

The emphasis on acentricity in the ligand field experienced by the cobalt atoms is in connection with the intensity of the visible absorption band observed in the oligomers. At the highest concentrations studied ϵ_{\max} is about 70 and this is necessarily a lower unit. On the other hand, for $\text{CoA}_2 \cdot 2\text{H}_2\text{O} - \text{CoA}_2 \cdot 2\text{CH}_3\text{OH}$, as shown in Fig. 4, the ϵ_{\max} values are only about 40% of this. Since it is known that acentricity can lead to enhancement of intensities by relaxing the Laporte selection rule, and since the structure of $\text{CoA}_2 \cdot 2\text{H}_2\text{O}$ is quite similar in many respects to the sort of local environment of cobalt atoms in the structure we have suggested for the oligomers, we believe that in the oligomers there will be distortions not found in $\text{CoA}_2 \cdot 2\text{H}_2\text{O}$, such as twisting or bending of the plane of the four close oxygen atoms, which introduces an acentric component into the ligand field about the non-terminal cobalt atoms.

The effective magnetic moment previously reported⁴ for CoA_2 (4.93 B.M. at 300°) is quite consistent with the roughly octahedral environment of the cobalt atoms in the proposed structure for the oligomers. This structure, it may be noted, is similar in its gross features to the one proposed by Holm for the oligomers of certain nickel(II) salicylaldimine complexes.¹⁶

A few additional comments and observations may now be recorded. The ultraviolet spectrum of CoA_2 has been examined at concentrations between 10^{-3} and 10^{-5} M in chloroform at $\sim 25^\circ$. No deviations from Beer's law were detected. This supports the conclusion that virtually complete dissociation of oligomers has occurred already at concentrations of 10^{-2} – 10^{-3} M, so that Beer's law should be obeyed at all lower concentrations.

The tetrahedral structure of CoA_2 answers the question of whether steric factors play any significant role in producing the tetrahedral structure of $\text{Co}(\text{DPM})_2$,

(16) R. H. Holm, *J. Am. Chem. Soc.*, **83**, 4683 (1961).

in preference to a planar structure for this molecule. Using reasonable dimensions for the $\text{Co}(\text{DPM})_2$ molecule in a planar configuration, it appears that repulsion between *t*-butyl groups cannot be very great, so that if such repulsion is the critical factor, the relative stabilities of the two configurations must be little different. The results for CoA_2 , where no repulsive forces come into play in the monomer, show that the tetrahedral configuration is inherently the more stable at normal temperatures. At the same time, if our conjectures about the structures of the oligomers are correct, the energy of the tetrahedral configuration is not likely to be more than perhaps 20 kcal./mole below that of the planar one.

The results of another experiment permit us to estimate a lower limit for the enthalpy difference between planar and tetrahedral $\text{Co}(\text{DPM})_2$. Attempts were made to incorporate $\text{Co}(\text{DPM})_2$ in crystalline $\text{Ni}(\text{DPM})_2$ (in which the molecules are planar) by growing crystals of the latter from solutions containing comparable concentrations of $\text{Co}(\text{DPM})_2$ and $\text{Ni}(\text{DPM})_2$. No cobalt could be detected spectroscopically in the crystals obtained, and we estimate that the limit of detectability must be a Co/Ni ratio of about 10^{-2} . Using an elementary statistical mechanical treatment,¹⁷ it can easily be shown that for the process of replacing a mole fraction, X , of $\text{Ni}(\text{DPM})_2$ molecules by $\text{Co}(\text{DPM})_2$ molecules at 300°K., the quantity $T\Delta S$ is about 3.0 kcal./mole of $\text{Co}(\text{DPM})_2$ when $X \approx 10^{-2}$. Assuming that the enthalpy of substituting *planar* $\text{Co}(\text{DPM})_2$ for $\text{Ni}(\text{DPM})_2$ would be ~ 0 , the equilibrium condition, $\Delta F = 0$, for the actual process can be assumed to hold when the above $T\Delta S$ term equals $-\Delta H$ for the process of changing tetrahedral $\text{Co}(\text{DPM})_2$ to planar $\text{Co}(\text{DPM})_2$, giving 3.0 kcal./mole as a lower limit on this enthalpy.

