J. Am. Chem. Soc. 1982, 104, 4073–4076

Thermodynamic Constants of Complexes of Crown Ethers and Uncharged Molecules and X-ray Structure of the 18-Crown-6·$(CH_3NO_2)_2$ Complex

Jan A. A. de Boer,[†] David N. Reinhoudt,*[,†] Sybolt Harkema,[‡] Gerrit J. van Hummel,[‡] and Feike de Jong[§]

Contribution from the Laboratories of Organic Chemistry and Chemical Physics, Twente University of Technology, 7500 AE Enschede, The Netherlands, and Kon./Shell-Laboratorium (Shell Research B.V.), 1031 CM Amsterdam-N, The Netherlands. *Received May 15, 1981*

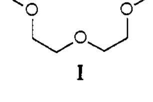
Abstract: In the solid state 18-crown-6 (**1**) forms a 1:2 complex with nitromethane, the structure of which has been determined by X-ray diffraction. The conformation of the crown found is a regular one with almost D_{3d} symmetry. Close contacts are found between the methyl carbon atom and oxygen atoms of the ring (mean value 3.28 Å). The final R value was 13.0%. In solution **1** forms both 1:1 and 1:2 complexes with nitromethane, acetonitrile, and malonitrile, as can be shown by dynamic ^1H NMR spectroscopy. The thermodynamic constants of complexation for the 1:1 complexes were obtained from plots of log K vs. T^{-1} for the following compounds: nitromethane, $\Delta H° = -7.6$ kcal mol^{-1}, $\Delta S° = -25$ cal mol^{-1} K^{-1}; acetonitrile, $\Delta H° = -6.0$ kcal mol^{-1}, $\Delta S° = -22$ cal mol^{-1} K^{-1}; malonitrile, $\Delta H° = -14.2$ kcal mol^{-1}, $\Delta S° = -37$ cal mol^{-1} K^{-1}. 1,3-Xylyl-18-crown-5 (**2**) only forms a 1:1 complex with nitromethane in solution with $\Delta H° = -3.6$ kcal mol^{-1} and $\Delta S° = -13$ cal mol^{-1} K^{-1}.

Whereas most of the work on crown ether complexation deals with complexes of metal cation and ammonium salts, recently a number of well-defined stoichiometric complexes with uncharged molecules have been reported.[1] Uncharged molecules that form such complexes all contain either polar O–H bonds (alcohols[2] and water[3]), polar N–H bonds [(thio)urea[4] and (sulfon)amides[5,6]], or polar C–H bonds (acetonitrile,[7] malonitrile,[8] dimethyl acetylenedicarboxylate[9a–c] dimethyl sulfone,[9d] dimethyl sulfate,[10] dimethyl carbonate,[10] dimethyl oxalate,[10] and dimethyl fumarate[10]).

Detailed information about the structure of these complexes in the crystalline state is available in a number of cases from single-crystal X-ray analysis.[4b,5b,8a,9c,d] A preliminary conclusion is that hydrogen bonds between the crown ether donor atoms and the guest molecule determine the structure of the complexes in the crystalline state. To our knowledge there are no previous reports on the thermodynamic stabilities of complexes of crown ethers and uncharged guest molecules.

We report the results of a quantitative study of the thermodynamic stability of complexes of uncharged guest molecules and crown ethers in benzene. As representative model substrates we prepared the crystalline 18-crown-6–nitromethane (1:2) complex that has been reported previously by McLachlan[11] but without details about its structure and the 1:2 18-crown-6–malonitrile complex as described by Kaufmann et al.[8a]

Table I gives the positional parameters determined by X-ray diffraction. The atom numbering can be found in Figure 1, which gives two views of an 18-crown-6 ring (**1**) and the nitromethane molecules associated with it. The resulting bond lengths and angles are collected in Table II. The bond lengths and angles in the macrocycle compare very well with the mean values given for a number of 18-crown-6 molecules by Goldberg.[12]



