A Calorimetric Study of the Interaction in Aqueous Solution of Several Uni- and Bivalent Metal Ions with the Cyclic Polyether Dicyclohexyl-18-crown-6 at 10, 25, and 40° [1a,b]

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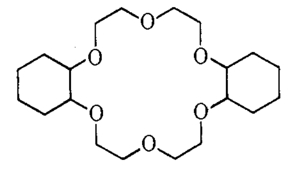
Abstract: Log K, ΔH°, and ΔS° values are reported for the interaction in aqueous solution of K^+, Rb^+, Cs^+, NH_4^+, Ag^+, Sr^{2+}, and Ba^{2+} ions with the two isomers of the cyclic polyether, dicyclohexyl-18-crown-6 (I). Little or no reaction with I was found for H^+, Li^+, Na^+, $(CH_3)_4N^+$, guanidinium, Mg^{2+}, Ca^{2+}, Co^{2+}, and Cu^{2+} ions. The stability sequences of the alkali and alkaline earth metal ions with either isomer are $K^+ > Rb^+ > Cs^+$, $Na^+ > Li^+$ and $Ba^{2+} > Sr^{2+} > Ca^{2+}$, Mg^{2+}. The alkali metal ion stability sequence is identical with the permeability sequences for these metal ions with the structurally related antibiotics valinomycin and monactin.

We recently[2] proposed 2,5,8,15,18,21-hexaoxatricyclo[20.4.0.0^{9,14}]hexacosane (I), abbreviated dicyclohexyl-18-crown-6,[3] as a model compound for thermodynamic investigations of active transport processes. This compound is one in a series of cyclic polyethers synthesized recently by Pedersen[3] which have the unusual property of forming complexes with certain of the alkali and alkaline earth metal ions. Pedersen indicates that one of the factors influencing the stabilities of the complexes is the ratio of the size of the cation to that of the hole in the polyether ring. In our earlier study the stability sequence for alkali metal ions reacting with I was reported to be

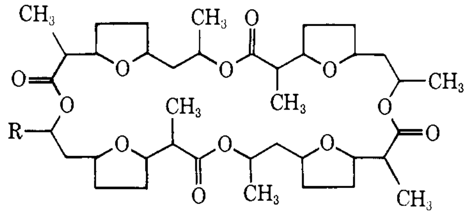
$$K^+ > Rb^+ > Cs^+ > Na^+ > Li^+$$

which is identical with the permeability sequence for these metal ions with I[4] and with the structurally related antibiotics monactin (II) and valinomycin[5] (III).



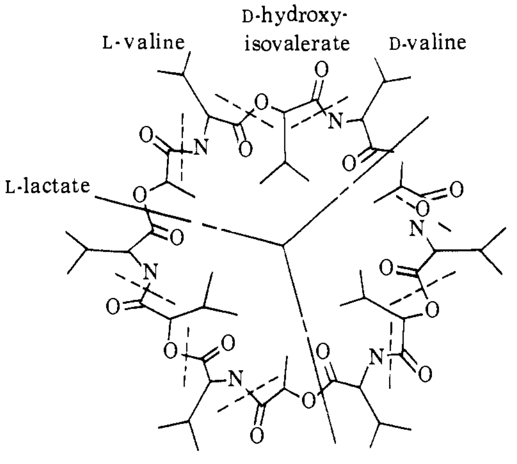
I

dicyclohexyl-18-crown-6
$C_{20}H_{36}O_6$



II

R = CH_3, nonactin
R = CH_3CH_2, monactin
$C_{40}H_{64}O_{12}$



III

valinomycin
$C_{54}H_{90}O_{18}N_6$

Cyclic polyethers, valinomycin, nonactin (II), monactin, and other macrocyclic molecules, both biological and synthetic in origin, exhibit varying degrees of biological activity as related to the processes of active ion transport,[6] photosynthesis,[7] and oxidative phosphorylation.[6,8] The biological activity of these compounds appears to be related to their macrocyclic structure which consists of a lipophilic exterior and a hydrophilic central cavity ringed with electronegative donor atoms, and their ability to assume highly specific conformations in the presence of metal ions. The macrocyclic nature of these compounds allows charged cations to be bound in the central cavity thus rendering the cation soluble in the lipid region of the membrane. The extent to which macrocyclic molecules influence alkali metal ion trans-

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port, *in vitro*, across intact mitochondrial and chromatophore membranes has been treated.[6-8] Permeability and conductance studies on artificial bilayer membranes prepared from a variety of lipid materials also indicate that these macrocyclic compounds promote selective transport of alkali metal cations[4,9,10] across membranes.