(17) See G. S. Rushbrooke, "Introduction to Statistical Mechanics," Oxford University Press, 1949, Chapter 14, for a discussion of almost exactly the problem we have treated.

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Relative Enthalpies of Formation of Some Tetrachlorometallate Ions^{1a}

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The heats of solution of the series of compounds $[\text{As}(\text{C}_6\text{H}_5)_3\text{CH}_3]_2[\text{MCl}_4]$, $\text{M} = \text{Mn, Fe, Co, Ni, Cu, Zn}$, have been measured. Using these results, the problem of the relative stabilities of the $[\text{MX}_4]^{2-}$ species is discussed, with particular reference to the reaction $[\text{MCl}_4]^{2-}(\text{aq}) + \infty\text{H}_2\text{O} = [\text{M}(\text{H}_2\text{O})_6]^{2+}(\text{aq}) + 4\text{Cl}^-(\text{aq})$. It is concluded that the differences in crystal field stabilization energies of the $[\text{MCl}_4]^{2-}$ and $[\text{M}(\text{H}_2\text{O})_6]^{2+}$ ions vary in about the same way as the enthalpies of the overall process and thus provide a fairly good first approximation to the relative enthalpies of these reactions. The role of other energy contributions is also discussed briefly.

Introduction

In order to determine the relative enthalpies of formation of $[\text{MCl}_4]^{2-}$ ions, in which the metal, M, is Mn, Fe, Co, Ni, Cu, and Zn, calorimetric measure-

ments have been carried out on the series of salts $[(\text{C}_6\text{H}_5)_3\text{CH}_3\text{As}]_2\text{MCl}_4$. All of these except the one containing copper have been shown by Pauling² to be isomorphous, belonging to the space group $\text{P}2_13$ (No. 198).

(1) (a) Research supported by the United States Atomic Energy Commission; (b) Fellow of the Alfred P. Sloan Foundation.

(2) (a) P. Pauling, Ph.D. Thesis, University College, London, 1960; for partial reports see (b) N. S. Gill, R. S. Nyholm, and P. Pauling, *Nature*, **182**, 168 (1958); (c) N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959).

The MCl_4^{2-} ions lie along body diagonals of the unit cube; three of the M-Cl bonds are then required to be equivalent, but the fourth is permitted to be different. However, in the nickel compound, which was investigated in great detail, the two sorts of Ni-Cl distances were found to be equal (2.27 Å.) within the standard deviations (0.01 Å.). In addition, the ClNiCl angles were all found to be equal at 109.5° to well within the standard deviation (0.5°). For the series of compounds, Pauling has obtained the cubic cell parameters listed in Table I. The Cu(II) compound was definitely shown not to be isomorphous with the others, but no investigation of its structure has been reported.

TABLE I
PAULING'S VALUES FOR UNIT CELL EDGES OF $[(\text{C}_6\text{H}_5)_3\text{CH}_2\text{As}]_2^+[\text{MCl}_4]^{2-}$ COMPOUNDS^a AND CALCULATED CORRECTIONS TO LATTICE ENERGIES^b

	Mn	Fe	Co	Ni	Zn
a_0 , Å. ^c	15.597	15.621	15.497	15.526	15.516
ΔH_L correction, kcal./mole	...	-0.96	0.64

^a Private communication from P. Pauling. ^b Method of calculation explained in text. ^c Pauling estimates standard deviation at 0.01 Å.

Now the quantities $2\Delta H_f[\text{RCl}(s)]$, $2\Delta H_f[\text{R}^+(g)]$, and $4\Delta H_f[\text{Cl}^-(g)]$ are constants independent of the metal ion concerned. We will also make the initial assumption that ΔH_L may be treated as either independent of M or as only slightly and smoothly varying with M. The "constant" quantity, C, may thus be defined

$$C = -2\Delta H_f[\text{RCl}(s)] + 2\Delta H_f[\text{R}^+(g)] + 4\Delta H_f[\text{Cl}^-(g)] - \Delta H_L[\text{R}_2\text{MCl}_4(s)] \quad (5)$$

