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.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
STATE UNIVERSITY OF NEW YORK AT BUFFALO, BUFFALO, NEW YORK 14214

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

BY GEORGE H. NANCOLLAS AND ANDREW C. PARK[1b]

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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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measured by means of a sensitive differential calorimeter and, for magnesium and calcium, stepwise enthalpies of formation of M(MIDA) and M(MIDA)$_2^{2-}$ are reported. When this work was almost completed, the results of some calorimetric measurements were published by Anderegg[2] for a number of bivalent metal MIDA complexes. For magnesium and calcium, however, data were reported for only the 1:1 complexes. Since one of the aims of the present work was to discuss the chelate effect of (EDTA) *vs.* 2(MIDA), it was necessary to know the values of the thermodynamic functions for the formation of the rather unstable M(MIDA)$_2^{2-}$ complexes. Trends in all of the available thermodynamic functions for the formation of MIDA, EDTA, iminodiacetate (IDA), and dicarboxylate complexes of Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+} are discussed.

Experimental Section

Potentiometric Experiments.—Grade A glassware and AR reagents were used whenever possible, and carbon dioxide was excluded from all solutions by bubbling with nitrogen. N-Methyliminodiacetic acid was prepared following the method of Schwarzenbach, *et al.*[3] *Anal.* Calcd for $C_5H_9O_4N$: C, 40.82; H, 6.17; N, 9.52. Found: C, 40.62; H, 5.91; N, 9.63. Magnesium and calcium solutions were analyzed by EDTA titrations and strontium and barium by gravimetric precipitation as their sulfates. Emf measurements were made at 25 ± 0.02° with cells of the type

glass electrode | solution under study | 0.1 *N* KCl | Hg_2Cl_2, Hg

using a Beckman Research pH meter and Beckman Type 42 glass electrodes; reproducibility was ±0.1 mv. Each cell incorporated a pair of glass electrodes so that any irregularity in the behavior of one of them was immediately apparent. The electrode systems were standardized before and after each experiment with NBS standard buffer solutions prepared according to Bates:[4] 0.05 *M* potassium hydrogen phthalate, pH 4.008; 0.008695 *M* potassium dihydrogen phosphate–0.03043 *M* disodium hydrogen phosphate, pH 7.413; and 0.01 *M* sodium borate, pH 9.180. Measurements were made in solutions containing the alkaline earth chloride, MIDA, and potassium hydroxide, together with sufficient potassium chloride to maintain an ionic strength within 1% of 0.1 *M;* pH values were converted to hydrogen ion concentration by using an f_{H^+} value (0.7815) calculated from the Davies equation.[5]

Calorimetric Experiments.—The calorimeter and general experimental technique have been described previously.[6,7] Temperature changes were measured on dilution, in a nitrogen atmosphere, of small volumes (approximately 10 ml) of a relatively concentrated solution of the potassium salt of MIDA with (i) 300 ml of a solution of the alkaline earth chloride together with sufficient potassium chloride to give a final ionic strength of 0.1 *M* and (ii) a similar volume of 0.1 *M* potassium chloride. The pH values of the solutions were measured at the end of each calorimetric experiment.

Results and Discussion

Concentrations of solutions for potentiometric measurement were such that not more than two complexes, MA and MA_2^{2-}, were formed with association constants K_1 (= $[MA]/[M^{2+}][A^{2-}]$) and K_2 (= $[MA_2^{2-}]/[MA][A^{2-}]$) at an ionic strength of 0.1 *M*. The concentrations of ionic species were calculated from equations for total MIDA

$$T_A = [HA^-] + [A^{2-}] + [MA] + 2[MA_2^{2-}]$$

total metal

$$T_M = [M^{2+}] + [MA] + [MA_2^{2-}]$$

and for electroneutrality

$$[K^+] + [H^+] + 2[M^{2+}] = [HA^-] + 2[A^{2-}] + 2[MA_2^{2-}] + [OH^-] + [Cl^-]$$

The dissociation constant for HA^-, k_2, was calculated from the results of potentiometric experiments at 25° with mixtures of MIDA, potassium hydroxide, and potassium chloride at an ionic strength of 0.1 *M;* the mean of 16 determinations gave $k_2 = (2.68 \pm 0.01) \times 10^{-10}$ mole l.$^{-1}$. K_1 and K_2 were obtained graphically[8] by plotting X against Y in $Y = XK_1 + K_1K_2$, where