Structural determinations of the K^+–nonactin[11] and K^+–valinomycin[12] complexes in the solid and solution states, respectively, indicate that the cyclic backbones of these large macrocycles possess considerable flexibility and are capable of extensive folding in order to assume an ideal steric orientation about the central metal ion.

Few thermodynamic studies have been reported for the reaction of metal ions with macrocyclic compounds despite the obvious importance of such studies in establishing a basis for understanding the selective binding of cations by these ligands. Marked preferences by macrocyclic compounds for K^+ over Na^+ have been shown for nonactin and monactin in methanol[13] and for I in methanol[14] and aqueous solution.[2] In order to systematically define and investigate the factors which determine cation selectivity and complexation by macrocyclic molecules, we have initiated a calorimetric titration study of the reaction of cations of various sizes and types with cyclic polyethers. The cyclic polyethers possess the advantage for such a study over the cyclic antibiotics and other natural substances that they are readily synthesized from inexpensive starting materials leading to a wide variety of available compounds with various ring sizes, substituents, and numbers and types of donor atoms.

In the present study a calorimetric titration investigation is reported for the reaction of cations of various sizes with I in aqueous solution at 25°. Log K, $\Delta H°$, and $\Delta S°$ values are reported for those cases where appreciable reaction occurred. The reaction of selected cations with I was also studied at 10 and 40° and $\Delta C_p°$ values are estimated from the temperature dependence of the $\Delta H°$ values.

Experimental Section

Materials. The following chemicals were obtained in the best available purity from the sources indicated: KCl and $MgCl_2 \cdot 6H_2O$ (Mallinkrodt, AR ACS), LiCl (Mallinkrodt AR), NaCl (Wasatch Chemical Co., ACS analytical reagent), CsCl (Research Inorganics, 99.9%), RbCl (Research Inorganics, 99.9%), RbBr (K & K, 99.9%), $AgNO_3$ (Goldsmith Division of National Lead Co., ACS reagent 99.999%), NH_4Cl (Merck ACS Reagent), guanidine monohydrochloride (Baker, Baker grade), $HClO_4$, $SrCl_2 \cdot 6H_2O$ (Baker Analyzed reagent), $N(CH_3)_4I$ (Matheson Coleman and Bell, 99+%), $CaCl_2 \cdot 2H_2O$, $BaCl_2 \cdot 2H_2O$ (Baker and Adamson, reagent, ACS), $Co(ClO_4)_2 \cdot 6H_2O$., $Cu(ClO_4)_2 \cdot 6H_2O$ (G. Frederick Smith Chemical Co.). Dicyclohexyl-18-crown-6 was obtained as a mixture of isomers from Dr. H. K. Frensdorff, E. I. du Pont de Nemours and Co., Wilmington, Del.

Isomer Separation. The two isomers of I which were used in this study can be distinguished by their melting points (isomer A, 61–62°; isomer B, 69–70°) and infrared spectra; however, the specific configurations of these isomers are not presently known. Isomer B exists in two crystalline forms as has also been observed by others.[15] These forms are obtainable through modifications of the crystallization procedure. The second crystalline form, B′, has a mp of 83–84° and is slightly denser than B. B and B′ are identical in solution.

Separation of the isomers of I was accomplished by column chromatography on Woelm Alumina (activity grade I) using $n\text{-}C_6H_{14}$–$(C_2H_5)_2O$ mixtures (increasing the mole fraction of ether with time) as the eluents.[15] After removal of the main portion of isomer A the column was stripped with methanol to recover the bulk of isomer B. After removal of the solvent used in the elution, isomers A and B were purified by recrystallization from ether and hexane, respectively.

