XXXI	Dicyclohexyl-18-crown-6 (a mixture of two two-ring juncture isomers)	36–56
XXXIA	Pure isomer	61–62
XXXIB	Pure isomer	69–70
XXXV	Dibenzo-24-crown-8	113–114
S-1	Thiourea	180–182
S-2	*N*-Phenylthiourea	154
S-3	1-Phenylsemicarbazide	174–176
S-4	1-Phenylthiosemicarbazide	200–201
S-5	4-Phenylthiosemicarbazide	140
S-6	2-Thiazolidinethione	104–105
S-7	Thiobenzamide	115–116
	Sodium thiocyanate	287
	Potassium thiocyanate	173
	Potassium iodide	723
	Rubidium thiocyanate	188–190

The action of thiourea was determined simply by warming the polyethers with different proportions of a saturated (at 25°) methanol solution of thiourea, filtering the warm (40–50°) solution to remove undissolved polyether, and recovering any crystalline product that formed on cooling, taking care to minimize evaporation which would cause the thiourea to precipitate. The results obtained with several polyethers are shown in Table II. No other technique was used for the preparation of these products, and it is possible that other complexes could be formed under different conditions. Whether the composition of the complexes could be varied by precipitating the crystals at different fixed temperatures was not determined.

Thiourea did not form any complex with the following compounds: dibenzo-14-crown-4 (XV), 1,3-bis(*o*-methoxyphenoxy)propane (equivalent to an open XV), bis[2-(*o*-methoxyphenoxy)ethyl] ether (open XXV), and 1,14-dimethoxy-1,2,13,14-bis(tetramethylene)-3,6,-9,12-tetraoxatetradecane (open XXXI).

When thiourea was found to complex with several macrocyclic polyethers, some compounds related to thiourea were tested in connection with IV, XXVIII, and XXXI. The results obtained are shown in Table III. The proportions of reactants given in Table III were warmed in methanol and the mixtures treated as in the case of the thiourea complexes. Note that 4-phenylsemicarbazide which does not contain sulfur also forms a complex with XXXI. Dibenzo-18-crown-6 did not form an isolable complex with *N*-phenylurea and *N*-phenylthiourea, and no complex was formed between XXXI and the following compounds: Thiocarbanilide, *N*,*N*,*N*′-trimethylthiourea, tetramethylthiuram sulfide, tetraethylthiuram disulfide, 2-imidazolidinethione, and *N*-methyl-2-thiazolidinethione.

Finally, salt complexes of the polyethers or mixtures of salts and polyethers were treated with thiourea in methanol as described in detail in the Experimental Section. The results obtained are summarized in Table IV. Although some complexes of sodium and potassium salts add thiourea without decomposing, thiourea tends to displace ammonium, rubidium, and cesium from their complexes.

Discussion

The exact nature of the complexes of the macrocyclic polyethers with thiourea and related compounds is yet unknown. Their infrared spectra contain bands due to the components and appear to give little information on the probable mode of their interaction. The ultraviolet spectrum of the 1:1:1 complex of dibenzo-18-crown-6, potassium thiocyanate, and thiourea in methanol at a concentration which can be handled in a spectrophotometer is similar to that of the 1:1 complex of dibenzo-18-crown-6 and potassium thiocyanate, indicating that thiourea has no significant effect at very low concentrations. Higher concentrations of thiourea cannot be tested by this method because of interference in the region of 275 mμ.

They are not likely to be inclusion compounds of thiourea because the macrocyclic polyethers measure more than 6 × 7 Å in their smallest dimensions, the usual upper limit for the size of a guest molecule accommodated by thiourea.[3] Moreover, thiourea inclusion compounds usually consist of one molecule of guest compound and six or more molecules of thiourea.[4]

These complexes were then thought to be crystals with thiourea and related compounds present as interstitial components and that different numbers of molecules were required to fill the different vacancies in the crystals of the polyethers. This hypothesis seemed to be demolished when it was found that both urea and thiourea increase the solubility of dibenzo-18-crown-6 in methanol as shown in Table V.

