Polarographic Studies on Complex Formation of Cryptand[2.2] and a Macrocyclic Polythioetheramine with Alkali or Alkaline-Earth Metal Ions in Acetonitrile

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The formation constants for 1 : 1 complexes between Li^+ or Na^+ and a monocyclic polyetherdiamine, cryptand[2.2], were evaluated in acetonitrile at $25 \pm 0.2^\circ \text{C}$ by three d.c. polarographic analyses: the positive shift in $E_{1/2}$ of the anodic (mercury dissolution) wave induced from cryptand[2.2] in the presence of a large excess of LiClO_4 and NaClO_4 ; the positive shift in $E_{1/2}$ of the cathodic wave of the $[\text{HgL}]^{2+}$ complex ($\text{L} = \text{cryptand[2.2]}$) in the presence of a large excess of alkali metal ions; and the negative shift of the cathodic wave of Li^+ or Na^+ in the presence of a large excess of cryptand[2.2]. The above three analyses gave complex formation constants that were consistent with each other within experimental error. In a less solvating medium (benzonitrile), stronger interactions were observed between the cations and cryptand[2.2]. The interaction between alkali metal ions and 1,10-diaza-4,7,13,16-tetrathiacyclooctadecane (ATCO) was very small, even in benzonitrile. The complex formation constants of $[\text{SrL}]^{2+}$ and $[\text{BaL}]^{2+}$ ($\text{L} = \text{ATCO}$) in acetonitrile were both $\text{ca. } 10^{2.5}$ by the first two methods mentioned above.

Keywords Cryptand[2.2], macrocyclic polythioetheramine, polarography, anodic wave, acetonitrile, complex formation

We have found the formation of new species, $\text{RCOO}^-(\text{M}^+)_2$ ($\text{R} = \text{CH}_3$ and C_6H_5 ; $\text{M}^+ = \text{Li}^+$ and Na^+), in acetonitrile by means of a newly developed polarographic analysis.¹ Complex ions, $\text{M}^+(\text{C}_6\text{H}_5\text{COO}^-)_2$ ($\text{M}^+ = \text{Li}^+$, Na^+ and K^+), were also observed¹ by the usual polarographic analysis. The presence of such "extraordinary" species has been convinced by further investigations with spectrophotometry² and conductometry.³

In previous papers, we have reported on the complex formation of Li^+ and Na^+ with acyclic polyamines⁴ as well as cyclic polyamines (cyclam and tetramethylcyclam)^{5,6} by utilizing the anodic waves of amines. Although one of the crown ethers, 18-crown-6, was found to give a well-defined anodic wave, the $E_{1/2}$ was too close to the positive potential limit to evaluate the interaction between M^+ and the crown ether.⁶ Introduction of nitrogen atoms into a crown ether may provide sufficient coordination ability towards Hg^{2+} .

Interactions of cryptand[2.2] with ions⁷ and neutral molecules⁸ have been extensively investigated and been reviewed by Izatt *et al.* Very recently, the complexation of alkali metal ions with crown ethers and cryptands in acetone was examined based on potentiometric and calorimetric titrations.⁹ Effective solvent extractions of "soft" metals with cyclic polythioethers (including

monoaza- and diaza-derivatives) have been reported by Chayama *et al.*^{10,11}

In the present study, a monocyclic polyetherdiamine, (cryptand[2.2]) and its sulfur derivative (ATCO) were examined by polarography in acetonitrile. It is predicted that the small affinity of sulfur atoms towards alkali metal ions may cause a weak interaction between ATCO and alkali metal ions.

Cryptand[2.2]

ATCO

Experimental

(Cryptand[2.2]) 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane from Aldrich was used as received. 1,10-Diaza-4,7,13,16-tetrathiacyclooctadecane (ATCO) was prepared by the method of Dietrich *et al.*¹² Acetonitrile and benzonitrile (both Wako, GR grade) were used without further purification. Anhydrous lithium per-

