Table II. Rates of Transformation of Blue Magnesium Tetracyanoplatinate to Red-Green[16] Magnesium Tetracyanoplatinate

Saturated salt solution	Relative humidity	Transformation time
NH_4Cl and KNO_3	72% at 23° [a]	~1 h
$(NH_4)_2SO_4$	80% at 25° [10]	~1 day
$BaCl_2 \cdot 2H_2O$	90% at 25° [10]	~4 days

[a] G. Edgar and W. O. Swan, *J. Am. Chem. Soc.*, **44**, 570 (1922).

by the addition of H_2O_2 to a solution of **4** in the presence of HBr, yielded only green crystals. These green crystals were shown by chemical analysis[6] to be unoxidized $Ba[Pt(CN)_4] \cdot 4H_2O$, in agreement with the previous report by Levy.[7]

The "blue magnesium tetracyanoplatinate" described by Krogmann and Ringwald[3] was easily prepared by their method and an x-ray diffraction powder pattern of this material was identical with that which they reported (see Table I). However, chemical analysis for chlorine revealed that only trace amounts (<0.1%) were present.[8] In addition, no Cl^- was detected by x-ray fluorescence spectroscopy.[9] Subsequently it was discovered that when the "blue $Mg[Pt(CN)_4]Cl_{0.28} \cdot 7H_2O$" was removed from the solution in which it was prepared, and stored over a saturated barium chloride solution (relative humidity[10] of 90% at 25 °C), the blue crystals transformed slowly to red-green[16] crystals. An x-ray diffraction powder pattern of this red-green material was identical with the pattern of the nonhalogenated red $Mg[Pt(CN)_4] \cdot 7H_2O$ prepared by the authors, and to the pattern of **2** reported by Krogmann and Ringwald[3] (see Table I).

Handling of the blue magnesium tetracyanoplatinate is difficult because the hydration state apparently changes easily and rapidly; e.g., addition of water to the blue material in its preparative solution results in the formation of a white precipitate. This handling problem greatly complicates the chemical analysis, but the material does appear to be nearly a 7-8 hydrate. The relative rate at which the blue material transforms to the red-green variety, at room temperature under differing relative humidities, is shown in Table II. Our attempts to grow large crystals of the blue magnesium tetracyanoplatinate have been unsuccessful, in agreement with a report by Krogmann.[2b]

Other hydration states which we have observed for the transformed blue material include a blue-green phase, a violet phase, and a bright-red phase. These complex hydrate phases of $Mg[Pt(CN)_4] \cdot 7H_2O$ have previously been reported.[11] The wide range of color changes exhibited by **2** is related to the interplanar $Pt(CN)_4{}^{2-}$ distances as was first pointed out by Yamada,[12] and the great ease with which many of the platinocyanides "dehydrate (below 100 °C) and thereby reorganize themselves in order to form a new structure . . . as shown by spectacular color changes" has been reported by Moreau-Colin.[13]

An additional report which corroborates our results with Mg^{2+} platinocyanide complexes is based on an 1856 report by Weselsky[14] who mentioned a "blackish violet" partially oxidized magnesium pentacyanoplatinate, $Mg[Pt(CN)_5] \cdot 7H_2O$, prepared by the partial oxidation of $Mg[Pt(CN)_4] \cdot 7H_2O$ by HNO_3. In an alternate attempt to prepare this Mg^{2+} platinocyanide complex, we have prepared a dark purple solid by the addition of H_2O_2 to a solution of **2**. We were surprised to find that an x-ray diffraction powder pattern of this material was nearly identical with the x-ray powder pattern of blue compound **1** reported by Krogmann and Ringwald[3] (see Table I). When this dark purple material was removed from the solution in which it was prepared, it transformed to green crystals. Thus it appears that this dark purple magnesium platinocyanide is also a different hydrate of $Mg[Pt(CN)_4] \cdot 7H_2O$.