I

Table I. Fractional Atomic Coordinates (×10⁴)

atom	x	y	z
O(1)	9556 (4)	5926 (6)	7822 (5)
C(2)	8659 (6)	6764 (10)	7600 (9)
C(3)	7905 (6)	5683 (11)	6667 (10)
O(4)	8049 (3)	5694 (6)	5153 (6)
C(5)	7384 (6)	4673 (10)	4171 (12)
C(6)	7577 (6)	4804 (11)	2606 (11)
O(7)	8477 (4)	3998 (5)	2588 (5)
C(8)	8753 (7)	4060 (11)	1163 (8)
C(9)	9676 (8)	3153 (11)	1276 (9)
C(10)	5026 (5)	7882 (8)	9341 (8)
N(11)	5425 (6)	6632 (8)	8520 (10)
O(12)	6200 (7)	6077 (11)	8978 (12)
O(13)	5033 (8)	6346 (11)	7228 (10)

Table II. Bond Distances (Å) and Angles (deg)

	A. Distances, Å		
O(1)–C(2)	1.42 (1)	C(6)–O(7)	1.44 (1)
O(1)–C(9)′	1.44 (1)	O(7)–C(8)	1.43 (1)
C(2)–C(3)	1.51 (1)	C(8)–C(9)	1.49 (1)
C(3)–O(4)	1.43 (1)	C(10)–N(11)	1.46 (1)
O(4)–C(5)	1.43 (1)	N(11)–O(12)	1.18 (1)
C(5)–C(6)	1.50 (1)	N(11)–O(13)	1.21 (1)
	B. Angles, deg		
C(2)–O(1)–C(9)′	111.3 (8)	C(6)–O(7)–C(8)	113.6 (8)
O(1)–C(2)–C(3)	106.8 (7)	O(7)–C(8)–C(9)	108.5 (7)
C(2)–C(3)–O(4)	108.3 (7)	C(8)–C(9)–O(1)′	108.3 (8)
C(3)–O(4)–C(5)	113.1 (9)	C(10)–N(11)–O(12)	121.7 (11)
O(4)–C(5)–C(6)	108.9 (7)	C(10)–N(11)–O(13)	119.2 (10)
C(5)–C(6)–O(7)	108.0 (8)	O(12)–N(11)–O(13)	117.9 (12)

Table III. Torsion Angles (deg) in the Ring, Standard Deviation 1°

C(9)′–O(1)–C(2)–C(3)	−179
O(1)–C(2)–C(3)–O(4)	−74
C(2)–C(3)–O(4)–C(5)	179
C(3)–O(4)–C(5)–C(6)	179
O(4)–C(5)–C(6)–O(7)	72
C(5)–C(6)–O(7)–C(8)	−179
C(6)–O(7)–C(8)–C(9)	−179
O(7)–C(8)–C(9)–O(1)′	−72
C(2)–O(1)–C(9)′–C(8)′	−177

Due to the inaccuracy indicated in the experimental section, no detailed information on the interaction between the crown ether and nitromethane could be obtained, but some conclusions can be drawn. From Figure 1 it can be seen that the methyl group is in close contact with the atoms of the ring. The shortest dis-

---

[†] Laboratory of Organic Chemistry.
[‡] Laboratory of Chemical Physics.
[§] Kon./Shell-Laboratorium.

0002-7863/82/1504-4073$01.25/0

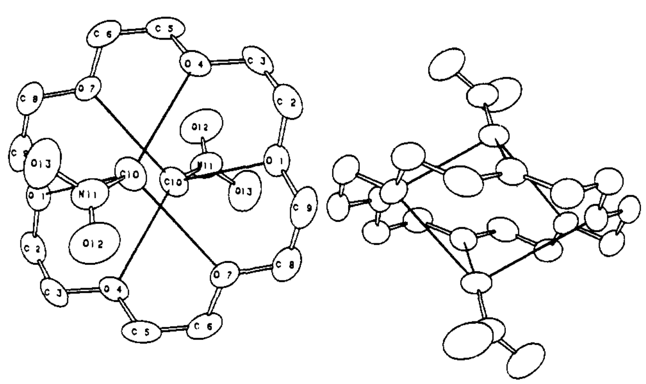


Figure 1. Crystal structure of the 18-crown-6 nitromethane (1:2) complex. The thermal ellipsoids are scaled to include 25% probability. Short C···O contacts are indicated by thin lines.

tances between the methyl carbon atom and the atoms of the ring are the C···O distances indicated by thin lines in Figure 1. The distances found are as follows: 3.26(2), 3.25(2) and 3.33(2) Å, to be compared with 3.55(2), 3.54(2), and 3.50(2) Å for the distances between the methyl carbon atom and the remaining three oxygen atoms. From the C···O distances given, it can be concluded that C–H···O hydrogen bonds play an important role in the interaction between host and guest. The torsion angles for the macrocycle are given in Table III.