Anal. Calcd for $C_{20}H_{36}O_6$: C, 64.45; H, 9.74. Found (isomer A): C, 64.58; H, 9.97. Found (isomer B): C, 64.69; H, 9.89. Found (isomer B′) C, 64.53; H, 9.85.

Solution Preparation. Solutions 0.2–0.8 *M* in each cation were prepared by dissolving the appropriate weight of each salt in boiled, doubly distilled water. The $AgNO_3$, KCl, RbCl, RbBr, and CsCl salts were dried at 125° prior to weighing. The Sr^{2+} and Ba^{2+} solutions were standardized gravimetrically as the monohydrogen phosphate and chromate, respectively. The NH_4^+ solutions were standardized gravimetrically by precipitation of AgCl.

Solutions of each isomer of I were prepared by dissolving known amounts of A and B, assuming a molecular weight of 372.5 g/mol and no molecules of solvation, in boiled, doubly distilled water to give final concentrations of ~0.01 *M*.

Procedure and Calculations. The calorimetric determinations were made in a precision titration calorimeter[16] at 10, 25, and 40° by titrating into aqueous solutions of I aqueous solutions of $HClO_4$ and of each cation salt listed in the Materials section. Excess cation was present in the reaction vessel at the conclusion of each titration. The approximate final ionic strength, μ, in the calorimeter was 0.03 to 0.09, depending on the titrant used.

In those cases where a sufficient heat change was observed, log K, $\Delta H°$, and $\Delta S°$ values were calculated from the calorimetric titration data by methods similar to those previously described[17] with the aid of an IBM 360 computer. At the low μ values used, ΔH values have been found in previous studies[18] not to vary significantly with μ; therefore, in the present study they are assumed to be equal to $\Delta H°$ values. In the cases of the K^+–IA, Rb^+–IA, and NH_4^+–IA systems changes up to threefold in final cation concentration resulted in no significant change in the log K values, indicating that the species assumed correctly define the systems. Although the calorimetric method of determining equilibrium constants used here is limited to reactions for which log K lies between 0 and 4 the method has wide applicability since by judicious selection of reactants[19,20] one can generally obtain competitive equilibria with ΔH and log K values within the range of accurate determination.

Results

In Figure 1 corrected heat of reaction values, $-Q_i$(corr), for sample runs are plotted *vs.* the number of millimoles of titrant added to a solution containing IA. The data in Figure 1 show that the reactions become less exothermic in the order $Ba^{2+} > Sr^{2+} > K^+ > Rb^+ > NH_4^+ > Cs^+ > Na^+, Li^+ > Mg^{2+} > Ca^{2+}$. The Q_i(corr) values of Na^+, Li^+, and Mg^{2+} as well as those of H^+, $(CH_3)_4N^+$, guanidinium ion, Co^{2+}, and Cu^{2+} are zero.

With respect to the magnitudes of their Q_i(corr) values, the reactions studied can be placed in two cate-

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Table I.[a] Log K, $\Delta H°$, and $\Delta S°$ Values for the Reaction $M^{n+} + I = MI^{n+}$