It therefore appears that POTCP complexes of *divalent* cations have yet to be prepared. In the specific case of the magnesium tetracyanoplatinates, the bulky, hydrated magnesium cations may sufficiently hinder the close approach of planar $Pt(CN)_4{}^{2-}$ groups, and concomitant overlap of the $Pt(5d_{z^2})$ orbitals, which appears to be essential for the formation of short Pt-Pt chains observed in the *monovalent* alkali metal salts.[2b] The observed inability to prepare POTCP salts of *divalent* cations may provide invaluable insight into the relative importance of cation charge and cation solvation effects on the formation of these salts. Such effects should be considered in future synthetic efforts directed toward the formation of highly conducting one-dimensional tetracyanoplatinates.

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(1) Work performed under the auspices of the U.S. Energy Research and Development Administration.

(2) See, for example, (a) L. A. Levy, *J. Chem. Soc.*, **101**, 1081 (1912); T. W. Thomas and A. W. Underhill, *Chem. Soc. Rev.*, **1** (1), 99 (1972); (b) K. Krogmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 35 (1969); (c) J. M. Williams, J. L. Petersen, H. M. Gerdes, and S. W. Peterson, *Phys. Rev. Lett.*, **33** (18), 1079 (1974); (d) K. D. Keefer, D. M. Washecheck, N. P. Enright, and J. M. Williams, *J. Am. Chem. Soc.*, **98**, 233 (1976).

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(5) All chemical analyses were performed by Midwest Microlab, Indianapolis, Ind.

(6) Anal. Calcd for $C_4H_8N_4O_4BaPt$: C, 9.45; H, 1.59; N, 11.02. Found: C, 9.60; H, 1.59; N, 11.17; Br, 0.0.

(7) L. A. Levy, *J. Chem. Soc.*, **93**, 1454 (1908).

(8) Anal. Calcd for $C_4H_{14}N_4O_7Cl_{0.28}MgPt$: C, 10.45; H, 3.07; N, 12.20; O, 24.37; Cl, 2.16. Calcd. for $C_4H_{14}N_4O_7MgPt$: C, 10.69; H, 3.14; N, 12.46; O, 24.91. Found: C, 10.82; H, 2.49; N, 12.90; O, 24.77; Cl, 0.0.

(9) X-Ray fluorescence spectroscopy performed by Dr. A. Reis, Jr., and R. L. Maffly at the Chemistry Division, Argonne National Laboratory.

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(14) P. Weselsky, *J. Prac. Chem.*, **69**, 279 (1856); ref 11c, p 271.

(15) Research participant sponsored by the Argonne Center for Educational Affairs from Coe College, Cedar Rapids, Iowa.

(16) In visible light small needle crystals of this material appear red when viewed along the needle axis and green when light is reflected from the faces parallel to the needle axis.

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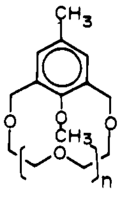
Synthesis and Binding Characteristics of Macrocyclic Polyethers Containing Convergent Methoxyaryl or Phenolic Groups[1]

Sir:

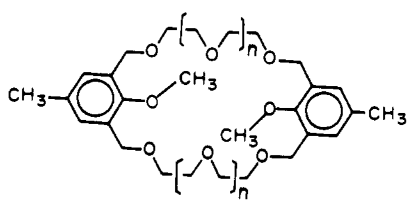
Convergence of binding sites and of potential catalytic functional groups is a problem central to the design and synthesis of nonpeptide catalysts that might imitate enzymes. Hydroxyl groups of phenols are found in active sites of enzymes (e.g., carboxypeptidase)[2] and play important roles in organization of ionophores that wrap around metal ions (e.g., antibiotic X-537A).[3] Phenolic ether groups as parts of crown ether rings are fairly good ligands for the alkali metal ions,[4a] and the crown ethers have been widely used as lipophilizers of salts and anion activators.[5a] Association constants of the simple crown ethers with alkali metal ions have been measured.[5b,c] In prior work we have reported the synthesis of macrocyclic polyethers containing inward-turning furan,[6a] pyridyl,[6b] and phenyl-