The sequence of torsion angles (O–C, C–C, C–O, etc.) for the independent part of the ring is ag$^-$a ag$^+$a ag$^-$a, in accordance with a regular (almost D_{3d}) conformation of the ring. The same conformation of the ring is found in a number of complexes of 18-crown-6 with inorganic ions and organic molecules.[12,13]

When the complex was dissolved in deuteriobenzene we found a downfield shift of the nitromethane protons in the ^{1}H NMR spectrum. The addition of excess of 18-crown-6 caused a further downfield shift of the nitromethane methyl protons, and we concluded that the 1:2 complex in benzene is partly dissociated. We used the chemical shift difference between free nitromethane and nitromethane in the presence of 18-crown-6 to determine the thermodynamic stability of the complex. Knöchel and co-workers[8b] have previously also reported downfield chemical shifts upon the addition of 18-crown-6 to solutions of α,ω-dinitriles (e.g., malonitrile) in benzene, but they did not use these observations to obtain association constants and thermodynamic constants of the complexation.

Table IV. 1:1 vs. 1:2 Complexes of Nitromethane and 1 at Different Concentration at 300 K

concn of 18-crown-6, mol L^{-1}	concn of CH_3NO_2, mol L^{-1}	δ_{obsd}	% 1:1 complex[a]	% 1:2 complex[a]
1.5634	0.2027	4.317	52.9	8.2
0.7658	0.0993	3.970	41.7	5.0
0.1445	0.3788	3.413	8.4	6.3
0.0571	0.1498	3.145	5.1	1.8

[a] Calculated on nitromethane.

Because 18-crown-6 forms a 1:2 complex with nitromethane in the solid state, the problem of the determination of the association constants in solution is complicated because either the exclusively 1:1 complexation (model I, eq 1 or both 1:1 and 1:2 complexation (model II, eq (2a,b) can exist. The concentrations

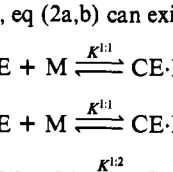
$$\mathrm{CE} + \mathrm{M} \overset{K^{1:1}}{\rightleftharpoons} \mathrm{CE{\cdot}M} \qquad (1)$$

$$\mathrm{CE} + \mathrm{M} \overset{K^{1:1}}{\rightleftharpoons} \mathrm{CE{\cdot}M} \qquad (2a)$$

$$\mathrm{CE{\cdot}M} + \mathrm{M} \overset{K^{1:2}}{\rightleftharpoons} \mathrm{CE{\cdot}M_2} \qquad (2b)$$

of free and complexed uncharged molecules cannot be determined independently because the rates of exchange are fast on the ^{1}H NMR time scale. Therefore the observed chemical shift of the protons of the uncharged guest molecules is a function of the association constant(s), the chemical shift of free uncharged guest molecules, and the unknown chemical shift of the complexed uncharged molecules. As outlined in the Experimental Section, the observed chemical shifts have been compared with the calculated chemical shifts by using both models. In the case of nitromethane the experimental data are only in agreement with the calculated chemical shifts of model II. The results are given in Tables IV and V.