		Isomer A			Isomer B		
M^{n+}	Temp, °C	Log K	$\Delta H°$, kcal/mol	$\Delta S°$, cal/(deg mol)	Log K	$\Delta H°$, kcal/mol	$\Delta S°$, cal/(deg mol)
K^+	10	2.15 ± 0.02	−4.14 ± 0.10	−4.8	1.79 ± 0.02	−5.78 ± 0.03	−12.2
	25	2.02 ± 0.03 (2.18)[b]	−3.88 ± 0.04	−3.8	1.63 ± 0.03 (1.78)[b]	−5.07 ± 0.03	−9.6
	40	1.91 ± 0.03	−3.58 ± 0.01	−2.7	1.50 ± 0.05	−4.19 ± 0.03	−6.5
Rb^+	10	1.61 ± 0.01	−3.43 ± 0.03	−4.8	0.95 ± 0.05	−4.6 ± 0.2	−11.9
	25	1.52 ± 0.01	−3.33 ± 0.01	−4.2	0.87 ± 0.01	−3.97 ± 0.03	−9.3
	40	1.40 ± 0.02	−3.29 ± 0.03	−4.1	0.86 ± 0.04	−3.30 ± 0.16	−6.6
Cs^+	10	1.00 ± 0.07	−2.40 ± 0.10	−3.9			
	25	0.96 ± 0.06 (1.25)[b]	−2.41 ± 0.04	−3.7	(0.9)[b]		
	40	0.96 ± 0.03	−2.38 ± 0.07	−3.2			
NH_4^+	25	1.33 ± 0.02 (1.4)[b]	−2.16 ± 0.03	−1.2	0.80 ± 0.03 (0.8)[b]	−3.41 ± 0.02	−7.8
Ag^+	25	(2.3)[b]			1.59 ± 0.04 (1.8)[b]	−2.09 ± 0.02	0.3
Sr^{2+}	10	3.43 ± 0.01	−3.68 ± 0.01	2.7	2.80 ± 0.01	−3.45 ± 0.01	0.6
	25	3.24 ± 0.02	−3.68 ± 0.02	2.5	2.64 ± 0.03	−3.16 ± 0.03	1.5
	40	3.16 ± 0.10	−3.70 ± 0.10	2.6	2.56 ± 0.04	−2.91 ± 0.04	2.4
Ba^{2+}	10	3.84 ± 0.03	−4.97 ± 0.02	0.0	3.44 ± 0.09	−6.82 ± 0.05	−8.3
	25	3.57 ± 0.02	−4.92 ± 0.02	−0.2	3.27 ± 0.02	−6.20 ± 0.02	−5.8
	40	3.47 ± 0.01	−4.85 ± 0.14	0.4	3.12 ± 0.02	−5.78 ± 0.03	−4.2

[a] Values given in each case are valid at $\mu = 0$ and are the average of those taken from four to six determinations. The uncertainties are given as the standard deviations. The $\Delta S°$ values were calculated from the corresponding log K and $\Delta H°$ values. [b] Reference 14; determined potentiometrically using ion selective electrodes. Reactant concentrations <0.01 M.

gories. (a) For the systems Cs^+ with IA; Ag^+ with IB; K^+, Rb^+, NH_4^+, Sr^{2+}, and Ba^{2+} with both IA and IB, the $-Q_i$(corr) values are sufficiently large that log K and $\Delta H°$ values of good precision are obtained within each individual run indicating that reaction 1 which was

$$M^{n+} + I = MI^{n+} \qquad (1)$$

assumed in their calculation is correct. Log K, $\Delta H°$, and $\Delta S°$ values for reaction 1 in the cases of these systems are given in Table I. (b) In the systems Ag^+ with IA; Cs^+ with IB; and Ca^{2+}, Mg^{2+}, Na^+, Li^+, H^+, $(CH_3)_4N^+$, guanidinium ion, Co^{2+}, and Cu^{2+} with both IA and IB, the Q_i(corr) values were very small and no attempt was made to calculate log K values.

The calorimetric data from which the log K, $\Delta H°$, and $\Delta S°$ values were calculated are available.[1b]

Values of $\Delta C_p°$ [cal/(deg mol)] calculated from the temperature dependence of $\Delta H°$ for reaction 1 are as follows: (isomer A) K^+, 20; Rb^+, 5; Cs^+, 0; Sr^{2+}, 0; Ba^{2+}, 4; (isomer B) K^+, 53; Rb^+, 44; Sr^{2+}, 17; Ba^{2+}, 35.

Discussion

The agreement of the log K values in Table I with those determined by Frensdorff[14] is fair considering the different experimental methods and reactant concentrations used in the two studies.

