tions, the equilibrium constants are much more influenced by the nature of the solvent than the rate constants, as can be seen in the slope (2.26) of the lines in Figure 3, which is, in fact, the difference between the slopes of the lines in Figure 1.

Experimental Section

All of the complexes used in this study were prepared and purified in ways previously described.[1,5] The solvents were pure commercial samples (chromatographic grade), dried according to the methods reported in the literature. The methods used to follow the kinetics were similar to those reported previously.[1] Known volumes of thermostated solutions of the complex and the reagent were mixed in the spectrophotometer cell which was placed in the thermostated compartment of an Optica CF-4 recording spectrophotometer. The spectrum changes characteristic of the reacting system were first determined by scanning the near-ultraviolet region at known intervals. Once the spectra changes were characterized and suitable wavelengths were chosen to study the reaction, the kinetics were followed by looking at the wavelength at the chosen value and recording the change of optical density as a function of time.

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Electronic Structures and Spectra of Square-Planar Gold(III) Complexes

BY W. ROY MASON, III, AND HARRY B. GRAY

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The electronic spectra of $AuCl_4^-$, $AuBr_4^-$, and $Au(SCN)_4^-$ have been measured in the visible and near-ultraviolet regions at 300 and 77°K in a 2:1 2-methyltetrahydrofuran–methyl alcohol solvent mixture. Improved resolution at low temperature revealed d–d transitions in each case, and the assignment of these transitions has been given based on a d-MO ordering of $b_{1g}(x^2 - y^2) > b_{2g}(xy) > e_g(xz, yz) > a_{1g}(z^2)$. The electronic spectrum of $Au(CN)_4^-$ has also been measured to 54,000 cm^{-1} at room temperature in water and acetonitrile.

Introduction

The interpretation of the electronic spectra of gold(III) complexes has not been fruitful in aiding solution of the square-planar electronic structural problem.[1-3] One reason has been poor resolution of the ligand field spectra from which information regarding the d-MO leveling ordering can be extracted. For example, the d–d transitions are almost completely obscured by intense charge-transfer transitions in the $AuCl_4^-$ and $AuBr_4^-$ complexes.[3] Another reason is that aqueous solution spectra of gold(III) complexes are subject to question because of the known tendency of these complexes to hydrolyze.[4]

In this paper, as part of our investigations of the electronic structures of a number of square-planar complexes, we present measurements of the electronic spectra of some gold(III) complexes of the type MX_4^-, where X is chloride, bromide, thiocyanate, and cyanide. To avoid the possibility of hydrolysis, our measurements were made in nonaqueous media. Also, where possible, measurements were made in a medium that forms a rigid, transparent glass when cooled to liquid nitrogen temperature. By cooling samples to near liquid nitrogen temperature, the resolution of the weaker ligand field spectra was markedly improved.

Experimental Section

The gold complexes, except $Au(CN)_4^-$, were prepared from reagent grade hydrogen tetrachloroaurate(III), $HAuCl_4 \cdot 3H_2O$ (Mallinckrodt). Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

***n*-Butylammonium Tetrachloroaurate(III), $[(n\text{-}C_4H_9)_4N][AuCl_4]$.**—An excess of concentrated hydrochloric acid was added to a concentrated aqueous solution of $HAuCl_4$. A stoichiometric amount of *n*-butylammonium chloride as a concentrated aqueous solution was then added at ice-bath temperatures. Golden needles of product formed immediately. These were washed with cold water and then with ether and dried under vacuum. *Anal.* Calcd for $[(n\text{-}C_4H_9)_4N][AuCl_4]$: Au, 33.89; C, 33.06; H, 6.24. Found: Au, 33.66; C, 33.29; H, 6.45.

***n*-Butylammonium Tetrabromoaurate(III), $[(n\text{-}C_4H_9)_4N][AuBr_4]$.**—An excess of concentrated hydrobromic acid was added to a concentrated aqueous solution of $HAuCl_4$, followed by the addition of a stoichiometric amount of *n*-butylammonium bromide as a concentrated aqueous solution. Dark red plates formed immediately. These were collected and washed with cold water and then ether, and finally dried under vacuum. *Anal.* Calcd for $[(n\text{-}C_4H_9)_4N][AuBr_4]$: Au, 25.95; C, 25.32; H, 4.78. Found: Au, 26.20; C, 25.43; H, 4.62.