These experiments were carried out at four different temperatures and showed that the association constants of both the 1:1 and the 1:2 complex increase with decreasing temperature (Table V). Similar experiments were also carried out with 1′,3′-xylyl-18-crown-5 (**2**) of which no solid nitromethane complex could be



2

obtained. The downfield chemical shift of the nitromethane methyl protons in mixtures of **2** and nitromethane in deuteriobenzene, at four different temperatures, was used to calculate K of the 1:1 complex of nitromethane and **2** (Table V). The contribution of a 1:2 complex to the complexation in this case was negligible. This difference between 18-crown-6 and 1′,3′-xylyl-18-crown-5 can be attributed to the presence of an intraannular aromatic proton in **2**. Complexation of a nitromethane molecule at one face of **2** will cause steric shielding at the opposite face of **2**. The same steric shielding forces the complex of **2** and *tert*-butylammonium hexafluorophosphate into a "nesting" conformation, as was recently established by X-ray analysis.[14]

The same experiments were carried out with **1** and acetonitrile and malonitrile (Table VI). In the case of acetonitrile at 309

---

(1) For recent reviews on the complexing properties of crown ethers, see: (a) *Top. Curr. Chemi.* **1981**, *98*. (b) De Jong, F.; Reinhoudt, D. N. *Adv. Phys. Org. Chem.* **1980**, *17*, 279.

(2) (a) Cram, D. J.; Helgeson, R. C.; Koga, K.; Kyba, E. P.; Madan, K.; Sousa, L. R.; Siegel, M. G.; Moreau, P.; Gokel, G. W.; Timko, J. M.; Sogah, C. D. Y. *J. Org. Chem.* **1978**, *43*, 2758. (b) Weber, E.; Vögtle, F. *Angew. Chem.* **1980**, *92*, 1067.

(3) (a) De Jong, F.; Reinhoudt, D. N.; Smit, C. J. *Tetrahedron Lett.* **1976**, 1371. (b) Koenig, K. E.; Helgeson, R. C.; Cram, D. J. *J. Am. Chem. Soc.* **1976**, *98*, 4018.

(4) (a) Pedersen, C. J. *J. Org. Chem.* **1971**, *36*, 1690. (b) Harkema, S.; Van Hummel, G. J.; Daasvatn, K.; Reinhoudt, D. N. *J. Chem. Soc., Chem. Commun.* **1981**, 368.

(5) (a) Takayama, K.; Nambu, N.; Nagai, T. *Chem. Pharm. Bull.* **1979**, *27*, 215. (b) Knöchel, A.; Kopf, J.; Oehler, J.; Rudolph, G. *J. Chem. Soc., Chem. Commun.* **1978**, 595.

(6) (a) Vögtle, F.; Müller, W. M.; Weber, E. *Chem. Ber.* **1980**, *113*, 1130. (b) Vögtle, F.; Müller, W. M. *Naturwissenschaften* **1980**, *67*, 255.

(7) Gokel, G. W.; Cram, D. J.; Liotta, C. L.; Harris, H. P.; Cook, F. L. *J. Org. Chem.* **1974**, *39*, 2445.

(8) (a) Kaufmann, R.; Knöchel, A.; Kopf, J.; Oehler, J.; Rudolph, G. *Chem. Ber.* **1977**, *110*, 2449. (b) El Basyony, A.; Klimes, J.; Knöchel, A.; Oehler, J.; Rudolph, G. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1976**, *31B*, 1192.

(9) (a) Timko, J. M.; Cram, D. J. *J. Am. Chem. Soc.* **1974**, *96*, 7159. (b) Timko, J. M.; Moore, S. S.; Walba, D. M.; Hiberty, P. C.; Cram, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 4207. (c) Goldberg, I. *Acta Crystallogr., Sect. B* **1975**, *31B*, 754. (d) Bandy, J. A.; Truter, M. R.; Vögtle, F. *Acta Crystallogr.* **1981**, 1337, 1568.

(10) Van Zon, A.; De Jong, F.; Reinhoudt, D. N.; Torny, G. J.; Onwezen, Y. *Recl. Trav. Chim. Pays-Bas* **1981**, *100*, 453.

(11) McLachlan, R. D. *Spectrochim. Acta, Part A* **1974**, *30*, 2153. Personal communication from F. P. Boer and P. P. North.

(12) Goldberg, I. "The Chemistry of Ethers, Crown Ethers, Hydroxyl Groups and their Sulphur Analogues", Supplement E1; Patai, S., Ed.; Wiley: London, 1981.

(13) (a) Dale, J. *Isr. J. Chem.* **1980**, *20*, 3. (b) Bovill, M.; Chadwick, D. J.; Sutherland, I. O.; Watkin, D. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1529.