The data in Table I show several interesting trends. In all cases studied log K values for metal complexes of isomer A are larger than those for the corresponding metal complexes of isomer B. This observation suggests that the essentially zero $-Q_i$(corr) values for the reaction of Ag^+ with IA are due, not to the low log K value, since a log K value could be obtained for the reaction of Ag^+ with IB, but rather to the small $\Delta H°$ value for the reaction of Ag^+ with IA. Although log K values could not be calculated for Li^+, Na^+, Mg^{2+}, and Ca^{2+}, the small Q_s(corr) values (see Figure 1) indicate that either the log K or $\Delta H°$ values for reaction 1 are small. Log K values for reaction 2 reported by Frensdorff[14] indicate that $Na^+ > Cs^+$; however, he notes a large change in log K with μ in the case of Na^+. Since the μ values used in our study (0.03–0.09) are considerably higher than those used by Frensdorff[14] (0.001–0.008), the two sets of results may not be strictly comparable. Combination of data from the two studies leads to the revised stability sequence

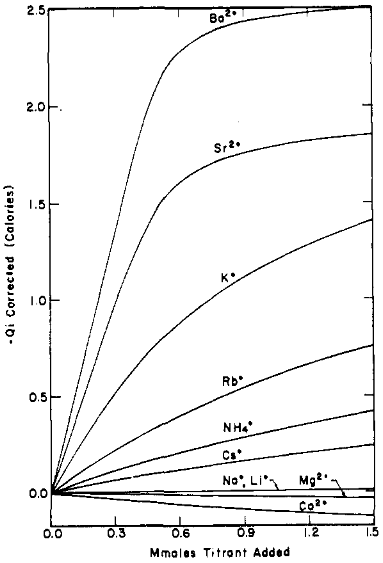

Figure 1. Plot of $-Q_i$(corr) (cal) values *vs.* millimoles of titrant added for the reaction $M^{n+} + IA = MIA^{n+}$ at 25°. The titrant in each case was the metal chloride. The Q_i(corr) values have been corrected for all heat effects except that for the above reaction.

$$K^+ > Rb^+ > Cs^+, Na^+ > Li^+$$

for the alkali metal ions, with some uncertainty in the relative positions of Na^+ and Cs^+. The stability se-

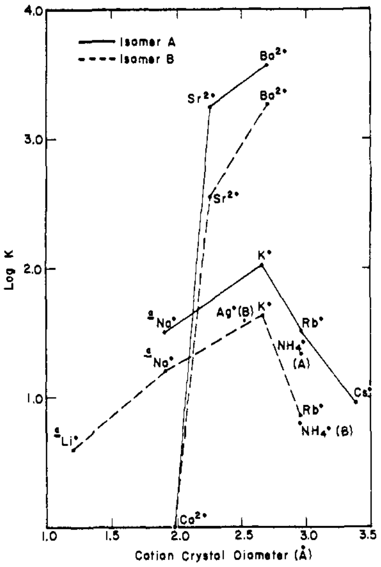

Figure 2. Plot of log K for the reaction $M^{n+} + I = MI^{n+}$ at 25° *vs.* cation diameter.[22] Log K values were not determined for Ca^{2+} because the Q_i(corr) value in this case was too small to permit the calculation of a reliable log K value. It is assumed that the log K value in this case is small. (Values for ions marked with superscript *a* were taken from ref 14.)

quence for the alkaline earth cations with both IA and IB is

$$Ba^{2+} > Sr^{2+} > Ca^{2+}, Mg^{2+}$$

Except for Sr^{2+}, $\Delta H°$ values for isomer B are more negative than are those for isomer A. The relatively low $\Delta S°$ values suggest a near compensation in most cases of the factors which determine the magnitude of $\Delta S°$, *i.e.*, ligand conformational changes upon complexation, changes in ligand and metal ion hydration, and changes in total particle number. Finally, the $\Delta C_p°$ values for the formation of the metal complexes of isomer B are larger than are those for isomer A. These trends in the $\Delta H°$, $\Delta S°$, and $\Delta C_p°$ values suggest that significant differences exist in the solvation or solvent structuring properties of the two isomers. This dissimilarity in the behavior of the two isomers in aqueous solution may have its origin in the differences between the steric orientations of the hydrophobic cyclohexyl groups in the two cases.