Table I. Association Constants (K_a) of Host and Picrate Salts in Chloroform at 25°

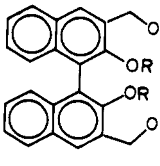
Host	$K_a \times 10^{-3}$ for guest picrates					
	Li^+	Na^+	K^+	Rb^+	Cs^+	NH_4^+
1	3.8	14.2	21.1	—	4.98	4.23
2	9.9	46.8	1 810	—	115	367
3	2.9	46	184	—	654	134
12	1.2	2.4	80.1	—	37.8	73.9
13	20.1	897	1 220	—	475	500
4	0.86	2.0	3.9	1.7	1.9	1.9
5	0.56	5.01	8.76	4.24	6.07	8.53
6	16.1	1 240	3 740	—	560	803
7	18.8	42.9	953	976	954	479
8	12.8	33.4	227	195	361	114
9	2.2	7.9	40.4	—	25.0	5.85
10	7.1	15.4	236	222	198	70.7
11	4.9	30.7	105	87.1	224	51.3
14	22	1 420	41 300	—	2 920	302



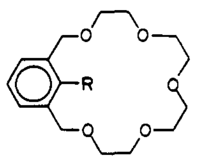
1, n = 2
2, n = 3
3, n = 4



4, n = 0
5, n = 1



6, n = 2, R = CH3
7, n = 3, R = CH3
8, n = 4, R = CH3
9, n = 2, R = H
10, n = 3, R = H
11, n = 4, R = H



12, R = H
13, R = CO2CH3

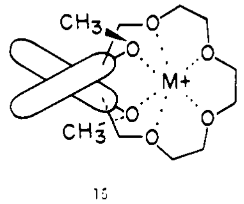
carboxyl[6c] groups, as well as their complexation constants in chloroform toward *tert*-butylammonium ions.[6d] Here we report the syntheses and ion-binding properties of 11 new macrocyclic polyethers containing one or two ArOH or $ArOCH_3$ groups whose oxygens when complexed lie above or below the best plane of the macroring. No oxygen systems possessing these geometries have been prepared and studied previously, although two sulfur-containing 18-crown-6 hosts with $ArOCH_3$ groups as parts of the ring system have been reported.[4b]

Host compounds **1–5**[7] were prepared at reflux in dry tetrahydrofuran by adding to a sodium hydride suspension a mixture of 2,6-bis(bromomethyl)-4-methylanisole[7,8] and the appropriate diol.[9] Triethylene glycol provided **1**, 58%, oil; tetraethylene glycol, **2**, 49%, mp 70–72°; pentaethylene glycol, **3**, 59%, mp 71–73°; ethylene glycol, **4**, 14%, mp 148–151°; and diethylene glycol, **5**, 26%, mp 88–90°. Compounds **6–8**[7] were prepared similarly[9] from 2,2′-bismethoxy-3,3′-bis(hydroxymethyl)-1,1′-binaphthyl[7,10] and the appropriate glycol ditosylate. Triethyleneglycol ditosylate gave **6** (40%, glass), tetraethylene glycol ditosylate gave **7** (40%, glass), and pentaethylene glycol ditosylate gave **8** (20%, glass). Similarly, 2,2′-bis(methoxymethoxy)-3,3′-bis(hydroxymethyl)-1,1′-binaphthyl[7,11] and glycol ditosylates gave cycles[9] which when hydrolyzed[12] gave **9–11**.[7] Triethylene glycol ditosylate gave **9** (40%, mp 214–215°), tetraethylene glycol ditosylate gave **10** (30%, mp 188–189°), and pentaethylene glycol ditosylate gave **11** (15%, mp 162–163°).