(14) Reinhoudt, D. N.; Den Hertog, H. J., Jr.; De Jong, F. *Tetrahedron Lett.* **1981**, 2513.

Table V. Association Constants of Crown Ether·Nitromethane Complexes at Different Temperatures

	18-crown-6[a]			1',3'-xylyl-18-crown-5[b]	
temp, K	$K^{1:1}$,[c] L mol^{-1}	$K^{1:2}$,[d] L mol^{-1}	$\delta_{\mathrm{CH_3NO_2}}{}^{\mathrm{complex}}$	$K^{1:1}$,[c] L mol^{-1}	$\delta_{\mathrm{CH_3NO_2}}{}^{\mathrm{complex}}$
309	0.9	1.5	4.96	0.53	4.78
300	1.2	2.5	4.92	0.61	4.75
290	1.8	4.0	4.88	0.76	4.73
282	3.0	4.9	4.83	0.93	4.72

[a] Calculated from 10 independent experimental δ_{obsd} values; ratio $0.1297 < [\mathrm{CH_3NO_2}]/[\mathrm{CE}] < 2.6235$; $0.0993 < [\mathrm{CH_3NO_2}] < 0.3788$. [b] Calculated from 17 independent experimental δ_{obsd} values. [c] Accuracy ±10%. [d] Accuracy ±25%.

Table VI. Association Constants of 1 with Acetonitrile and Malonitrile in Deuteriobenzene at Different Temperatures

	$\mathrm{CH_3CN}$[a]			$\mathrm{CH_2(CN)_2}$[a]		
temp, K	$K^{1:1}$,[b] L mol^{-1}	$K^{1:2}$,[c] L mol^{-1}	$\delta_{\mathrm{CH_3CN}}{}^{\mathrm{complex}}$	$K^{1:1}$,[b] L mol^{-1}	$K^{1:2}$,[c] L mol^{-1}	$\delta_{\mathrm{CH_2(CN)_2}}{}^{\mathrm{complex}}$
309	0.36		3.19	77	9	4.52
300	0.48		3.00	150	11	4.58
290	0.60	0.90	2.93	390	12	4.62
282	0.80	1.70	2.72	670	14	4.68

[a] Calculated from 10 independent experimental δ_{obsd} values. [b] Accuracy ±10%. [c] Accuracy ±25%.

Table VII. Thermodynamic Constants of Complexes of Crown Ethers with Nitromethane, Acetonitrile, and Malonitrile in Deuteriobenzene

complex	$\Delta H°$, kcal mol^{-1}	$\Delta S°$, cal mol^{-1} K^{-1}
$1\cdot\mathrm{CH_3CN}$	−6.0	−22
$1\cdot\mathrm{CH_3NO_2}$	−7.6	−25
$1\cdot\mathrm{CH_2(CN)_2}$	−14.2	−37
$2\cdot\mathrm{CH_3NO_2}$	−3.6	−13

and 300 K, the exclusive 1:1 complexation, in agreement with model I, is observed. At lower temperatures, 290 and 282 K, both 1:1 and 1:2 complexation is found. It is reasonable to assume that also at 309 and 300 K 1:2 complexation occurs, but in a concentration too low to contribute substantially to the total complexation.

For malonitrile a remarkable strong 1:1 association is found compared with nitromethane and acetonitrile, which can be attributed to the two cyano groups, which render the two hydrogen atoms much more capable in forming strong hydrogen bonds with 18-crown-6.

From a plot of log K vs. T^{-1} the thermodynamic constants $\Delta H°$ and $\Delta S°$ of all the 1:1 complexes were obtained; the results are given in Table VII. The association constants of the 1:2 complexes are less accurate, and they have not been used to calculate the $\Delta H°$ and $\Delta S°$ values of these complexes.