The cation has been shown to be coordinated in the center of the cavity by X-ray crystallography in the case of the K^+–nonactin[11] system and by spectral methods in the case of the aqueous K^+–valinomycin[12] system. A recent X-ray crystallographic study of Rb^+–dibenzo-18-crown-6 shows the Rb^+ to lie slightly above the center of the plane of the ring.[21] The stable bonds in these systems have been attributed[3] to ion–dipole interactions between the positively charged cation and the dipole created by the inwardly oriented oxygen atoms. This assumption is supported by the log K values in Table I which show that for cations of approximately the same ionic diameters, *i.e.*, K^+ (2.66 Å)[22] and Ba^{2+} (2.70 Å),[22] the log K values increase with increasing cation charge. The $\Delta H°$ values for K^+ and Ba^{2+} interaction with either isomer indicate, however, that factors other than electrostatic attraction are involved in the bonding since electrostatic theory alone predicts[23] a more positive $\Delta H°$ value for reaction 1 in the case of Ba^{2+}, whereas the opposite is the case, *i.e.*, the $\Delta H°$ value for the K^+ being the more positive.

The ability of a cation to form stable complexes with I in aqueous solution is very dependent on cation diameter as can be seen in Figure 2, where log K values from Table I for the reactions at 25° are plotted against cation diameter.[22] To examine more closely the apparent size specificity in aqueous solution of IA and IB toward cations which are approximately 2.5 Å in diameter, determinations were made using cations (a) near, *i.e.*, NH_4^+ (2.96 Å)[22] and Ag^+ (2.52 Å),[22] (b) much larger than, *i.e.*, $(CH_3)_4N^+$ (6.94)[24] and guanidinium ion ($CN_3H_6^+$), and (c) much smaller than, *i.e.*, Cu^{2+} (1.44)[25] and Co^{2+} (1.48),[22] the apparent optimum diameter. No reaction was observed in case b or c. Reaction was observed in the cases of NH_4^+ and Ag^+ with both IA and IB; however, the thermodynamic values were not calculated in the case of the Ag^+–IA system for reasons given earlier. In Figure 2 the experimental log K values for the NH_4^+–IA, NH_4^+–IB, and Ag^+–IB systems are seen to lie close to the predicted values. Our data suggest that in aqueous solution other cations having ionic diameters within the range indicated in Figure 2 should complex significantly with I. These ions would include (ionic diameters,[22] Å, in parentheses) La^{3+} (2.30), Hg^{2+} (2.20), Pb^{2+} (2.40), and Tl^+ (2.80). We are presently investigating the complexing properties of these and other ions.

That the magnitude of the thermodynamic quantities is strongly solvent dependent is shown in reported K values for NaCl–IB[14] and KCl–IB[14] interactions and K and $\Delta H°$ values for NaSCN–IB[1a] and KSCN–IB[1a] interactions in methanol and ethanol. These data show that very stable complexes are formed with large negative $\Delta H°$ values in both cases as compared to the aqueous systems. For example, for the NaCl–IB reaction in methanol log K = 3.68[14] and for the NaSCN–IB reaction in methanol $\Delta H° = -6$ kcal/mol.[1a] The $\Delta H°$ values for the reactions of IB with KSCN in methanol, NaSCN in ethanol, and KSCN in ethanol are −11, −9, and −13 kcal/mol, respectively.[1a] These results show that the solvent used is important in determining complex stability in these systems, although our data do not allow us at the present time to determine whether the ion pair or metal ion is reacting with the IB.

There are obvious similarities between I and the structurally related macrocyclic antibiotics (II, III). All are uncharged and have hydrocarbon backbones with interior cavities ringed with centrally oriented basic heteroatoms. The agreement of the stability and permeability sequences ($K^+ > Rb^+ > Cs^+ > Na^+ > Li^+$) for the reaction of alkali metal ions with I suggests that thermodynamic correlations between the ability of a macrocyclic compound (as measured by the log K value for complex formation) to complex a particular ion and its influence on the biological transport of that ion can be extended to the structurally related antibiotics. Furthermore, it suggests that the selectivity of the bio-

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logical ion transport mechanism may in part be due to the complexation properties of the macrocyclic carrier molecules.