***n*-Butylammonium Tetracyanoaurate(III), $[(n\text{-}C_4H_9)_4N][Au(CN)_4]$.**—This compound was prepared from $K[Au(CN)_4]$. The potassium salt was prepared by the method of Smith and co-workers.[5] The literature procedure was followed exactly except that the treatment of $Au(CN)_2Br_2^-$ with potassium cyanide was carried out at ice-bath temperature. The *n*-butylammonium salt was then prepared by adding a solution containing a stoichiometric amount of *n*-butylammonium chloride to a concentrated aqueous solution of the potassium salt. A white microcrystalline precipitate formed immediately. This was

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[3] A. K. Gangopadhayhay and A. Chakravorty, *J. Chem. Phys.*, **35**, 2206 (1961).

[4] W. Robb, *Inorg. Chem.*, **6**, 382 (1967).

[5] (a) J. M. Smith, L. H. Jones, J. K. Kessin, and R. A. Penneman, *ibid.*, **4**, 369 (1965); (b) L. H. Jones and J. M. Smith, *J. Chem. Phys.*, **41**, 2507 (1964).

washed with a small amount of cold water and then ether, and finally dried under vacuum. *Anal.* Calcd for $[(n\text{-}C_4H_9)_4N][Au(CN)_4]$: Au, 36.24; C, 44.20; H, 6.67; N, 12.88. Found: Au, 36.50; C, 44.40; H, 6.68; N, 13.04.

Potassium Tetrathiocyanatoaurate(III), $K[Au(SCN)_4]$.—A stoichiometric amount of potassium thiocyanate was added to a cold aqueous solution of $HAuCl_4$. A red precipitate formed immediately that was very insoluble in water, but soluble in alcohol, acetone, and acetonitrile. This precipitate was collected and washed with cold water and then with ether, and finally dried under vacuum. *Anal.* Calcd for $K[Au(SCN)_4]$: S, 27.32. Found: S, 27.19.

Attempts to make the *n*-butylammonium salt of $Au(SCN)_4^-$ were unsuccessful because solutions of the potassium salt were found to decompose soon after preparation. Spectral measurements on the potassium salt were made with fresh solution within minutes after preparation. The decomposition in the time required to obtain a spectrum was negligible.

Spectral Measurements.—Spectroquality solvents (Matheson Coleman and Bell) were used for the spectral measurements wherever possible. Solutions for liquid nitrogen measurements were prepared from a 2:1 mixture of 2-methyltetrahydrofuran and methyl alcohol. The 2-methyltetrahydrofuran was chromatoquality reagent (Matheson Coleman and Bell) which had been distilled from sodium to remove all traces of peroxides. The 2:1 mixture forms a rigid glass at liquid nitrogen temperature. The contraction of this mixture on cooling from room temperature to liquid nitrogen temperature was measured approximately by cooling a measured volume in a graduated tube. A volume of 1.00 ml at 300°K decreased to 0.79 ± 0.02 ml at 77°K giving a contraction of 21 ± 2%. This value is not precise, but the error introduced in solution concentration is probably less than 5%. The molar extinction coefficients of the spectra reported here have been corrected for solvent contraction using this value. The transparency of this mixture is suitable for measurements in the visible and near-ultraviolet regions; the cutoff point is approximately 41,000 cm^{-1}. As a check on spectra obtained in 2:1 $2\text{-}CH_3THF\text{-}CH_3OH$, spectra were measured at 300 and 77°K in 2:1 $2\text{-}CH_3THF\text{-}C_2H_5CN$. The results obtained in the latter solvent do not differ significantly from those reported in this paper.

Spectral measurements were made on a Cary Model 14RI using 1.00-cm quartz cells. Measurements on $Au(CN)_4^-$ were also made on a Cary Model 15 to 54,000 cm^{-1}. Liquid nitrogen measurements were made with a Cary low-temperature dewar which had been modified to hold a standard 1.00-cm cell. The path length contraction of a 1.00-cm cell on cooling to liquid nitrogen temperature was found to be negligible (0.05–0.1%).