These results show that although in the crystalline state the complexes of 18-crown-6 with nitromethane and malonitrile have a 1:2 stoichiometry, in solution 1:1 complexation is the most important. In both cases, however, 1:2 complexation occurs. For the acetonitrile complex, of which no X-ray study is available, 1:2 complexation occurs only at lower temperatures. The association constants of the 1:1 complexes of 18-crown-6 with nitromethane and acetonitrile are smaller as those reported for 18-crown-6 with a series of sulfonamides, for which K values of 3–8 L mol^{-1} in chloroform are reported.[15] With the exception of malonitrile the complexes of crown ethers with the uncharged molecules studied are less stable by several orders of magnitude than those of crown ethers and ammonium salts, for which in chloroform $\Delta G°$ values of −5.9 to −9.8 kcal mol^{-1} at 293 K have been reported.[16] The 18-crown-6·$\mathrm{CH_2(CN)_2}$ complex is moderately stable, with a value of $\Delta G°$ at 293 K in benzene of −3.3 kcal mol^{-1}. As with complexation of ammonium salts, the 1',3'-xylyl-18-crown-5·$\mathrm{CH_3NO_2}$ complex is less stable than the 18-crown-6·($\mathrm{CH_3NO_2}$) complex at room temperature.[16] A further analogy between ammonium salt–crown ether complexes[17] and the complexes with uncharged guest molecules is that a higher enthalpy of binding is accompanied by a more rigid complex structure, $-T\Delta S°$ ($1\cdot\mathrm{CH_3NO_2}$) > $-T\Delta S°$ ($2\cdot\mathrm{CH_3NO_2}$) and $-T\Delta S°$ ($1\cdot\mathrm{CH_3CN}$) < $-T\Delta S°$ ($1\cdot\mathrm{CH_3NO_2}$) < $-T\Delta S°$ ($1\cdot\mathrm{CH_2(CN)_2}$). The thermodynamic constants of complexation are quite similar to those of charge-transfer complexes, e.g., between 1,3,5-trinitrobenzene and hexamethylbenzene in carbon tetrachloride, for which $\Delta H°$ and $\Delta S°$ values of −3.6 kcal mol^{-1} and −8.8 eu have been reported.[18]

Experimental Section

Preparation of 18-Crown-6·$(\mathrm{CH_3NO_2})_2$. The 18-crown-6·$(\mathrm{CH_3NO_2})_2$ crystals that were used for the X-ray analysis were prepared by mixing a 10% solution (v/v) of nitromethane in diethyl ether with a solution of 18-crown-6 in chloroform. The white 18-crown-6·$(\mathrm{CH_3NO_2})_2$ solid precipitated immediately and was filtered off. This solid was dissolved in refluxing diethyl ether. A slow evaporation at 20 °C of the solvent with exposure to the atmosphere yielded colorless crystals that slowly precipitated from the solution, dec >40 °C.

X-ray Diffraction. Crystals of the 18-crown-6·nitromethane (1:2) complex belong to the monoclinic space group $P2_1/n$, with $a = 14.081$ (2), $b = 8.314$ (2), $c = 9.083$ (2) Å, $\beta = 101.90$ (3)°; $Z = 2$. The asymmetric part of the unit cell contains a nitromethane molecule and a half 18-crown-6 molecule. The other half of the crown is generated by a center of symmetry.

Intensities were measured on a single-crystal diffractometer using the θ–2θ scanning mode (Mo Kα radiation, graphite monochromator, $3 < \theta < 25°$; 1944 reflections measured). By coating the crystal with hair spray, the decomposition of the crystal (presumably due to the loss of nitromethane) could be reduced to make data collection possible. A correction for the decrease in intensity, based on the intensities of standard reflections, measured every hour, was performed.

The structure was solved by direct methods[20] and refined by full-matrix least squares[21] to an R factor of 13.0%. Reflections having an intensity greater than the estimated standard deviation (total number, 1276) were used in the refinement. Parameters refined were the positional and anisotropic thermal parameters of the heavy atoms. Hydrogen atoms have not been located. The weight for each reflection was taken to be $\omega = \sigma^{-2}$, where σ is the estimated standard deviation of the structure factor. σ was chosen as $\sigma = S + 0.01|F_0|$, in which S is the standard

---

(15) Takayama, K.; Nambu, N.; Nagai, T. *Chem. Pharm. Bull.* **1979**, *27*, 715.