$$X = (T_M - T_A + [HA^-] + [A^{2-}])/[A^{2-}](2T_M - T_A + [HA^-] + [A^{2-}])$$

and

$$Y = (T_A - [HA^-] - [A^{2-}])/[A^{2-}]^2(2T_M - T_A + [HA^-] + [A^{2-}])$$

Concentrations ranged from 1.5 to 5.5×10^{-3} *M* for T_A and 2.0 to 12.0×10^{-3} *M* for T_M; pH ranged from 7.6 to 9.8, with $\bar{n}$ values between 0.11 and 0.85. Some typical plots of X and Y are shown in Figure 1. A minimum of 30 determinations were made at 25 ± 0.02° with each system, and the lines were fitted by a least-squares procedure with the aid of an electronic computer. Values obtained for K_1 and K_2 are: for magnesium, $K_1 = (3.02 \pm 0.07) \times 10^3$, $K_2 = 225 \pm 87$; for calcium, $K_1 = (7.08 \pm 0.23) \times 10^3$, $K_2 = 519 \pm 50$; for strontium, $K_1 = 904 \pm 16$, $K_2 = 63.0 \pm 14$; and, for barium, $K_1 = 405 \pm 10$, $K_2 = 215 \pm 33$ l. mole^{-1}. A large number of experiments were necessary in order to obtain as reliable values as possible for the rather small association constants K_2 at high ligand concentrations. The concentrations of MOH^+ ion pairs were negligible in these potentiometric experiments. The K_1 values may be compared with those determined at 20° by Schwarzenbach, *et al.*:[9] K_1(MgMIDA) = 2.8×10^3, K_1(CaMIDA) = 5.6×10^3, K_1(SrMIDA) = 718, and K_1(BaMIDA) = 389 l. mole^{-1}.

The results of the calorimetric experiments are summarized in Table I. The concentration of metal ions was higher than in the potentiometric measurements in order to provide a sufficiently large temperature change for accurate measurement. Small corrections were made for the heat of formation of $MgOH^+$ (K = 144 l. mole^{-1}) and $CaOH^+$ (K = 8.9 l. mole^{-1}) using $\Delta H(CaOH^+)$ = 1.25 kcal mole^{-1} [10] and a value of 2.8

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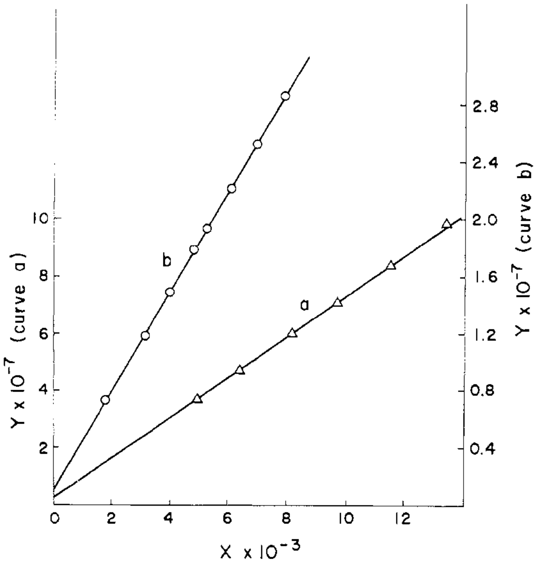

Figure 1.—Typical plots of X against Y in the determination of K_1 and K_2 for calcium (curve a) and magnesium (curve b) MIDA complexes.

TABLE I

CALORIMETRIC RESULTS AT 25° ($I = 0.1\ M$)