Approximate association constants (K_a) of **1–11**, **12**,[6c] and **13**[6c] with cation-picrate in $CHCl_3$ were determined at 25° by extracting aqueous solutions of Li^+, Na^+, K^+, Rb^+, Cs^+, and NH_4^+ picrates with $CHCl_3$ solutions of host.[13] In calculation of K_a values (Table I) it was assumed that the complexes involved one host and one guest (eq 1). No detectable amount of host was drawn into the aqueous layer (uv). The K_a values of the phenolic cycle **10** did not change when the pH of the aqueous solution extracted was changed from the usual 6 to 4 by addition of hydrochloric acid. The K_a values for 2,3-naphtho-18-crown-6 (**14**)[4a] are included for comparison.

$$\text{host in } CDCl_3 + M^+Pic^- \text{ in } CDCl_3 \overset{K_a}{\rightleftharpoons} \text{host}\cdot M^+Pic^- \text{ in } CDCl_3 \quad (1)$$

Generalizations derived from the results are as follows. (1) Values of K_a are highest when the diameters of the metal ions roughly match the hole diameters of the host.[14] The fit is especially good for K^+ and **2**, **6**, and **14**, where K_a values are the highest ($>10^6$). The fit is worst for Li^+ whose K_a values are the smallest (the highest is $\sim 10^4$). (2) To provide in models[14] contact between oxygens and metal ions, hosts **1–5**, **12**, and **13** must assume a conformation in which the plane of the benzene ring(s) is ~30° out of the best plane of the macroring. The K_a values of hosts **4** and **5** that contain two benzene rings opposite one another are the lowest for almost all ions (exceptions are **1** whose small hole cannot accommodate the large ions Cs^+ and NH_4^+). Models of **4** and **5** indicate many degrees of rotational freedom must be frozen out to generate cavities for the guests. (3) In **6–8** which also contain two $ArOCH_3$ groups, one methoxyl is held above and one below the best plane of the macroring, and little conformational change is needed to insert metal ions (see structure **15**). The K_a values of **6–8** are about 10 to 10^3 higher than those of **4** and **5**. In the approximately planar **14**, the K_a values are the highest observed for all the metal ions, but not for NH_4^+. In the 18-membered ring cycles **3**, **12**, and **13**, the 2-aryl substituents fall in the order $CO_2CH_3 > OCH_3 > H$ in enhancing binding toward all ions except K^+, for which the order is $OCH_3 > CO_2CH_3 > H$. (4) Among **6–11**, the methoxyl-containing hosts have K_a values consistently greater by factors up to about 10^2 than the corresponding hydroxyl-containing hosts. CPK molecular models indicate the OH groups of **9–11** are in positions to intramolecularly hydrogen bond transannularly located oxygens, particularly in **9** (see structure **16**), which is the poorest binder of the series. These hydrogen bonds must be broken before guest ions can maximize their contact oxygens. Secondary structuring by intramolecular hydrogen bonding of this sort might be useful in design of hosts for certain purposes. (5) Of the guests, only the ammonium ion can be substituted by organic residues, and its nonspherical character



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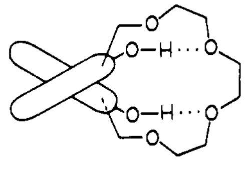

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lends itself to matching of shapes of hosts and guests. CPK molecular models of the complexes of **2, 13, 14, 6,** and **7**, which have the highest K_a values, indicate three linear $^+NH\cdots O$ bonds and three $^+N\cdots O$ interactions are possible. In no other hosts are these conditions met. Hosts **2, 13,** and **6** particularly lend themselves to structural modification that shape the cavity for binding selectively different alkylammonium ions.

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(1) This research was supported by ERDA Contract AT(04-3)34, P. A. 218.

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(7) (a) Carbon and hydrogen analyses were within 0.30% of theory; (b) ^1H NMR spectra in $CDCl_3$ were as expected; (c) 70 eV mass spectra gave parent ion.