(16) De Jong, F.; Reinhoudt, D. N.; Huis, R. *Tetrahedron Lett.* **1977**, 3985.

(17) Peacock, S. C.; Domeier, L. A.; Gaeta, F. C. A.; Helgeson, R. C.; Timko, J. M.; Cram, D. J. *J. Am. Chem. Soc.* **1978**, *100*, 8190.

(18) Foster, R.; Fijfe, C. A.; Moreman, M. I. *J. Chem. Soc., Chem. Commun.* **1967**, 913.

(19) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *27A*, 368.

(20) Busing, W. R.; Martin, K. O.; Levy, H. A. ORFLS, Report ORNL-TM-305, Oak Ridge National Laboratory, Tennessee, 1962.

(21) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, 1974; Vol. 4.

deviation of the observed structure factor ($|F_o|$) due to counting statistics. Scattering factors were taken from *International Tables for X-ray Crystallography*.[21]

In view of the rather high R value obtained and the anisotropy of some of the thermal ellipsoids, indicating disorder or inaccuracy of the data due to loss of nitromethane, we have decided to perform a low-temperature structure determination, the results of which will be published elsewhere.

Determination of the Association Constants. All ^{1}H NMR spectra were recorded on a Bruker 80-MHz apparatus with a B-VT-1000 temperature accessor. All measurements were carried out in deuteriobenzene with Me_4Si as the internal standard. Considering only 1:1 complexation (model I), the association constant can be expressed by eq 3 in which

$$K = \frac{[\mathrm{CE{\cdot}M}]}{([\mathrm{CE}]_0 - [\mathrm{CE{\cdot}M}])([\mathrm{M}]_0 - [\mathrm{CEM}])} \tag{3}$$

$[\mathrm{CE}]_0$ and $[\mathrm{M}]_0$ are the initial concentrations of respectively crown ether and uncharged molecules. The observed chemical shift of the protons of the uncharged guest molecules is given by eq 4, in which δ_M is the

$$\delta_\mathrm{obsd} = \chi_\mathrm{M}\delta_\mathrm{M} + \chi_\mathrm{CE{\cdot}M}\delta_\mathrm{CE{\cdot}M} \tag{4}$$

chemical shift of the uncharged molecule, $\delta_\mathrm{CE{\cdot}M}$ is the chemical shift of this molecule in the complex, $\chi_\mathrm{M} = ([\mathrm{M}]_0 - [\mathrm{CE{\cdot}M}])/[\mathrm{M}]_0$, and $\chi_\mathrm{CE{\cdot}M} = [\mathrm{CE{\cdot}M}]/[\mathrm{M}]_0$. For a series of samples in which both CE and M concentrations were varied, the chemical shift was measured, and in an iterative procedure a minimum is found by eq 5. By varying K and

$$F = \sum_i (\delta_{\mathrm{obsd}_i} - \chi_{\mathrm{M}_i}\delta_\mathrm{M} - \chi_{\mathrm{CE{\cdot}M}_i}\delta_\mathrm{CE{\cdot}M})^2 \tag{5}$$

$\delta_\mathrm{CE{\cdot}M}$, both χ_M and $\chi_\mathrm{CE{\cdot}M}$ are calculated from eq 6. If one takes into account that for the minimum $\partial F/\partial\delta_\mathrm{CE{\cdot}M}$ must be zero, then $\delta_\mathrm{CE{\cdot}M}$ can be expressed according to

$$[\mathrm{CE{\cdot}M}] = \tfrac{1}{2}\{([\mathrm{CE}]_0 + [\mathrm{M}]_0 + 1/K) - [([\mathrm{CE}]_0 + [\mathrm{M}]_0 + 1/K)^2 - 4[\mathrm{CE}]_0[\mathrm{M}]_0]^{1/2}\} \tag{6}$$

$$\delta_\mathrm{CE{\cdot}M} = \left(\sum_i \delta_{\mathrm{obsd}_i}\chi_{\mathrm{CE{\cdot}M}_i} - \sum_i \chi_{\mathrm{CE{\cdot}M}_i}\chi_{\mathrm{M}_i}\delta_\mathrm{M}\right)/\sum_i \chi^2_{\mathrm{CE{\cdot}M}_i} \tag{7}$$

By substitution of eq 7 into eq 5, F needs only to be minimized for K.