10^2T_M, M	10^3T_A, M	pH	$10^3[MA]$, M	ΔH_1, kcal mole^{-1}
		MgMIDA		
2.758	3.159	9.628	3.070	2.87
2.758	3.154	9.619	3.065	2.70
2.758	3.154	9.654	3.068	2.81
1.931	3.161	9.757	3.046	2.79
1.931	3.159	9.806	3.050	2.91
1.931	3.161	9.671	3.036	2.99
			Mean	2.85 ± 0.1
		CaMIDA		
1.973	2.808	9.777	2.767	−1.12
1.973	2.802	9.329	2.728	−1.05
1.973	3.156	9.878	3.113	−1.36
1.480	3.159	9.874	3.101	−1.11
1.973	3.150	9.878	3.106	−1.31
1.480	3.152	9.958	3.095	−1.33
1.973	3.152	9.861	3.101	−1.05
			Mean	−1.19 ± 0.12
		SrMIDA		
3.289	2.963	9.771	2.777	−0.90
3.289	2.981	9.720	2.784	−0.85
2.000	3.019	9.962	2.749	−0.81
2.000	3.019	9.970	2.750	−0.87
2.000	3.020	9.953	2.748	−0.69
2.000	3.020	9.983	2.754	−0.87
			Mean	−0.83 ± 0.06
		BaMIDA		
2.000	3.019	10.171	2.543	−1.10
2.000	3.024	9.991	2.499	−1.05
2.667	3.016	10.082	2.637	−0.78
2.667	3.016	10.150	2.651	−1.07
2.667	3.022	10.231	2.669	−1.23
2.667	3.019	10.104	2.645	−1.15
			Mean	−1.06 + 0.10

10^3T_M, M	10^3T_A, M	pH	$10^3[MA]$, M	10^3 $[MA_2^{2-}]$, M	ΔH_2, kcal mole^{-1}
			MgMIDA		
2.758	8.277	10.763	1.382	1.262	−0.54
2.758	8.286	10.737	1.384	1.260	−0.70
3.310	8.279	10.736	1.768	1.370	−1.03
2.758	8.274	10.684	1.385	1.259	−0.17
3.310	8.288	10.665	1.769	1.369	−0.89
				Mean	−0.67 ± 0.32
			CaMIDA		
2.960	8.272	10.655	9.777	1.938	−1.33
2.960	8.278	10.660	9.839	1.931	−0.85
3.552	8.290	10.590	13.720	2.099	−0.62
3.552	8.272	10.598	13.750	2.096	−0.36
2.565	8.279	10.670	7.721	1.763	−0.81
3.552	8.276	10.613	13.720	2.100	−0.70
2.565	8.270	10.662	7.739	1.761	−0.54
				Mean	−0.74 ± 0.30

kcal mole^{-1} for $\Delta H(\mathrm{MgOH})$ estimated from a consideration of the values for $CaOH^+$, $SrOH^+$, and $BaOH^+$ and a knowledge of the trends in ΔH shown in the interaction of other anions with these cations. The correction never amounted to more than 5% of the measured heat changes and was usually less than the experimental uncertainty. Allowances were also made for the heat of protonation of the ligand ($H^+ + MIDA^- \rightleftharpoons HMIDA$, $\Delta H = -6.8$ kcal mole^{-1} [11]) and for the heat of formation of water ($\Delta H = -13.36$ kcal mole^{-1} [7]). It was not possible to measure ΔH_2 for SrA_2^{2-} and BaA_2^{2-} because of precipitation of the hydroxides. The thermodynamic functions are collected in Table II in which the values of Anderegg[2] for 1:1 alkaline earth complexes are given in parentheses. It can be seen that in most cases the agreement with the present work is satisfactory; the thermodynamic data for the formation of $M(MIDA)_2$ are subject to greater uncertainties owing to the small values of K_2. The MIDA molecule constitutes half of the EDTA molecule and the availability of enthalpy and entropy data makes it possible to examine the source of the chelate effect in more detail than can be done from a consideration only of the free energy changes. The changes in thermodynamic properties for the reaction

$$M(MIDA)_2^{2-} + EDTA^{4-} \rightleftharpoons MEDTA^{2-} + 2MIDA^{2-} \quad (1)$$

are listed in Table III. For magnesium, zinc, and cadmium the formation of the additional chelate ring in the EDTA complexes is accompanied by appreciable entropy and small enthalpy changes. The chelate effect for these ions is clearly one of entropy reflecting the increase in the number of solute particles in reaction 1. The endothermic heat changes for magnesium and zinc are due to the greater strain involved in fitting another chelate ring around these small ions and the effect is larger for the smaller magnesium ion. In contrast to these results, it is seen from Table III that the chelate effect for the calcium complexes is principally one of enthalpy. The exothermicity of reaction 1 for both calcium and cadmium can be explained by the relatively strain-free structures of their EDTA complexes as compared with the smaller magnesium and zinc ions. In the calcium case, however, the entropy change is unusually small. Although no X-ray structural studies have yet been made with the alkaline earth aminopolycarboxylate complexes, some of the complexes with the transition metal ions have been shown to have coordination numbers in excess of six. In manganous EDTA, for instance, a water molecule is bound to the metal ion in a seven-coordinate complex.[12] If

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(11) N. E. Ockerbloom and A. E. Martell, *J. Am. Chem. Soc.*, **78**, 267 (1956).