After insertion of eq. 4 in eq. 1 and substitution of C as given in eq. 5, we obtain

$$\Delta H_{\text{com}} - C = \Delta H_S^A - \Delta H_S^B - \Delta H_f[\text{MCl}_2 \cdot n\text{H}_2\text{O}(s)] + n\Delta H_f[\text{H}_2\text{O}(l)] + \Delta H_f[\text{M}^{2+}(g)] \quad (6)$$

The quantities ΔH_S^A and ΔH_S^B were measured as described in the Experimental section and are recorded in Table II. The other quantities required on the right side of eq. 6 are recorded in Table III along with references to the sources of data.

The crystal field stabilization energies listed in Table III were obtained in two ways. For FeCl_4^{2-} , CoCl_4^{2-} , and NiCl_4^{2-} reliable experimental Δ values, 4000, 3100, and 3600 cm^{-1} , respectively, have been reported.³⁻⁵ A Δ value for $[\text{CuCl}_4]^{2-}$ has not yet been derived di-

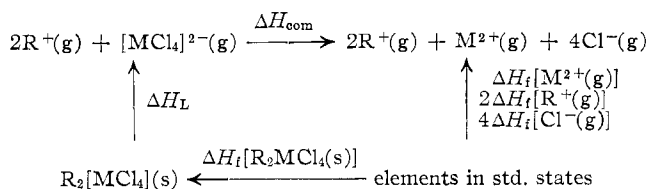
TABLE II
MEASURED VALUES^a OF ΔH_S^A AND ΔH_S^B , KCAL./MOLE
(Defined in eq. 2 and 3)

Metal	ΔH_S^A				ΔH_S^B			
	Measured values			Mean	Measured values			Mean
Mn	0.96	0.82	...	0.89	5.63	5.47	5.73	5.61
Fe	3.58	3.31	...	3.45	3.81	3.70	...	3.75
Co	1.17	1.32	1.26	1.25	10.57	10.46	...	10.52
Ni	11.67	11.64	11.59	11.63	8.68	8.55	8.35	8.53
Cu	-1.86	-1.69	-1.69	-1.75	3.26	2.95	2.73	3.00

^a Estimated uncertainty of a single measurement: ~ 0.1 kcal./mole.

Procedure

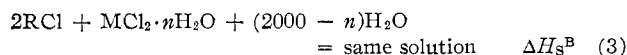
The thermochemical cycle shown below is to be considered



From this we obtain the thermochemical equation

$$\Delta H_{\text{com}} = -\Delta H_f[\text{R}_2\text{MCl}_4(s)] + 2\Delta H_f[\text{R}^+(g)] + \Delta H_f[\text{M}^{2+}(g)] + 4\Delta H_f[\text{Cl}^-(g)] - \Delta H_L[\text{R}_2\text{MCl}_4] \quad (1)$$

We further consider the two reactions, (2) and (3), whose enthalpies, ΔH_S^A and ΔH_S^B , are experimentally measurable



Using these, we may write the following expression for $\Delta H_f[\text{R}_2\text{MCl}_4(s)]$

$$\Delta H_f[\text{R}_2\text{MCl}_4(s)] = 2\Delta H_f[\text{RCl}(s)] + \Delta H_f[\text{MCl}_2 \cdot n\text{H}_2\text{O}] - n\Delta H_f[\text{H}_2\text{O}(l)] + \Delta H_S^B - \Delta H_S^A \quad (4)$$

TABLE III

$\Delta H_{\text{com}} - C$ AND AUXILIARY DATA^a

Metal	ΔH_f	n	$\Delta H_f[\text{MCl}_2 \cdot n\text{H}_2\text{O}(c)]$ ^c	$\Delta H_{\text{com}} - C$	CFSE, ^e
	$[\text{M}^{2+}(g)]$ ^b				
Mn	601.6	4	-407.0	728.9	0
Fe	658.9	4	-370.7	749.2	6.8
Co	681.2	6	-508.9	769.5	10.6
Ni	701.4	6	-505.8	777.3	~ 6.2
Cu	732.3	2	-193.0	787.5	5.2
Zn	782 ^d	0

^a $\Delta H_f[\text{H}_2\text{O}(l)] = -68.32$; ref. 12. ^b Taken from Table IXA of ref. 14. ^c Taken from ref. 12. ^d See text for an explanation of the source of this number. ^e Crystal field stabilization energies; sources are explained in the text.

rectly from spectra because the interpretation of spectral data is complicated by distortion of the tetrahedron and the rather large spin-orbit coupling.⁶ We

(3) C. Furlani, E. Cervone, and V. Valenti, *J. Inorg. Nucl. Chem.*, **25**, 159 (1963).