(8) In the preparation of **1–5,** a solution of 0.37 mol of diol and 0.37 mol of dibromide in dry $(CH_2)_4O$ was added (2.5 h) to a stirred mixture of 1 mol of NaH in dry $(CH_2)_4O$ at reflux under N_2. The mixture was stirred at 25° for 12 h. In the preparation of **6–11,** NaH was added to the stirred mixture of diol and ditosylate in dry $(CH_2)_4O$, and the resulting mixture was refluxed for 48 h. Products **1–8** were purified by gel permeation chromatography with a 100 Å styragel column (10 or 20 ft by ⅜ in.) packed in $(CH_2)_4O$.

(9) Treatment of *p*-cresol with K_2CO_3 and $H_2O–CH_2O$ at 50° for 3.5 h gave (45%) 2,6-bis(hydroxymethyl)-4-methylphenol, mp 123–124° (note 7), which with $(CH_3)_2SO_4$ in acetone and K_2CO_3 gave (95%) 2,6-bis(hydroxymethyl)-4-methylanisole, mp 103–104° (note 7). This diol with thionyl bromide in $CHCl_3$ at 25° gave (95%) 2,6-bis(bromomethyl)-4-methylanisole, mp 66–68° (note 7).

(10) Treatment of racemic 2,2′-bishydroxy-3,3′-bis(hydroxymethyl)-1,1′-binaphthyl (R. C. Helgeson, J. M. Timko and D. J. Cram, *J. Amer. Chem. Soc.*, **95,** 3023 (1973)) and CH_3I in acetone with K_2CO_3 at reflux (24 h) gave (90%) 2,2′-bismethoxy-3,3′-bis(hydroxymethyl)-1,1′-binaphthyl, mp 178–179° (note 7).

(11) Treatment of racemic 2,2′-bishydroxy-3,3′-bis(hydroxymethyl)-1,1′-binaphthyl with $KOC(CH_3)_3$ and $ClCH_2OCH_3$ in $(CH_2)_4O$ at 25° gave (55%) 2,2′-bis(methoxymethoxy)-1,1′-binaphthyl as an oil (note 7).

(12) The initially formed cycles were hydrolyzed in a mixture of 1:40:80 concentrated HCl, $CHCl_3$, and CH_3OH at 25° (2 h), and **9–11** were purified by silica gel chromatography and crystallization.

(13) The method was suggested by the work of C. J. Pedersen (*Fed. Proc.*, **27,** 1305 (1968)) and developed by Thomas L. Tarnowski, whom we thank. Stock solutions were prepared at 25° of 0.075 M host in $CDCl_3$, and of 0.0150 M (Li, Na, K, and NH_4 picrates) or 0.0100 M (Rb and Cs picrates) salt solutions in deionized water. In a 12-ml centrifuge tube were placed 0.10 ml of the $CDCl_3$ and 0.50 ml of the more or 0.75 ml of the less concentrated salt solutions. The mixture successively was stirred magnetically, centrifuged, stirred, and centrifuged. If very yellow, 0.010 ml, and if light yellow 0.050 ml, of the $CDCl_3$ layer was diluted to 5.0 ml with spectrograde CH_3CN (for blanks, deionized water-saturated $CDCl_3$ stock solutions were similarly diluted). The uv absorbance at 380 nm of the solutions was determined and that of the blanks (~0.003) subtracted (Beckman DU spectrophotometer, slit 0.6). The extinction coefficients in CH_3CN of standard solutions of the six picrates prepared similarly from the stock aqueous solutions were found to be 16 900 and cation and concentration independent over the range used for K_a determinations. The distribution coefficients $\times 10^3$ (K_d = [picrate in $CDCl_3$]/[picrate in H_2O]) of the six salts in the absence of host were found to be: Li, 1.42; Na, 1.74; K, 2.55; Rb, 6.37; Cs, 5.41; NH_4, 4.02. For each host and guest, values of R were determined [in H_2O-saturated $CDCl_3$ at equilibrium, R = (equivalents of guest)/(equivalents of host) = 5 (blank-corrected absorbance)/(16 900)], and ranged from 0.000 18 to 0.256. Values of K_a were calculated from the equation, $K_a = R/[K_d(a - 0.075cR)^2(1 - R)]$, where a = molarity of the stock aqueous solutions and c = (volume of $CDCl_3$ layer)/(volume of H_2O layer). Values of K_a calculated from similarly treated aliquots of the equilibrated aqueous layer gave within experimental error the same values as those determined from the $CDCl_3$ layer.