Urea and thiourea both increase the solubility of dibenzo-18-crown-6 in methanol, suggesting that there is some interaction between them although the forces involved might have nothing to do with the presence of thiourea in the crystaline complexes. It is interesting that, in spite of the effect of urea shown in Table V, crystalline complexes of urea with the polyethers were not obtained when urea was handled in exactly the same way as thiourea. Possibly some other technique might have induced the formation of urea complexes.

Complexes such as $(\mathrm{XXXV})_2(\text{thiourea})_7$ (Table II), $(\mathrm{XXVIII})_1(\mathrm{KCNS})_1(\text{thiourea})_6$ (Table IV), and $(\mathrm{XXVIII})_1(\mathrm{RbCNS})_1(\text{thiourea})_4$ (Table IV) have been included because the analytical results are reasonably good, and the melting point of the first is sharp although those of the others are not satisfactory. They may suggest that crystalline complexes of different thiourea content could be obtained by precipitating them from solutions of different compositions and at different temperatures.

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(3) R. W. Schiessler and D. Flitter, *J. Amer. Chem. Soc.*, **74**, 1720 (1952).

(4) H. M. Powell, *J. Chem. Soc.* (*London*), 2658 (1954).

TABLE II

CRYSTALLINE COMPLEXES WITH THIOUREA

Reactants		Products												
							Carbon, %		Hydrogen, %		Nitrogen, %		Sulfur, %	
Polyether	Ratio[a]	Yield,[b] %	Ratio[a]	Registry no.	Mp, °C	Formula	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
XV	15			No complex										
IV	5 to 7	74	4/1	28595-77-9	152–164	$C_{18}H_{36}N_8O_5S_4$	37.7	38.1	6.3	6.2	19.6	19.6	22.4	22.6
XXV	5 to 7	50	1/1	28595-78-0	115–117	$C_{19}H_{24}N_2O_5S$	58.2	58.5	6.1	6.0	7.1	7.0	8.2	8.4
XXI	5 to 7	93	1/3	28595-79-1	123–124	$C_{58}H_{70}N_2O_{15}S$	65.3	65.5	6.6	6.3	2.6	2.5	3.0	3.4
X	5 to 7	99	1/1	28595-80-4	127	$C_{17}H_{28}N_2O_6S$	52.6	53.3	7.2	7.3	7.2	7.6	8.3	9.5
XXVIII	12[c]	48	1/1	28595-81-5	165–166	$C_{21}H_{28}N_2O_6S$	57.8	57.7	6.4	6.4	6.4	6.3	7.3	7.6
XXIX			6/1	28595-82-6	178–180	$C_{34}H_{64}N_{12}O_6S_6$	44.0	43.1	6.9	7.0	18.1	18.1	20.7	20.5
LII	9 to 10	22[d]	6/1	28595-83-7	175–180	$C_{26}H_{54}N_{12}O_6S_6$	37.9	37.9	6.6	6.5	20.4	20.4	23.4	23.8
		36[e]	5/1	28595-84-8	167–174	$C_{25}H_{50}N_{10}O_6S_5$	40.2	41.5	6.7	6.6	18.8	17.7	21.5	21.7
XXXI[f]	9 to 10	66	6/1	28670-79-3	168–173	$C_{26}H_{60}N_{12}O_6S_6$	37.7	37.3	7.2	6.9	20.3	21.3	23.2	23.3
XXXI	5 to 7[g]	82	6/1		175–176	$C_{26}H_{60}N_{12}O_6S_6$	37.7	37.3	7.2	7.3	20.3	20.5	23.2	24.9
XXXI	2	21	6/1		189–193	$C_{26}H_{60}N_{12}O_6S_6$	37.7	38.7	7.2	7.1	20.3	20.3	23.2	27.1[h]
XXXIA	9 to 10	49	6/1		168–172	$C_{26}H_{60}N_{12}O_6S_6$	37.7	36.9	7.2	7.3	20.3	20.2	23.2	24.4
XXXIB	9 to 10	82	6/1		197–198	$C_{26}H_{60}N_{12}O_6S_6$	37.7	37.9	7.2	7.5	20.3	20.4	23.2	23.3
XXXV	5 to 7	78	7/2	28739-87-9	105–106	$C_{55}H_{92}N_{14}O_{16}S_7$	46.3	46.3	6.4	6.1	13.7	13.4	15.7	15.9