chlorate (Wako, GR grade) was used as received. Anhydrous sodium perchlorate was prepared from $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ (Wako, EP grade), and was dried *in vacuo* at 180°C over P_2O_5 . Tributylammonium perchlorate ($\text{Bu}_3\text{NHClO}_4$) was prepared from tributylamine and HClO_4 . The crystals were dried *in vacuo* at 60°C . $\text{Mg}(\text{ClO}_4)_2$ and $\text{Ba}(\text{ClO}_4)_2$ (both Wako, GR grade) were dried *in vacuo* at 200°C and 180°C , respectively. $\text{Ca}(\text{ClO}_4)_2$ and $\text{Sr}(\text{ClO}_4)_2$ were prepared from $\text{Ca}(\text{OH})_2$ and SrCO_3 with HClO_4 , respectively, and were dried *in vacuo* at 200°C . $\text{Hg}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ (Wako, EP grade) was used as received. A solution of 0.1 mol dm^{-3} HClO_4 -MeCN was prepared by diluting HClO_4 (Wako, GR grade, 60%) with acetonitrile. The minor effects of water from $\text{Hg}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ and 60% HClO_4 were ignored. Other chemicals were used as mentioned previously.⁴⁻⁶

Direct-current polarograms were recorded by a Yanagimoto polarograph (Model P-1000) and a Graphtec X-Y recorder (Model WX-4410-L0). The rate of the potential sweep was 5 mV/s . The dropping mercury electrode had the following open-circuit characteristics: $m=2.56 \text{ mg/s}$ and $\tau=5.14 \text{ s}$ in a 0.1 mol dm^{-3} Et_4NClO_4 -MeCN solution at $h=50 \text{ cm}$. The drop time was regulated to be 1.0 s by means of a Yanagimoto (P-1000-ST) drop-timer. The reference electrode was an $\text{Ag}/0.1 \text{ mol dm}^{-3} \text{ AgClO}_4$ -MeCN electrode. All of the polarographic measurements were carried out at $25 \pm 0.2^\circ\text{C}$.

Results and Discussion

Anodic wave of cryptand[2.2] and cathodic wave of the mercury complex

An anodic (mercury dissolution) wave was produced at -0.29 V by 0.3 mmol dm^{-3} cryptand[2.2] in acetonitrile containing 0.1 mol dm^{-3} Et_4NClO_4 as the supporting electrolyte (*cf.* $E_{1/2}=-0.41$ and $+0.22 \text{ V}$ for tetramethylcycram and 18-crown-6, respectively).⁶ A wave analysis [E vs. $\log\{i/(i_d-i)\}$, 36 mV] suggested a reversible 2-electron process. The alternation of the supporting electrolyte to Bu_4NClO_4 gave no change in the wave. When using Na^+ , Li^+ or Bu_3NH^+ , however, the anodic wave was shifted positively (Fig. 1). The half-wave potential ($E_{1/2}$) and current values are listed in Table 1. The waves were all diffusion controlled ($i \propto \sqrt{h}$). It should be mentioned that it has been reported that a bicyclic polyetherdiamine, cryptand[2.2.2]¹³, gives an anodic wave at -0.29 V vs. $\text{Ag}/0.1 \text{ mol dm}^{-3} \text{ AgClO}_4$ -MeCN. However, by the addition of 0.1 mol dm^{-3} LiClO_4 or NaClO_4 to 0.2 mmol dm^{-3} cryptand[2.2.2], the (anodic) wave was deformed and its height was much decreased, although the $E_{1/2}$ was shifted positively. The polarographic irreversibility (slow reaction) in the complexation between cryptand[2.2.2] and the alkali metal ions prevented us from obtaining formation constants by means of polarography.

Amperometric titration was performed for 0.5

Fig. 1 D.c. polarograms of $0.30 \text{ mmol dm}^{-3}$ cryptand[2.2] in acetonitrile containing various supporting electrolytes (all 0.1 mol dm^{-3}). (1) Base current of Et_4NClO_4 , (2) NaClO_4 , (3) LiClO_4 , (4) $\text{Bu}_3\text{NHClO}_4$, (5) Et_4NClO_4 , (6) Bu_4NClO_4 .