Results and Discussion

A portion of the room-temperature and low-temperature spectra of $AuCl_4^-$ and $AuBr_4^-$ in 2:1 2-methyltetrahydrofuran–methyl alcohol is presented in Figures 1 and 2. It is seen that in each case the absorption decreases and the resolution is markedly improved at low temperature; two bands are revealed, at 21,740 and 26,320 cm^{-1} for $AuCl_4^-$, and 18,520 and 21,230 cm^{-1} for $AuBr_4^-$. The left pair of curves in Figure 3 shows also the resolution of two bands at low temperature for the $Au(SCN)_4^-$ anion. The more intense charge-transfer band at 31,000 cm^{-1} is also shown in Figure 3. In contrast to the weaker bands at lower energy, this band sharpens and increases in maximum molar extinction. This behavior was found to be characteristic of the charge-transfer transitions at 25,000 and 39,000 cm^{-1} for $AuBr_4^-$ and also the one at 31,000 cm^{-1} for $AuCl_4^-$. The acetonitrile solution spectrum of $AuCl_4^-$ also shows a second intense band at 44,000 cm^{-1}, but low-temperature measurements at this energy could not be made because of the absorption of the $2\text{-}CH_3THF\text{-}CH_3OH$ solvent. The band positions and molar extinction coefficients extracted from these spectra are collected in Table I, together with the bands observed at room temperature in acetonitrile solutions.

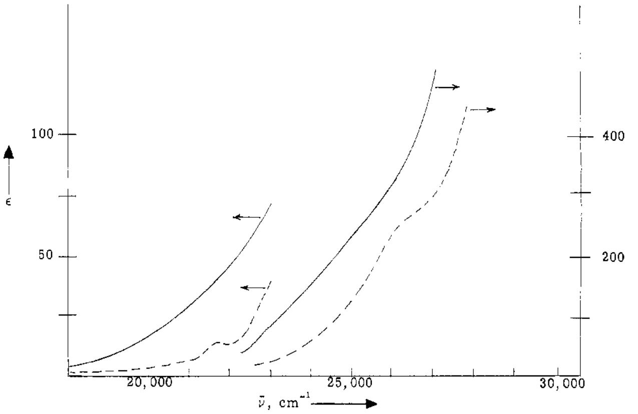

Figure 1.—Electronic spectra of $[(n\text{-}C_4H_9)_4N][AuCl_4]$ in 2:1 2-methyltetrahydrofuran–methyl alcohol: ———, 300°K; – – – –, 77°K.

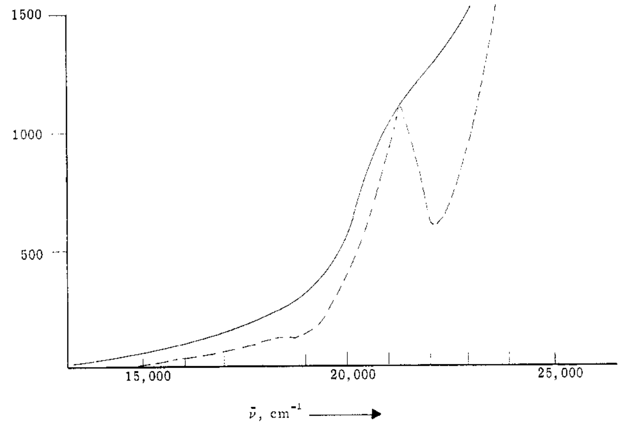

Figure 2.—Electronic spectra of $[(n\text{-}C_4H_9)_4N][AuBr_4]$ in 2:1 2-methyltetrahydrofuran–methyl alcohol: ———, 300°K; – – – –, 77°K.

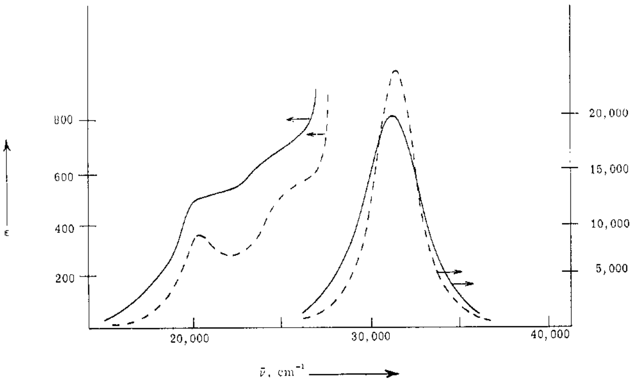

Figure 3.—Electronic spectra of $K[Au(SCN)_4]$ in 2:1 2-methyltetrahydrofuran–methyl alcohol: ———, 300°K; – – – –, 77°K.