When both 1:1 and 1:2 complexation (model II) takes place, the equations can be easily modified. In this model we have assumed that the chemical shifts of the uncharged molecule in the 1:1 and 1:2 complex are the same.[22] The modified function F has to be minimized now for $K^{1:1}$, $K^{1:2}$, and $\delta_\mathrm{CE{\cdot}M}$.

The chemical shifts of uncharged molecules in benzene depend on concentration and temperature. There is a linear relation between concentration and chemical shift at a certain temperature. The chemical shifts of the free uncharged molecules at different temperatures were corrected by using that linear relation. For a series of measurements, the data were fitted for both 1:1 complexation (model I) and 1:1 and 1:2 complexation (model II). The best model was the one in which the calculated data agree with the experimental data.

Registry No. I (CH_3NO_2), 82064-74-2; **1** ($(CH_3NO_2)_2$), 55075-34-8; I (CH_3CN), 60336-83-6; I ($(CH_3CN)_2$), 55075-35-9; **1** [$CH_2(CN)_2$], 63726-93-2; **1** [$CH_2(CN)_2]_2$, 61994-85-2; **2** (CH_3NO_2), 82064-75-3.

Supplementary Material Available: Tables of atomic thermal parameters and a list of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

---

[22] In the case of nitromethane, calculations were also carried out in which the chemical shift of the 1:1 complex was taken different from that of the 1:2 complex. Both types of calculations give the same results (within experimental error).

Dithizone Adsorption at Metal Electrodes. 4. Voltammetric and Surface Raman Spectroelectrochemical Investigation at a Copper Electrode

Jeanne E. Pemberton† **and Richard P. Buck***

Contribution from the Kenan Laboratories of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514. Received September 8, 1981

Abstract: Cyclic voltammetric and surface Raman spectroelectrochemical behavior of the anion of dithizone (diphenylthiocarbazone), HDz^-, has been characterized at a Cu electrode in aqueous alkaline media. The cyclic voltammetry suggests very strong interaction of HDz^- with the Cu surface. In the presence of HDz^-, significant oxidation of the Cu surface does not take place until potentials greater than 0.2–0.3 V are reached. The surface Raman spectroelectrochemical data are consistent with strong adsorption of HDz^- at the Cu surface at potentials negative of the oxidation potential. Very little control of surface HDz^- population can be realized through alteration of the potential. This is in contrast to the previous behavior observed at Ag. The surface species observed at potentials more positive than the oxidation potential of HDz^- is the disulfide. The effect of solubility on the extent of adsorption was also investigated. The surface Raman data indicate that adsorption of HDz^- in pH 10 solution is significantly greater than that in pH 12 solution in which HDz^- is more soluble. On the basis of the similarity of the surface spectra obtained and the spectrum of copper(II) dithizonate, an approximate orientation of HDz^- at the Cu/solution interface is proposed.

The utility of Raman spectroscopy as a probe of molecules at or near electrode surfaces has been amply demonstrated in the recent literature.[1,2] The sensitivity constraints imposed by the normal Raman scattering process for surface species can be overcome by exploitation of surface-enhanced Raman scattering (SERS), resonance Raman scattering (RRS), or a combination of these two phenomena (SERS + RRS) to enhance the Raman intensities to a readily measured level. The use of SERS requires the proper choice of both metal substrate and excitation frequency. SERS has been verified only at Ag,[1] Cu, and Au[3-6] metal surfaces,

---

† Present address: Department of Chemistry, University of Arizona, Tucson, Arizona 85721

(1) Van Duyne, R. P. In "Chemical and Biochemical Applications of Lasers", Moore, C. B., Ed.; Academic Press: New York, 1979; Vol. 4, pp 101.

(2) Furtak, T. E.; Reyes, J. *Surf. Sci.* **1980**, *93*, 351.

(3) Wenning, U.; Pettinger, B.; Wetzel, H. *Chem. Phys. Lett.* **1980**, *70*, 49.

0002-7863/82/1504-4076$01.25/0 © 1982 American Chemical Society