Table 1 D.c. polarographic data for anodic waves of cryptand[2.2] and ATCO in acetonitrile containing various supporting electrolytes at 25°C

Supporting electrolyte ^a	$E_{1/2}^b/\text{V}$	$i_i/\mu\text{A}$
[Cryptand[2.2]]= $0.30 \text{ mmol dm}^{-3}$		
Et_4NClO_4	-0.29	1.9
Bu_4NClO_4	-0.29	1.9
NaClO_4	-0.19	1.8
LiClO_4	-0.20	1.9
$\text{Bu}_3\text{NHClO}_4$	-0.21	1.5
[ATCO]= $0.30 \text{ mmol dm}^{-3}$		
Et_4NClO_4	-0.42	1.9
Bu_4NClO_4	-0.41	1.9
NaClO_4	-0.41	1.9
LiClO_4	-0.41	1.7
$\text{Bu}_3\text{NHClO}_4$	-0.38	1.5
$\text{Mg}(\text{ClO}_4)_2$	— ^c	—
$\text{Ca}(\text{ClO}_4)_2$	-0.20	(0.3)
$\text{Sr}(\text{ClO}_4)_2$	-0.38	1.0
$\text{Ba}(\text{ClO}_4)_2$	-0.38	1.4

a. Concentrations of the supporting electrolytes are 0.1 mol dm^{-3} , except for alkaline-earth metal salts (0.05 mol dm^{-3}).

b. vs. $\text{Ag}/0.1 \text{ mol dm}^{-3} \text{ AgClO}_4$ -MeCN electrode.

c. The anodic wave disappeared completely.

mmol dm^{-3} (10 ml) cryptand[2.2] with 0.1 mol dm^{-3} $\text{Hg}(\text{ClO}_4)_2$ in acetonitrile (Fig. 2). Upon the addition of a small amount of Hg^{2+} , some portion of the anodic wave changed to the cathodic portion. The wave changed entirely to the cathodic portion at the equivalent point ($[\text{L}]:[\text{Hg}^{2+}]=1:1$ where $\text{L}=\text{cryptand[2.2]}$, *cf.* Eq. (1)). No shift in $E_{1/2}$ was observed, although the wave height of

Fig. 2 Changes in current position in polarograms of 0.50 mmol dm⁻³ cryptand[2.2] in acetonitrile with the addition of Hg(ClO₄)₂. (1) 0, (2) 0.1, (3) 0.2, (4) 0.3, (5) 0.4, (6) 0.5, (7) 0.6 mmol dm⁻³ of Hg²⁺. The supporting electrolyte was 0.1 mol dm⁻³ Et₄NClO₄.

the cathodic wave was slightly smaller than that of the initial anodic wave. Unreacted Hg²⁺ was found after the equivalent point. The above results suggested that the combination of Hg²⁺ and L gave the HgL²⁺ species in the solution, which could be reduced by 2-electrons to Hg and L:

and

Figure 3 shows the shift in $E_{1/2}$ of the anodic wave of cryptand[2.2] with increasing concentration of (Lewis) acids. When 10–200 mmol dm⁻³ LiClO₄ was added to 0.3 mmol dm⁻³ cryptand[2.2], the $E_{1/2}$ of the anodic wave shifted by 29 mV positively due to the increase of a 10-fold Li⁺ concentration. The magnitude of the shift in $E_{1/2}$ ($\Delta E_{1/2}/\Delta \log[\text{Li}^+] = 29$ mV) indicated the formation of the [LiL]⁺ complex with a formation constant of 10^{3.9}. Similar $E_{1/2}$ shifts were observed for the cathodic wave of HgL²⁺ in the presence of a large excess of Li⁺. The formation constant of the [LiL]⁺ complex was obtained to be 10^{3.8} by the cathodic wave of HgL²⁺. Equation (3) was utilized for evaluating the complex formation constants by the anodic wave of L (or the cathodic wave of [HgL]²⁺):

$$(E_{1/2})_o = (E_{1/2})_s + (0.059/2) \log K_p + (0.059/2) p \log [\text{M}^+], \quad (3)$$

Fig. 3 Shift in $E_{1/2}$ of the anodic wave of 0.30 mmol dm⁻³ cryptand[2.2] in acetonitrile with increasing concentration of (Lewis) acids. (○) NaClO₄, (□) LiClO₄, (Δ) Bu₃NHClO₄. The ionic strength was kept to be 0.1 by Et₄NClO₄, except for 0.2 mol dm⁻³ MClO₄.