The low-energy bands resolved in the spectra in Figures 1–3 are logically assigned as d–d transitions from the occupied d-MO levels to the empty $b_{1g}(x^2 -$

y^2) level. The relatively high molar extinction coefficients for these transitions (except the band at 21,740 cm^{-1} for $AuCl_4^-$) are probably due to the close proximity of intense charge-transfer transitions, which are responsible for the poor resolution at room temperature. The assignments of these low-energy bands are given in Table I. These assignments are based on a d-MO energy ordering of $b_{1g}(x^2 - y^2) > b_{2g}(xy) > e_g(xz, yz) > a_{1g}(z^2)$, in agreement with recent work on $PtCl_4^{2-}$.[1,6] The low position of $a_{1g}(z^2)$ may be rationalized because halide ligands are good π donors but relatively weak in $\sigma \rightarrow$ d bonding. In this respect, the thiocyanate ligand is similar to halide ligands when bound to the metal through the sulfur atom. Infrared evidence has been presented recently indicating the thiocyanate ligand in $Au(SCN)_4^-$ is sulfur bound.[7] Therefore, it is reasonable to assume that the d-MO level energy ordering for the halides is also suitable for the S-bonded thiocyanate.

TABLE I

ELECTRONIC SPECTRA OF GOLD(III) COMPLEXES[a] IN 2:1 2-METHYLTETRAHYDROFURAN–METHYL ALCOHOL

CH_3CN	300°K	77°K	Assignments
	$[(n\text{-}C_4H_9)_4N][AuCl_4]$		
		21,740 (15)	$^1A_{1g} \rightarrow {}^1A_{2g}$
25,000 (304)[b]	25,000 (330)[b,c]	26,320 (267)[b]	$^1A_{1g} \rightarrow {}^1E_g$
31,050 (5020)	30,770 (5200)	30,390 (6500)	$^1A_{1g} \rightarrow {}^1A_{2u}, {}^1E_u(1)$
44,250 (42,500)			$^1A_{1g} \rightarrow {}^1E_u(2)$
	$[(n\text{-}C_4H_9)_4N][AuBr_4]$		
	17,800 (170)[b,c]	18,520 (101)[b]	$^1A_{1g} \rightarrow {}^1A_{2g}$
21,740 (1560)[b]	21,740 (1230)[b,c]	21,230 (1230)	$^1A_{1g} \rightarrow {}^1E_g$
25,250 (4620)	24,880 (3200)	24,810 (4750)	$^1A_{1g} \rightarrow {}^1A_{2u}, {}^1E_u(1)$
39,060 (33,200)	39,220 (27,450)	39,680 (29,120)	$^1A_{1g} \rightarrow {}^1E_u(2)$
	$K[Au(SCN)_4]$		
20,000 (490)[b]	22,200 (561)[b]	19,960 (375)	$^1A_{1g} \rightarrow {}^1A_{2g}$
24,600 (727)[b]	25,320 (704)[b]	25,180 (534)[b]	$^1A_{1g} \rightarrow {}^1E_g$
31,150 (30,000)	31,050 (21,500)	31,250 (25,400)	$^1A_{1g} \rightarrow {}^1A_{2u}, {}^1E_u(1)$
	$[(n\text{-}C_4H_9)_4N][Au(CN)_4]$		

No maxima or shoulders with $\epsilon > 1.5$ were observed to energies of 54,000 cm^{-1}: ϵ at 40,000 cm^{-1}, ~2.5; ϵ at 50,000 cm^{-1}, ~7000

[a] $\bar{\nu}$ is in cm^{-1} (ϵ is in l. mole^{-1} cm^{-1}). [b] Shoulder (ϵ is for value of $\bar{\nu}$ given). [c] Very poorly resolved.