(12) S. Richards, B. Pedersen, J. V. Silverton, and J. L. Hoard, *Inorg. Chem.*, **3**, 27 (1964).

TABLE II
THERMODYNAMIC FUNCTIONS ($I = 0.1\ M$)

Reaction	$-\Delta G$, kcal mole^{-1}	ΔH, kcal mole^{-1}	ΔS, cal deg^{-1} mole^{-1}	$\Delta S + S°(M^{2+})$, cal deg^{-1} mole^{-1}
$Mg^{2+} + MIDA^{2-}$	4.75 ± 0.02 (4.62)	+2.85 ± 0.10 (3.12)	25.6 ± 0.5 (26.4)	−2.6
$Ca^{2+} + MIDA^{2-}$	5.25 ± 0.02 (5.03)	−1.19 ± 0.12 (−1.64)	13.6 ± 0.4 (11.58)	+0.4
$Sr^{2+} + MIDA^{2-}$	4.02 ± 0.02 (3.82)	−0.83 ± 0.06 (−1.23)	10.7 ± 0.2 (8.85)	+1.3
$Ba^{2+} + MIDA^{2-}$	3.56 ± 0.01 (3.47)	−1.06 ± 0.10 (−0.79)	8.4 ± 0.4 (9.17)	+11.4
$MgMIDA + MIDA^{2-}$	3.17 ± 0.25	−0.67 ± 0.32	8.4 ± 2.0	...
$CaMIDA + MIDA^{2-}$	3.83 ± 0.07	−0.74 ± 0.30	10.0 ± 2.0	...
$Mg^{2+} + IDA^{2-}$	3.94	+2.94[13]	23.5	−4.7
$Ca^{2+} + IDA^{2-}$	3.47	+0.3[13]	12.7	−0.5
$Sr^{2+} + IDA^{2-}$	2.99	+0.1[13]	10.5	+1.1
$Ba^{2+} + IDA^{2-}$	2.24	+0.1[13]	8.0	+11.0

TABLE III
THE CHELATE EFFECT

$M(MIDA)_2^{2-} \rightarrow MEDTA^{2-}$	$-\Delta G$, kcal mole^{-1}	ΔH, kcal mole^{-1}	ΔS, cal deg^{-1} mole^{-1}
Mg^{2+}	3.65	+1.31	+17.1
Ca^{2+}	5.27	−4.62	+2.7
Zn^{2+}	3.23	+0.98	+14.6
Cd^{2+}	6.87	−1.78	+11.9

we can assume similar structures in solution and if the calcium ion behaves similarly, then the abnormally small entropy and exothermic enthalpy changes in Table III may reflect the binding of an additional water molecule in reaction 1 to form $Ca(OH_2)EDTA^{2-}$. In the comparison of thermodynamic functions for the formation of cadmium and lanthanum complexes of the type $M(IDA)_2$ and MEDTA, Anderegg[13] has also drawn attention to the importance of both ΔH and ΔS in interpreting the chelate effect.

It is of interest to examine the stepwise ΔH and ΔS values in Table II for the formation of $Mg(MIDA)_2^{2-}$ and $Ca(MIDA)_2^{2-}$. It can be seen that almost the same endothermicity is involved in dehydrating the small Mg^{2+} ion for both the tridentate MIDA and the higher dentate EDTA ($\Delta H = +3.49$ kcal mole^{-1}).[7] The second MIDA is coordinated to both MgMIDA and CaMIDA in "normal" exothermic steps and this is the first time that an exothermicity has been observed in the formation of a magnesium complex. It is clear that much of the important dehydration had taken place in the formation of the monocomplex which could retain a degree of charge separation.