(4) D. M. L. Goodgame, M. Goodgame, and F. A. Cotton, *J. Am. Chem. Soc.*, **83**, 4161 (1961).

(5) F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *ibid.*, **83**, 4690 (1961).

(6) See the recent note by A. G. Karipides and T. S. Piper, *Inorg. Chem.*, **1**, 970 (1962).

have therefore made use of a semiempirical relation,^{3,7} viz.

$$\frac{\Delta \text{ in } [\text{MCl}_4]^{2-}}{\Delta \text{ in } [\text{M}(\text{H}_2\text{O})_6]^{2+}} \approx 0.40 \quad (7)$$

Taking the Δ value⁸ for $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ to be 11,200 cm.^{-1} and using eq. 7, for $[\text{CuCl}_4]^{2-}$ we obtain a Δ of 4500 cm.^{-1} , from which the crystal field stabilization energy was calculated⁹ and recorded in Table III.

It will be noted in Table I that the lattice parameters do not vary monotonically from Mn to Zn; rather, if a smooth curve is drawn through the values for the Mn, Ni, and Zn compounds, the value for the Fe compound lies 0.06 Å. above it and that for the Co compound lies 0.04 Å. below. In order that these slight deviations should not defeat our assumption of a smooth variation in pseudo-lattice energies, ΔH_L , through the series of compounds, small correction energies have been calculated and applied to the $\Delta H_{\text{com}} - C$ values in Table III prior to plotting them. These corrections, which are specified in Table I, were obtained assuming a mean lattice energy of 250 kcal./mole. Taking interionic distances, r , to be proportional to unit cell edges, the anomalous deviations of the unit cell edges, Δa_0 , divided by the interpolated a_0 gives the fractional correction to r . Since ΔH_L is inversely proportional to r , we calculate the corrections to ΔH_{com} as

$$\Delta(\Delta H_{\text{com}}) = \left(1 - \frac{\Delta a_0}{a_0}\right) \Delta H_L \quad (8)$$

It may be seen that these corrections are very small. It also follows from eq. 8 that the over-all change in lattice energy through the series as a result of change in lattice parameter is also quite small, namely, about 1.6 kcal./mole from R_2MnCl_4 to R_2ZnCl_4 .

Finally, it is necessary to comment on the manner in which the quantity $\Delta H_{\text{com}} - C$ for $[\text{ZnCl}_4]^{2-}$, recorded in Table III, was obtained. Serious difficulties were encountered in finding appropriate reactions for calorimetric measurement. None was found which met all requirements, including the one that they go to completion in a relatively short time (say < 0.5 hr.). From a system utilizing $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ we obtained data (which varied from run to run, all runs suffering from some degree of incompleteness of reaction) leading to a $\Delta H_{\text{com}} - C$ value of ≤ 788 kcal./mole. The value of 782 kcal./mole given in Table III is obtained by assuming that the lattice energies of R_2CoCl_4 and R_2ZnCl_4 differ negligibly, both for $\text{R} = [(\text{C}_6\text{H}_5)_3\text{CH}_2\text{As}]$ and for $\text{R} = \text{Cs}$ (assumptions which are certainly valid to within less than 1 kcal./mole) and using the result¹⁰ reported elsewhere that ΔH_{com} for $[\text{ZnCl}_4]^{2-}$ is 12 kcal./mole greater than that for $[\text{CoCl}_4]^{2-}$.