[a] Mole(s) of thiourea per mole(s) of polyether. [b] Yield based on polyether. [c] Twice the normal amount of methanol was used. [d] First crop. [e] Second crop. [f] XXXI was a mixture of two isomers. [g] Only 0.7 the normal amount of methanol was used. [h] No more sample for reanalysis.

TABLE III

CRYSTALLINE COMPLEXES WITH COMPOUNDS RELATED TO THIOUREA

Reactants			Products												
								Carbon, %		Hydrogen, %		Nitrogen, %		Sulfur, %	
Polyether	Other	Ratio[a]	Yield,[b] %	Ratio[a]	Registry no.	Mp, °C	Formula	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
IV	S-7	2	68	2	28595-85-9	81–82	$C_{28}H_{34}N_2O_5S_2$	62.0	61.4	6.3	6.1	5.2	5.1	11.8	12.3
XXXI[c]	S-7	2	70	2	28595-86-0	154–156	$C_{34}H_{50}N_2O_6S_2$	63.2	63.1	7.7	7.3	4.3	4.5	9.9	10.0
XXXI	S-2	1	38	2	28595-87-1	179–180	$C_{34}H_{52}N_4O_6S_2$	60.3	60.0	7.7	7.6	8.3	8.3	9.5	9.8
XXXI	S-3	1	16	2	28670-80-6	150–158	$C_{34}H_{54}N_6O_8$	60.5	61.1	8.0	8.1	12.5	12.4		
XXXI	S-4	1	32	1	28595-88-2	155–165	$C_{27}H_{45}N_3O_6S$	60.1	60.3	8.4	8.4	7.8	7.9	5.9	6.0
XXXI	S-5	1	38	2	28595-89-3	144–145	$C_{34}H_{54}N_6O_6S_2$	57.8	57.9	7.6	7.8	11.9	11.8	9.1	8.8
XXXI	S-6	1	38	2	28595-90-6	125–127	$C_{26}H_{46}N_2O_6S_4$	51.2	51.1	7.5	7.4	4.6	4.7	21.0	21.3

[a] Mole(s) of additive per mole of polyether. [b] Yield based on polyether. [c] XXXI was a mixture of two isomers.

TABLE IV

CRYSTALLINE COMPLEXES WITH SALTS PLUS THIOUREA

					Carbon, %		Hydrogen, %		Nitrogen, %		Sulfur, %		Iodine, %	
Complex[a]	Yield,[b] %	Registry no.	Mp, °C	Formula	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$(IV)_2(KCNS)_1(S\text{-}1)_1$	36	28575-61-3	159–162	$C_{30}H_{44}N_3O_{10}S_2K$	50.8	50.8	6.2	6.1	5.9	6.2	9.0	9.6		
$(XXVIII)_1(NaCNS)_1(S\text{-}1)_1$	38	28575-62-4	230–231	$C_{22}H_{28}N_3O_6S_2Na$	51.0	49.4	5.4	5.3	8.1	8.4	12.4	12.7		
$(XXVIII)_1(KCNS)_1(S\text{-}1)_1$[c]	52	28575-63-5	242–253	$C_{22}H_{28}N_3O_6S_2K$	49.5	49.9	5.3	5.1	7.9	8.0	12.0	12.3		
$(XXVIII)_1(KCNS)_1(S\text{-}1)_6$[d]	20	28575-64-6	164–183	$C_{27}H_{48}N_{13}O_6S_7K$	35.5	35.9	5.3	5.0	19.9	19.5	24.5	24.5		
$(XXVIII)_1(KI)_1(S\text{-}1)_1$	46	28575-65-7	208–210	$C_{21}H_{28}N_2O_6SIK$	41.8	42.0	4.7	4.5	4.7	4.9	5.3	5.8	21.1	19.7
$(XXVIII)_1(RbCNS)_1(S\text{-}1)_4$	28	28575-66-8	160–190	$C_{25}H_{40}N_9O_6S_5Rb$	37.2	37.5	5.0	5.0	15.6	16.0	19.8	21.3		