In order to compare trends in the thermodynamic data, it is useful to remove the variable cationic aqueous entropy and values of the term

$$\Delta S + S°(M^{2+}) = \underbrace{[S_g(MA) - S_g(A^{2-})]}_{\text{I}} + \underbrace{[S_{hyd}(MA) - S_{hyd}(A^{2-})]}_{\text{II}}$$

are also given in Table II. In this expression S_g and S_{hyd} refer to the gaseous and hydration entropies respectively. Term I reflects the change in configurational and librational entropy of the ligand molecule when it enters into complex formation and will be expected to be negative. Term II on the other hand will be positive since $\Delta S_{hyd}(A^{2-})$ will be more negative than $\Delta S_{hyd}(MA)$ in which some charge neutralization has taken place. The absence of any large differences in the values of $\Delta S + S°(M^{2+})$ for magnesium, calcium, and strontium indicates a similar structure for their complexes. However, a common feature of these and other data for alkaline earth complexes[14] is the relatively high $\Delta S + S°(M^{2+})$ values for the barium complexes. The large barium ion has a small charge density and will bond less effectively to the ligand thus allowing the latter to retain some of its librational entropy in the complex. Consequently, term I will be less negative than for complexes involving the other metal ions. In addition, the large barium ion in its complexes will retain some of the solvent structure of the free ion owing to the inability of the ligands to surround the metal ion completely. The ionic entropy of the complex will thus follow $S°(Ba^{2+})$ which is relatively larger than that of the other alkaline earth ions.

The divalent alkaline earth ions have rare gas electronic configurations and will be expected to form essentially ionic bonds in their complexes with ligands. The results of nmr studies with the MIDA complexes, however, suggest that a certain degree of covalency is present, especially in bonds between nitrogen and the magnesium ion.[15] Further evidence for nitrogen bonding may be seen from the enhanced stability of MIDA and IDA complexes over those formed with the analogous dicarboxylic acids having a CH_2 group in place of the nitrogen. If electrostatic interactions were the only factor to be considered, then the magnesium complex would be expected to have a greater stability than that of the calcium. This is not the case for the MIDA and NTA complexes, and a number of other polyaminocarboxylate ligands behave similarly.[7] The effect of introducing a methyl group in MIDA as compared with IDA is seen in Table II as a greater exothermicity in the formation of the complexes. The inductive effect of the methyl group enhances the bonding of the nitrogen to the metal ion. In contrast to MIDA, the magnesium complexes of IDA are more stable than the calcium. The CaIDA is formed with a more endo-

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(13) G. Anderegg, *Helv. Chim. Acta*, **46**, 1833 (1963); **47**, 1801 (1964).

(14) G. Anderegg, *ibid.*, **48**, 1718 (1965).

(15) G. H. Nancollas and A. C. Park, *J. Phys. Chem.*, **71**, 3678 (1967).

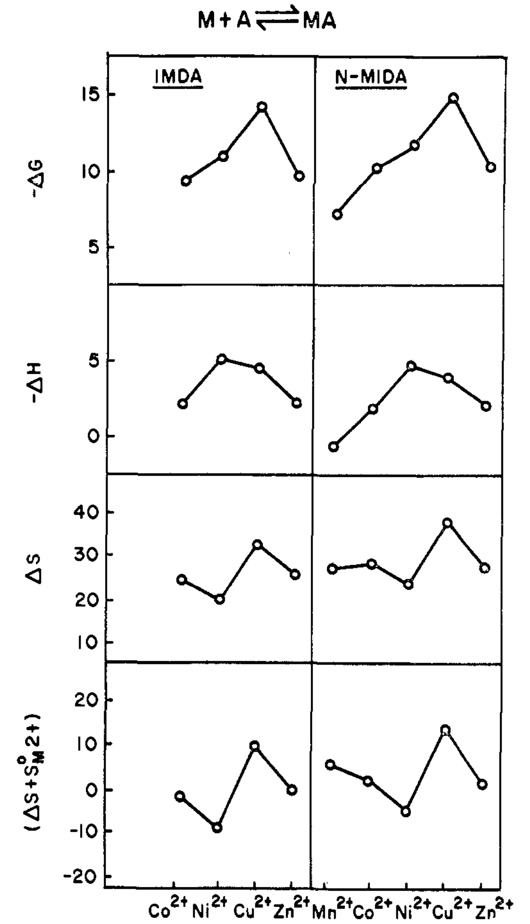

Figure 2.—Thermodynamic functions for the formation of transition metal monocomplexes in the reaction $M^{2+} + A^{2-} \rightleftharpoons MA$.