The central cavities of valinomycin and monactin are considerably larger (36 and 32 ring atoms, respectively) than that for I (18 ring atoms), yet they show preferences for cations of the same size as indicated by similar stability[13] and permeability[4,5] sequences. It would thus appear that these larger molecules possess considerable flexibility in order to be able to assume that orientation about the metal ion which is required for maximum complex stability. Such conformational differences between the noncomplexed and complexed ligands have been demonstrated by several workers.[11,12,21] The efficiency and high ion selectivity of the complexation reactions in the antibiotics appear to be determined by the possible conformational states of these compounds.[12] Nuclear magnetic resonance data in the case of nonactin indicate that complexation is accompanied by changes in the dihedral angles between adjacent hydrogens which are sufficient to account for the necessary changes in the diameter of the central cavity required to fit the metal ion.[26]

The macrocyclic ligands discussed here have interest not only from the standpoint of their application as model carriers in investigations of ion transport processes, but also in selective coordination chemistry and in ion selective resins and electrodes. The possible range of complexation properties and individual specificities of macrocyclic compounds has recently been greatly extended through the introduction of nitrogen and sulfur atoms into the macrocyclic rings,[27,28] and the preparation of analogs of the cyclic polyethers containing bridgehead nitrogen atoms.[29] Synthesis of these new macrocyclic ligands opens a new area of coordination chemistry with wide application in biological, industrial, and analytical fields.

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Photochemical Reactions of Copper(II)–1,3-Diketonate Complexes[1]

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Abstract: When alcohol solutions of bis(1,3-diketonate)copper(II) are exposed to 254-nm radiation the copper(II) ions are reduced to metallic copper. The photochemistry of five copper chelates was studied as a function of irradiating wavelength, light intensity, and chelate concentration. On this basis, the primary photochemical process was determined to be a reduction of Cu(II) to Cu(I) followed by a thermal reduction of Cu(I) to copper metal. The quantum yield was found to be a function of the ligand ionization potential. Mechanisms are proposed and discussed.

In recent years a number of photochemical studies involving coordination compounds have been published.[2] However, as yet there is little quantitative information about reactions that take place during irradiation of charge-transfer bands. We have chosen the 1,3-diketonate chelates to study these reactions for several reasons; both metal-to-ligand and ligand-to-metal charge-transfer absorptions are present in the spectra, the energies of the charge-transfer bands may be systematically varied by changing the metal ion and the chelate ring substituents, and a large amount of absorption and emission spectral data is available in the literature. To date only two quantitative studies on the photochemistry of 1,3-diketonate chelates have appeared.[3,4] These papers deal with Co(III) and Fe(III) 1,3-diketonates. The work presented herein is part of our continuing research on photochemically induced redox reactions of metal chelates.

Very few photochemical studies on the coordination complexes of copper have been undertaken. In 1966, Shagisultanova[5,6] reported the photoreduction of Cu(II) chelates of ethylenediamine, oxalate, and glycinate. The reduction observed was from Cu(II) to Cu(I). However, in preliminary irradiations of bis(1,3-diketonate)copper(II) chelates we observed complete reduction in alcoholic solvents to metallic copper. The Cu(II) ions reduced in this manner produce a lustrous metallic mirror on the irradiated cell face. This work was begun to study these photoinduced redox reactions with several bis(1,3-diketonato)copper(II) chelates.

The ultraviolet absorption spectra of bis(1,3-diketonato)copper(II) have been studied and the transitions assigned.[7,8] The spectra in this region consist of two

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(1) Presented in part at the 11th International Conference on Coordination Chemistry, Haifa, Israel, Sept 1968.

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(6) G. A. Shagisultanova and L. A. Ill'yikevitch, *Zh. Neorg. Khim.*, **11**, 945 (1966).

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