It is to be noted that the first well-resolved band in each of the three complexes—$AuCl_4^-$, $AuBr_4^-$, and $Au(SCN)_4^-$—is assigned as the spin-allowed transition $^1A_{1g} \rightarrow {}^1A_{2g}$. This may seem somewhat unsatisfying in view of the fact that the lowest energy spin-forbidden bands should have appreciable intensity, as they do in the related $PtCl_4^{2-}$ case.[1,8] The dilemma is most acute for $AuCl_4^-$; here the assignment of the 21,740-cm^{-1} band in the low-temperature spectrum as a spin-forbidden transition cannot be ruled out entirely, in view of the rather small molar extinction coefficient. The small value of this coefficient at 77°K may be misleading, however, as it is probably higher at 300°K. Measurements[9] on the first spin-allowed band of $PtCl_4^{2-}$ (at 25,000 cm^{-1})[1,6,8] showed a decrease in molar extinction of 40% (from 60.3 to 36.0) when cooled to 77°K in 2-CH_3THF–CH_3OH solution. Furthermore, the assignment of the 21,740-cm^{-1} band in $AuCl_4^-$ as a spin-allowed transition seems preferable because of the consistency with the assignment of the lowest energy bands observed for $AuBr_4^-$ and $Au(SCN)_4^-$. In the latter two cases, the intensities of the bands in question are much larger than for the well-documented spin-forbidden bands in analogous Pt(II) complexes.[1,8,9] For this reason, we prefer the $^1A_{1g} \rightarrow {}^1A_{2g}$ assignment for all three complexes; it is certainly not unreasonable in these cases to expect the weaker spin-forbidden structure to be lost in the large charge-transfer "tail" characteristic of gold(III) spectra.

The assignments of the charge-transfer bands in $AuCl_4^-$ and $AuBr_4^-$ have been made previously as ligand → metal (L→M).[2,3] The intense band at 31,000 cm^{-1} in $Au(SCN)_4^-$ has not been assigned. It is reasonable to assign this band as L→M because the first intense charge-transfer band in the isoelectronic platinum(II) complex, $Pt(SCN)_4^{2-}$, is observed at 41,150 cm^{-1} in acetonitrile solution.[8] Such a shift to higher energy on decreasing the oxidation number of the central metal is characteristic of L→M charge-transfer transitions.[10,11]

A comparison of the positions of the lowest energy band in Figures 1–3 with the positions of the first spin-allowed band ($^1A_{1g} \rightarrow {}^1A_{2g}$) of the corresponding platinum(II) complexes,[8] $PtCl_4^{2-}$ (25,000 cm^{-1}), $PtBr_4^{2-}$ (23,000 cm^{-1}), and $Pt(SCN)_4^{2-}$ (24,930 cm^{-1}), reveals that the transition in the gold(III) complex occurs at lower energy than in the platinum(II) complex. This trend indicates the splitting of the d-MO levels decreases as the central metal increases in oxidation number; this is just the reverse sort of trend observed for octahedral complexes of the earlier periodic groups. This inverse behavior was recently predicted for $PtCl_4^{2-}$ and $AuCl_4^-$ on the basis of a semiempirical MO calculation.[1] From a population analysis of the calculated d-MO levels for the two complexes, it was found that the empty $b_{1g}(x^2 - y^2)$ acceptor level, which is a σ type, increases markedly in metal character (65% for $PtCl_4^{2-}$ to 90% for $AuCl_4^-$) on increasing the oxidation number. The originating $b_{2g}(xy)$, which is a π type, increases in ligand character, though the increase is not large (50% for $PtCl_4^{2-}$ to 58% for $AuCl_4^-$). With the increase in ligand character of the b_{2g} level, it remains almost constant in energy on increasing the oxidation number, but the increase in metal σ character of the b_{1g} level

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(6) F. A. Cotton and C. B. Harris, *Inorg. Chem.*, **6**, 369 (1967).

(7) A. Sabatini and I. Bertini, *ibid.*, **4**, 959 (1965).

(8) D. S. Martin, M. A. Tucker, and A. J. Kassman, *ibid.*, **4**, 1682 (1965); as amended in *ibid.*, **6**, 1298 (1967).

(9) W. R. Mason and H. B. Gray, to be published.

(10) The positions of the bands in $Au(SCN)_4^-$ (Table I) and those reported recently[11] for $Au(N_3)_4^-$ are remarkably similar; the $Au(N_3)_4^-$ spectrum shows a shoulder at 20,600 cm^{-1} (ϵ 258) and a charge-transfer maximum at 30,000 cm^{-1} (ϵ 31,300). This result is surprising in view of the evidence for S-bound thiocyanate in $Au(SCN)_4^-$.[7] It has been generally thought that azide lies higher than S-bound thiocyanate in the spectrochemical series, in a position similar to N-bound thiocyanate. The explanation of this apparent spectrochemical similarity between S-bound thiocyanate and azide is not clear, and further investigation of this feature is in progress. However, it appears that comparisons of the electronic spectra of corresponding azide and thiocyanate complexes in order to determine whether the thiocyanate is S or N bonded should be viewed with caution in light of these results, particularly for square-planar complexes.