thermic enthalpy change than is CaMIDA while the enthalpy change for the formation of the magnesium complexes is almost the same for both of the ligands. These results can be explained if a relatively stronger covalent bond is formed between the magnesium ion and nitrogen atoms than that involving the calcium. This would be expected to be less enhanced by the inductive effect than is the calcium–nitrogen bond, and the nmr results provide support for this suggestion.[15]

Stepwise ΔG, ΔH, ΔS, and $\Delta S + S°(M^{2+})$ for bivalent transition metal complexes are plotted as a function of atomic number in Figures 2 and 3 for MIDA and IDA,[13] and a number of differences of behavior manifest themselves. The position of copper is particularly interesting since, although the ΔG values for the formation of CuA follow the well-established Irving-Williams order, it does not follow that the enthalpy changes, reflecting important crystal field effects, follow the same order. The 1:1 copper complexes are formed with unusually endothermic enthalpy changes and the high stability of these complexes is clearly an entropy effect. This observation was explained for the dicarboxylate complexes[16] by considering the influence

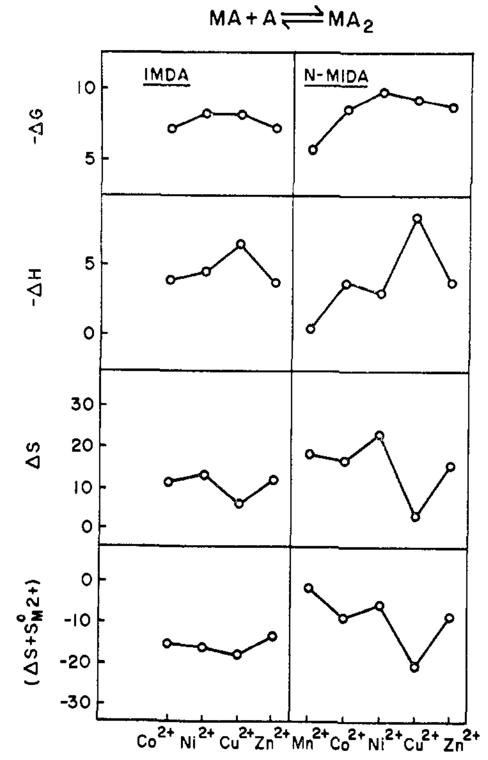

Figure 3.—Thermodynamic functions for the stepwise formation of transition metal dicomplexes in the reaction $MA + A^{2-} \rightleftharpoons MA_2^{2-}$.

of Jahn–Teller stabilization upon the thermodynamic properties and it is interesting to note that the effect appears to be of a much more general nature. The bonding of the first ligand molecule through short bonds in the *xy* plane of the metal ion would result in a more exothermic heat of formation but the accompanying closer contact of charged centers will lead to a more effective charge neutralization and a more positive entropy of formation. At the limit of tetragonal distortion, the two axial water molecules will be freed and the coordination will change from six in the aquo ion to four in the complex. This will also result in a more positive entropy of formation but with an increased endothermicity due to the breaking of metal–water bonds. This is seen to be the case in Figure 2 and the same trends are observed in the formation of copper monooxalate, monomalonate, and monosuccinate complexes.[16] In the latter systems, the increasing endothermicity of copper oxalate < malonate < succinate may reflect the increasing strain introduced in the ligand molecule in bringing the coordinating groups into close bonding with the metal in the *xy* plane. In the formation of $Cu(IDA)_2^{2-}$ and $Cu(MIDA)_2^{2-}$ from the corresponding monocomplexes (Figure 3), it is the exothermic enthalpy change accompanying Cu–N bond formation which stabilizes the complexes. The entropy change is now small compared with the other transition metal ions indicating that much of the water release had occurred, as suggested above, in the formation of the 1:1 complexes.

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(16) A. McAuley, G. H. Nancollas, and K. Torrance, *Inorg. Chem.*, **6**, 136 (1967).