[a] The preparation of these complexes is described in detail in the Experimental Section. [b] Yield based on polyether. [c] The first crop of crystals from a preparation. [d] The second crop of crystals from the same preparation.

TABLE V

EFFECTS OF UREA AND THIOUREA ON SOLUBILITY[a]

	Control	Urea	Thiourea
Undissolved polyether, g	2.651	2.330	2.156
Dissolved polyether, g	0.336	0.650	0.757
Dissolved polyether, mol	0.00093	0.0018	0.0021

[a] Polyether, 3 g of dibenzo-18-crown-6 (0.0083 mol); solvent, 100 ml of methanol; urea, 7.1 g (0.118 mol); thiourea, 9.0 g (0.118 mol); temperature, 59 ± 1°.

There appear to be certain inhibitions for the formation of the crystalline complexes; for example, if the polyether ring is too small (XV), no complex is formed, nor is one formed with open-chain equivalents of even the larger cyclic polyethers. Steric hindrance is also a factor since thiourea, *N*-phenylthiourea, and 2-thiasolidinethione form complexes but *N*,*N*,*N*′-trimethylurea, thiocarbanilide, and *N*-methyl-2-thiazolidinethione do not.

More work, probably in the field of single-crystal X-ray analysis, will be required for the elucidation of the structure of these crystalline complexes. Whatever forces are involved, they are not strong enough to displace a potassium ion from its complexes with 18-crown-6 polyethers.

Experimental Section

All inorganic compounds were reagent grade, and all solvents and available organic materials were commercial products used without purification. The macrocyclic polyethers were prepared according to published methods.[1]

The preparation of the thiourea complexes listed in Table II has been described in the text. The examples from Table III given below are typical for the preparation of these complexes.

Preparation of (Dicyclohexyl-18-crown-6)$_1$(2-thiazolidinethione)$_2$.—A mixture of 1.02 g (0.0086 mol) of 2-thiazolidinethione, 3.72 g (0.01 mol) of dicyclohexyl-18-crown-6, and 23 ml of methanol was heated, and the resulting clear solution was allowed to cool. The white crystals which formed were filtered, washed with methanol, dried, and weighed 2.0 g.

Preparation of (Dicyclohexyl-18-crown-6)$_1$(thiobenzamide)$_2$.—A mixture of 0.795 g (0.0058 mol) of thiobenzamide, 1.1 g (0.00296 mol) of dicyclohexyl-18-crown-6, and 10 ml of methanol was warmed, and the crystals which deposited were filtered, washed with methanol, and dried. The bright yellow crystals, 1.3 g, did not smell of thiobenzamide.

The preparations of the complexes given in Table IV are described below.

Preparation of (Benzo-15-crown-5)$_2$(potassium thiocyanate)$_1$(thiourea)$_1$.—A mixture of 10 ml of a saturated methanol solution of thiourea (0.97 g of thiourea, 0.013 mol) and 2 g (0.0032 mol) of (benzo-15-crown-5)$_2$(KCNS)$_1$ was warmed and the resulting clear solution was left at room temperature. The crystals which deposited within the solution in about 2 hr were filtered, washed with methanol, and dried. Colorless plates, 0.8 g, were obtained.