Table 2 Formation constants ($\log K_p$) between cations and cryptand[2.2] in acetonitrile, obtained by the three methods at 25°C

Cation	Anodic wave		M ⁺ reduction wave
	$\log K_1$	$\log K_2$	$\log K_1$
Li ⁺	3.9		4.1
	3.8 ^a		
Na ⁺	4.4		4.3
	4.3 ^a		
K ⁺	—		4.4
Bu ₃ NH ⁺	3.6	5.1	
	3.6 ^a	5.1 ^a	

a. The value by the cathodic wave of [HgL]²⁺.

where $(E_{1/2})_o$ is the $E_{1/2}$ of the anodic wave of L (or the cathodic wave of [HgL]²⁺) in the presence of M⁺, and $(E_{1/2})_s$ is that in the absence of M⁺; K_p is the (overall) formation constant, and p is the number of M⁺ to combine with L.

Sodium ions had effects similar to those of Li⁺. The formation constants for Na⁺ were obtained both by the anodic (L) and cathodic (HgL²⁺) in the presence of a large excess of Na⁺, and are listed in Table 2. The solubility of potassium perchlorate in acetonitrile was too small to be a large excess over the concentration of cryptand[2.2].

In benzonitrile, 0.7 mmol dm⁻³ cryptand[2.2] gave an anodic wave at -0.37 V vs. Ag/0.1 mol dm⁻³ Ag⁺PhCN (the reference electrode). The addition of LiClO₄ or NaClO₄ caused the $E_{1/2}$ to shift positively. The formation constants of [ML]⁺ were calculated to be 10^{6.3} and 10^{6.5} for Li⁺ (5–200 mmol dm⁻³, $p=1.36$) and Na⁺ (5–50 mmol dm⁻³, $p=1.0$), respectively. The very large formation constants of Li⁺ and Na⁺ in benzonitrile,

compared with those in acetonitrile, can be explained by the smaller solvation ability of PhCN ($DN=11.9$, $AN=15.5$) than that of MeCN ($DN=14.1$, $AN=19.3$).¹⁴

On the other hand, in the presence of a large excess of Bu_3NHClO_4 , the $E_{1/2}$ of the anodic wave of cryptand[2.2] shifted positively by 30 mV ($10-30 \text{ mmol dm}^{-3}$ of Bu_3NH^+) and 60 mV ($30-200 \text{ mmol dm}^{-3}$) in acetonitrile. The (anodic) wave height was not so affected by the presence of weak Brønsted acid (*cf.*, Fig. 1 or Table 1). Slopes of 30 mV ($p=1$) and 60 mV ($p=2$) suggested the formation of Bu_3NH^+L ($\log K_1=3.6$) and $(Bu_3NH^+)_2L$ ($\log K_2=5.1$), respectively. Tributylammonium ions may react successively with nitrogen atoms in the cryptand[2.2] molecule. The pK_a values of the conjugate acid ($L(H^+)_2$) of cryptand[2.2] in aqueous solution have been reported to be 8.94 and 7.81.¹⁵

However, the basicity in two amines of cryptand[2.2] could not be differentiated by a strong acid, $HClO_4$, in an acetonitrile solution. Figure 4 shows the amperometric titration of 0.5 mmol dm^{-3} cryptand[2.2] (10 ml) with 0.1 mol dm^{-3} $HClO_4$. The anodic wave height decreased linearly with increasing concentration of $HClO_4$, and completely disappeared at the second equivalent point ($[L]:[HClO_4]=1:2$). A cathodic wave newly appeared at around -1.95 V upon the addition of $HClO_4$, which was accompanied by a maximum wave. The wave height of the cathodic wave reached a constant value at the second equivalent point,

After the second equivalent point, another cathodic wave appeared at around -1.3 V . This cathodic wave must have been due to the reduction of unreacted $HClO_4$.¹⁶

Cathodic wave of alkali metal ions in the presence of a large excess of cryptand[2.2]