(14) Corey–Pauling–Koltun (CPK) molecular models of the hosts were fitted with a series of graded ball bearings whose diameters matched those of the alkali metal ions. We thank Professor J. M. Lehn for suggesting the use of ball bearings for this purpose.

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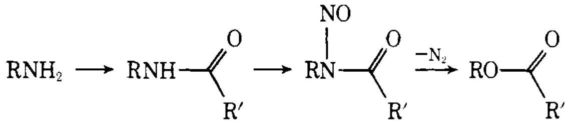
Effect of Pressure on the Stereochemistry of Ion Pair Collapse in the *N*-Nitrosamide Deamination

Sir:

The decomposition of *N*-nitrosamides (**1**) is a reaction useful for the conversion of amines into esters;[1] it involves the acylation of the amine, nitrosation of the amide, and, finally, the thermal decomposition of the nitrosamide:



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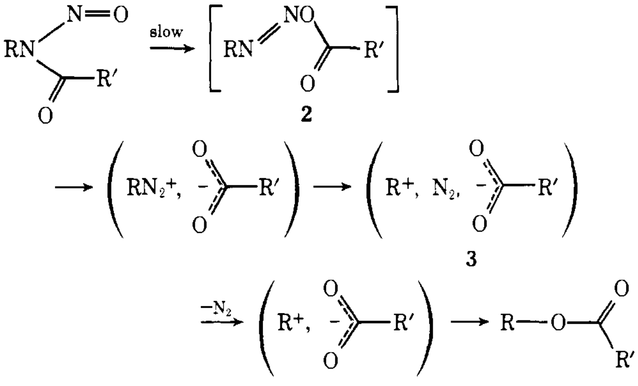
The mechanism of the last step in this sequence is thought to be formation of diazoester **2** in the rate controlling step, ionization, detachment of nitrogen to give loose (nitrogen-separated) ion-pair **3**, and, finally, collapse via the tight pair stage **4**. A variety of evidence has been amassed in support of this pathway. These studies have included the use of product and solvent studies,[1] bridgehead amino-substituted polycyclic compounds,[2] and optically active amines;[3] a comparison with the corresponding nitro derivatives;[4] ^{18}O-scrambling studies;[5] and a comparison with the same ion-pairs from other sources[6] and a comparison of secondary and tertiary amines.[3] While the reaction is characterized primarily by retention of configuration, some inversion (intramolecular[5]) does occur.[7] The inversion presumably results from rotation of the carbonium ion and circumnavigation of it by the anion prior to the ester forming step.



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3

4

Pressure effects on reactions involving ion-pairs have been described in several cases. All of these studies have a single feature in common: pressure promotes the formation of tight ion pairs from neutral compounds, of loose pairs from tight ones, and of separate ions from ion-pairs. Thus, the rate of isomerization which sometimes accompanies ester solvolysis (and which presumably results from internal return) is accelerated by pressure[8] but not as much as the rate of solvolysis itself;[9] the tight-loose equilibrium of lithium fluorenide in THF is shifted toward the latter species by pressure;[10] and the N/O-alkylation ratio of the sodium salt of fluorenone oxime under pressure shifts in the direction characteristic of the free ions rather than of the pair.[11] The ionic rate[12] and equilibrium constants[13] for literally hundreds of substances have been compiled, and not a single genuine case appears to be known in which ionization is suppressed by the application of high pressures.[14]

We have now made some measurements of the effect of pressure on the degree of racemization accompanying the deamination of optically active *N*-nitroso-*N*-*p*-chlorobenzhydrylbenzamide (**5**) in methylene chloride at 25° (50–100 mg in 20 ml). These solutions were allowed to decompose for 24 h; *ir* spectra were compared before and after to