Preparation of (Dibenzo-18-crown-6)$_1$(sodium thiocyanate)$_1$(thiourea)$_1$.—A mixture of 15 ml of a saturated methanol solution of thiourea (1.46 g, 0.019 mol), 0.45 g (0.0056 mol) of sodium thiocyanate, 2 g (0.0056 mol) of dibenzo-18-crown-6, and 10 ml of methanol was warmed and the clear solution was concentrated to 15 ml. The white solid which deposited shortly (0.5 g) was found to be thiourea. More crystals which formed within the solution were recovered by decanting and drying on a porous plate. A white powder, 1.1 g, was obtained.

Preparation of (Dibenzo-18-crown-6)$_1$(potassium thiocyanate)$_1$(thiourea)$_1$.—A mixture of 15 ml of a saturated methanol solution of thiourea (1.46 g, 0.019 mol) and 2 g (0.0044 mol) of (dibenzo-18-crown-6)$_1$(KCNS)$_1$ was warmed, and the clear solution was decanted into another beaker and allowed to stand at room temperature. The mass of white crystals which formed within the solution was filtered, washed with cold methanol, and dried. A white solid, 1.2 g, was obtained. This is the first crop shown in Table IV.

More crystals were recovered from the filtrate. This white solid product is the second crop shown in Table IV. In spite of the acceptable analysis of this product as (dibenzo-18-crown-6)$_1$(KCNS)$_1$(thiourea)$_6$, its existence as a specific compound has yet to be proven.

Preparation of (Dibenzo-18-crown-6)$_1$(potassium iodide)$_1$(thiourea)$_1$.—A mixture of 50 ml of a saturated methanol solution of thiourea (4.85 g, 0.065 mol), 2.3 g (0.014 mol) of potassium iodide, and 5 g (0.014 mol) of dibenzo-18-crown-6 was warmed, and the clear solution was filtered and left at room temperature. Clusters of hard needles formed within the solution and they were filtered, washed with methanol, and dried (3.8 g).

When an identical reaction was run using an equivalent amount of ammonium iodide instead of potassium iodide, a 41% yield of (dibenzo-18-crown-6)$_1$(thiourea)$_1$ was obtained. Apparently, ammonium thiocyanate was expelled from the complex by the thiourea. (Dibenzo-18-crown-6)$_2$(CsCNS)$_1$ under similar conditions gave the same product, (dibenzo-18-crown-6)$_1$(thiourea)$_1$. Another experiment using strontium iodide instead of potassium iodide did not give any complex of definite composition.

Preparation of (Dibenzo-18-crown-6)$_1$(rubidium thiocyanate)$_1$(thiourea)$_4$.—A mixture of 15 ml of a saturated methanol solution of thiourea (1.46 g, 0.019 mol) and 2.2 g (0.0044 mol) of (dibenzo-18-crown-6)$_1$(RbCNS)$_1$ was warmed and the clear solution was allowed to stand at room temperature. Crystals did not form within the solution but on the walls of the beaker, both above and below the liquid level. All the crystals were scraped into the solution, broken up, filtered, washed with methanol, and dried (0.5 g). More crystals, 0.5 g, were obtained on allowing the filtrate to evaporate.

The composition of the products, (dibenzo-18-crown-6)$_1$(RbCNS)$_1$(thiourea)$_4$, corresponds closely to the mole ratio of the reactants. This suggests the possibility of a coprecipitate of the two reactants.

Attempted Preparation of (Dibenzo-18-crown-6)$_2$(CsCNS)$_1$(thiourea)$_n$.—On warming a mixture of 8 ml of a saturated methanol solution of thiourea (0.76 g, 0.01 mol) and 1 g (0.0011 mol) of (dibenzo-18-crown-6)$_2$(CsCNS)$_1$, a clear solution was obtained within which crystals began to form. The mixture was cooled in ice–water, filtered, washed with cold methanol, and dried. The white crystals, 0.5 g, were those of (dibenzo-18-crown-6)$_1$(thiourea)$_1$. Here again, the salt was displaced in the complex by thiourea.

Registry No.—Thiourea, 62-56-6.

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