(11) H.-H. Schmidtke and D. Garthoff, *J. Am. Chem. Soc.*, **89**, 1317 (1967).

brings it to a lower energy as the oxidation number of the metal is increased. The net result is an increased L→M character of the transition and thus it shifts to lower energy as the oxidation number is increased.

The spectrum of the $Au(CN)_4^-$ ion was measured as the potassium salt in water and the *n*-butylammonium salt in acetonitrile. These measurements showed no band maxima or shoulders in the visible or ultraviolet region of the spectrum to energies of 54,000 cm^{-1}. It was noted, however, that the absorbance began increasing at energies greater than about 43,000 cm^{-1}. This result is entirely different from the spectrum previously reported,[12] which has been subsequently interpreted by several authors.[2,13] The explanation for this difference in experimental results is not known, but since no analytical data were given by the previous workers, it is possible that the sample they investigated was impure.[14]

The absence of band maxima in the $Au(CN)_4^-$ spectrum at energies lower than 54,000 cm^{-1} is a significant result when compared with the rich spectrum of charge-transfer bands between 34,000 and 47,000 cm^{-1} for $Pt(CN)_4^{2-}$.[2] The lower energy of the charge-transfer bands in platinum(II) as compared with gold(III) establishes these transitions as metal→ligand (M→L). The increase in energy of the transition as the oxidation number of the central metal increases is characteristic of M→L charge transfer. The ligand field transitions in these tetracyano complexes are expected to be at quite high energy from the high position of the cyanide ligand in the spectrochemical series.[15]

Acknowledgments.—We thank the National Science Foundation for support of this research.

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[13] J. R. Perumareddi, A. D. Liehr, and A. W. Adamson, *J. Am. Chem. Soc.*, **85**, 249 (1963).

[14] The infrared spectrum of the sample of $K[Au(CN)_4]$ used in this study was obtained as a Nujol mull on a Beckman IR 7 spectrometer between 550 and 3500 cm^{-1}. A single C≡N stretching band was observed at 2193 cm^{-1} in agreement with measurements of Jones and Smith.[5b] A thorough treatment of the vibrational spectrum of $Au(CN)_4^-$ based on D_{4h} symmetry has been given by these workers.[5b]

[15] C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in complexes," Addison-Wesley Publishing Co., Inc., Reading, Mass., 1962, p 109.

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Thermodynamics of Ion Association. XVI.[1a] Bivalent Metal Complexes Involving Nitrogen and Oxygen Coordination

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Ion association between alkaline earth cations and the methyliminodiacetate ion, MIDA, has been studied potentiometrically at 25°. Association constants have been determined for strontium and barium mono-MIDA and for both mono- and di-MIDA complexes of magnesium and calcium. The enthalpies of formation of the complex species have been measured directly by using a sensitive differential calorimeter, and ΔG, ΔH, and ΔS values have been calculated. All of the available thermodynamic functions, obtained calorimetrically, for the stepwise formation of bivalent metal complexes with iminodiacetate, MIDA, and dicarboxylates are presented and discussed. The influence of Jahn–Teller stabilization upon the thermodynamic functions for the formation of copper complexes is of particular interest. As might be expected, the 1:1 complex is entropy stabilized whereas in the second stepwise association to form CuA_2^{2-} the enthalpy change is the important factor.

There is considerable interest in studying the thermodynamics of formation of metal complexes in which the metal ion coordinates with different atoms within the ligand molecule. Many studies have been made of the association constants for such reactions and most discussions of the energetics have been based purely upon a knowledge of these K values. Although some limited correlations have emerged, it is important to recognize that the magnitude of the free energy changes reflects changes of enthalpy and entropy accompanying the reactions. Direct calorimetric studies yield precise values for the enthalpy of formation which can be used for the calculation of reliable entropy data. The alkaline earth complexes form a particularly suitable series for study since, if the bonding were purely electrostatic, the order of stability would be expected to follow closely the electrostatic potential of the cation. Frequently, however, the association constant for the formation, with a given ligand, of the magnesium complex is considerably smaller than that for the calcium complex.

In the present work, potentiometric measurements have been made of the association of alkaline earth cations with the N-methyliminodiacetate anion (hereafter, MIDA). Enthalpies of association have been

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