Lithium perchlorate gave a reversible cathodic wave ($n=1$) at -2.3 V in acetonitrile containing 0.1 mol dm^{-3} Et_4NClO_4 . Upon the addition of $5-50 \text{ mmol dm}^{-3}$ cryptand[2.2], the cathodic wave of Li^+ shifted negatively ($\Delta E_{1/2}/\Delta \log[L]=-62.5 \text{ mV}$). The waves were all diffusion controlled ($i_1 \propto \sqrt{h}$). The negative shift of the half-wave potential of the metal ion in the presence of the ligand was analyzed by the usual method:

$$(E_{1/2})_0 = (E_{1/2})_s - 0.059 \log K_p - 0.059p \log[L], \quad (5)$$

where $(E_{1/2})_0$ and $(E_{1/2})_s$ are the $E_{1/2}$ values of the cathodic wave of M^+ in the presence and absence of L , respectively; K_p is the (overall) formation constant, and p is the number of L to complex with M^+ . The slope of -62.5 mV ($p=1$) indicated the formation of $[LiL]^+$. The formation constant was $10^{4.1}$; this value is almost coincident with that obtained by the anodic wave of L (or the cathodic wave of $[HgL]^{2+}$). The cathodic waves of Na^+ and K^+ were also shifted negatively (-65 and -58 mV , respectively) by the presence of the ligand. The formation constants of $[NaL]^+$ and $[KL]^+$ were found

Fig. 4 Amperometric titrations of $0.50 \text{ mmol dm}^{-3}$ cryptand[2.2] (10 ml) with 0.1 mol dm^{-3} $HClO_4$ in acetonitrile. (●) Anodic wave from cryptand[2.2], (○) cathodic wave at -1.95 V , (Δ) cathodic wave of $HClO_4$ at $ca. -1.3 \text{ V}$.

to be $10^{4.3}$ and $10^{4.4}$, respectively. Formation constants similar to our values for Li^+ , Na^+ , and K^+ in acetonitrile by various techniques have been reported.^{7,17,18}

By the way, the addition of $Mg(ClO_4)_2$ and $Sr(ClO_4)_2$ of the equivalent amount to cryptand[2.2] caused the disappearance of the anodic wave of the ligand, without forming precipitation. These phenomena were explained by the strong, but slow, interactions between cryptand[2.2] and alkaline-earth metal ions. Boss and Popov¹⁹ have reported a $\log K$ value of >7 by NMR for the interaction between cryptand[2.2] and Ba^{2+} in MeCN.

ATCO (1,10-diaza-4,7,13,16-tetrathiacyclooctadecane)

The strong affinity of ATCO with mercury is predicted by the displacement of all the oxygen atoms in cryptand[2.2] with sulfur atoms. The $E_{1/2}$ of the anodic (mercury dissolution) wave of 0.3 mmol dm^{-3} ATCO (-0.42 V) is much more negative than that of cryptand[2.2] (-0.29 V) in acetonitrile with 0.1 mol dm^{-3} Et_4NClO_4 (or Bu_4NClO_4). The anodic wave of ATCO was a reversible 2-electron process (wave analysis: 30 mV), and was diffusion controlled ($i_1 \propto \sqrt{h}$).

The presence of 0.1 mol dm^{-3} $LiClO_4$ or $NaClO_4$ did not affect the $E_{1/2}$ and the height of the anodic wave (*cf.* Table 1); this fact indicates that interactions between ATCO and the alkali metal ions are very small. Even in benzonitrile, the anodic wave of ATCO with 0.1 mol dm^{-3} Et_4NClO_4 ($E_{1/2}=-0.50$) was not much affected by 0.1 mol dm^{-3} Li^+ or 0.05 mol dm^{-3} Na^+ ($E_{1/2}=-0.48 \text{ V}$).

However, alkaline-earth metal ions showed strong interactions with ATCO in acetonitrile (Fig. 5). The presence of 0.05 mol dm^{-3} $Mg(ClO_4)_2$ or $Ca(ClO_4)_2$ caused the anodic wave of ATCO to disappear. With $Sr(ClO_4)_2$ or $Ba(ClO_4)_2$, on the other hand, the anodic wave of ATCO was shifted positively. The formation

Fig. 5 D.C. polarograms of $0.30 \text{ mmol dm}^{-3}$ ATCO in acetonitrile containing various supporting electrolytes. (1) $0.1 \text{ mol dm}^{-3} \text{ Et}_4\text{NClO}_4$, (2) $0.05 \text{ mol dm}^{-3} \text{ Mg}(\text{ClO}_4)_2$, (3) $0.05 \text{ mol dm}^{-3} \text{ Ca}(\text{ClO}_4)_2$, (4) $0.05 \text{ mol dm}^{-3} \text{ Sr}(\text{ClO}_4)_2$, (5) $0.05 \text{ mol dm}^{-3} \text{ Ba}(\text{ClO}_4)_2$.

Table 3 Formation constants ($\log K_p$) between cations and ATCO in acetonitrile, obtained by the anodic wave of ATCO and the cathodic wave of Hg^{2+} -ATCO

Cation	Anodic wave of ATCO		Cathodic wave of Hg^{2+} -ATCO	
	$\log K_1$	$\log K_2$	$\log K_1$	$\log K_2$
Sr^{2+}	2.5 ₅		2.4	
Ba^{2+}	2.5		2.4	
Bu_3NH^+	2.0	3.2	—	—

constants of $[\text{SrL}']^{2+}$ and $[\text{BaL}']^{2+}$ ($\text{L}'=\text{ATCO}$) in acetonitrile were calculated using Eq. (3) to be $10^{2.55}$ and $10^{2.5}$, respectively. The slopes ($\Delta E_{1/2}/\Delta \log[\text{M}^{2+}]$) were 37 mV and 31 mV for Sr^{2+} and Ba^{2+} , respectively. The decreases (to some extent) in the reversibility and the wave-height due to the presence of Sr^{2+} and Ba^{2+} were ignored. The (overall) formation constant of $(\text{Bu}_3\text{NH}^+)\text{L}'$ and $(\text{Bu}_3\text{NH}^+)_2\text{L}'$ were also obtained (Table 3).

The cause for the disappearance of the anodic wave of ATCO in the presence of Mg^{2+} and Ca^{2+} was examined as follows: $0.50 \text{ mmol dm}^{-3}$ ATCO (10 ml) was titrated amperometrically with $0.1 \text{ mol dm}^{-3} \text{ Mg}(\text{ClO}_4)_2$. Upon the addition of Mg^{2+} , the wave-height decreased linearly up to the equivalent point ($50 \mu\text{l}$, $[\text{L}']:[\text{Mg}^{2+}]=1:1$). A further addition of Mg^{2+} did not reproduce the anodic wave. The titration curve with $\text{Ca}(\text{ClO}_4)_2$ (under conditions similar to the case of Mg^{2+}) gave a much more gentle slope. Even 100 or 200 μl of the Ca^{2+} solution did not decrease the wave-height very much. By a further addition, the wave-height gradually decreased, and became one-third at 2.0 ml of the Ca^{2+} solution. Precipitates were not observed during the titrations.

Based on the above observation, we have concluded that disappearance of the anodic wave in the presence of sufficient amounts of Mg^{2+} and Ca^{2+} should have been caused by strong, but slow (electrochemically irreversible) interactions between ATCO and the alkaline-earth cations of smaller ion sizes.

The anodic wave of ATCO at a rather negative potential indicated the strong affinity of ATCO with mercury. The formation constant of the $[\text{HgL}']^{2+}$ complex was roughly estimated to be $\log K=22.3$ (cf., $\log K=18.0$ for cryptand[2.2]) by the ΔE between $E_{1/2}$ of L' and the positive cut-off potential in the absence of L' . The addition of an equivalent amount of $\text{Hg}(\text{ClO}_4)_2$ to an ATCO-MeCN solution readily gave the $[\text{HgL}']^{2+}$ complex, as was the case for cryptand[2.2]. The cathodic wave of $[\text{HgL}']^{2+}$ was utilized to obtain the formation constants of $[\text{SrL}']^{2+}$ and $[\text{BaL}']^{2+}$ (cf. Table 3). The smaller solubility of ATCO in MeCN prevented us from utilizing the usual method to obtain the formation constants of the complexes.

An amperometric titration of ATCO with HClO_4 in acetonitrile gave results similar to those of cryptand[2.2] (cf. Fig. 4), except that a small second anodic-wave at -0.16 V was observed in addition to the original anodic wave at -0.42 V . The small second anodic-wave might have been caused by an interaction between mercury and the monoprotonated ATCO species, i.e., L'H^+ . We have observed⁶ a very clear second anodic-wave upon the addition of HClO_4 to tetramethylcyclam (TMC) in the same solvent, and attributed it to an interaction between mercury and monoprotonated TMC.

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