Experimental

Materials.—All of the inorganic salts were Mallinckrodt A.R. grade and were used without further purification, except in the

cases of the nickel and iron salts. $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ was recrystallized once from water. $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ was freed from surface contamination with Fe(III) by selecting crystals and allowing them to stand overnight under ether saturated with 37% aqueous HCl. The ether was decanted and the pale blue crystals were washed with ether. They were then dried in air for a few minutes, finely powdered, and used at once. Methyltriphenylarsonium chloride was prepared by ion exchange from the iodide, obtained from Eastman Organic Chemicals.

Each of the salts $[(\text{C}_6\text{H}_5)_3\text{CH}_2\text{As}]_2\text{MCl}_4$ ($\text{M} = \text{Mn, Fe, Co, Ni, Cu, Zn}$) was prepared by evaporating to dryness the aqueous solution of $\text{MCl}_2 + 2(\text{C}_6\text{H}_5)_3\text{CH}_2\text{AsCl}$ resulting from a heat-of-solution measurement and recrystallizing from ethanol. The nickel salt was precipitated from the ethanol solution by adding acetone. In the case of iron, the aqueous solution was evaporated at 60° under low pressure and the salt was recrystallized under nitrogen by dissolving it in hot ethanol containing 1% of 37% aqueous hydrochloric acid and adding an equal volume of ether dropwise, while allowing the solution to cool. The crystalline product was white. *Anal.* Calcd.: C, 54.4; H, 4.3; Fe, 6.7. Found: C, 53.9, 53.9; H, 3.9, 4.4; Fe, 7.4.

Apparatus.—This was of the type described by Daniels, *et al.*¹¹ The calorimeter consisted of two identical 500-ml. dewar vessels each with a Plexiglass cover, a heating coil, a 2-kilohm thermistor, and a stainless steel stirrer. Each heater was a coil of Chromel-A ribbon (1 ohm) enclosed in an oil-filled sheath made from two concentric brass tubes silver plated on the outside. The stirrer shaft was in two sections, separated at the water level by a 1-in. length of Teflon rod for thermal insulation, and the propellor-type stirrer rotated in the center of the heating coil. Both stirrers were driven by flexible cables from a two-drive constant-speed motor, thus assuring identical mechanical energy input to each dewar. Only one of the two units was heated in the experiments, the other serving as a continuous standard of temperature. Both dewars were placed side-by-side in an insulated box, in a room, the temperature of which was maintained at $25 \pm 1^\circ$.

The heater current of ca. 3.5 amp. was provided by a constant-voltage d.c. power supply and measured with an ammeter accurate to $\pm 0.25\%$. When not actually passing through the heater, the current flowed through a water-cooled Chromel coil adjusted to the same resistance as the heating coil. The time of heating was measured to within 0.1 sec. with a synchronous electric timer. The temperature difference between the thermistors was observed by means of a Wheatstone bridge circuit with a galvanometer of sensitivity 0.06 $\mu\text{a.}$ per 1-mm. scale division. The sensitivity of the whole arrangement was such that 1 cal. $\sim 0.003^\circ \sim 1$ galvanometer scale division ~ 0.5 sec. heating time at 3.5 amp.

Procedure.—In a typical experiment, 250 g. of water at $25 \pm 0.1^\circ$ was placed in each dewar and the stirrers were started. The very small change in the galvanometer reading with time was plotted graphically for about 20 min., and current was then passed through the heater for half of the estimated total time required to balance the heat of solution. The solute was immediately added through a funnel, and the galvanometer reading was adjusted by successively shorter applications of current to the value obtained by extrapolation from the fore period (the time required was about 10 min.) The total electrical energy used under these conditions is equal to the heat of solution.

In cases where heat was evolved, the heater in the reference calorimeter was used to reduce the temperature difference to zero. The ratio of the values of (current)² \times (time) required in the two units to produce the same temperature change was determined in separate experiments to be 1.053 ± 0.004 , which is identical, within the experimental error, with the ratio of the measured resistance of the reference heater (1.025 ± 0.002 ohms) to that of the solution heater (0.973 ± 0.002 ohm), indicating that the heat capacities of the two units were equal within the experimental error.

(7) F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *J. Am. Chem. Soc.*, **84**, 167 (1962).

(8) R. Pappalardo, *J. Mol. Spectry.*, **6**, 554 (1961).

(9) Cf. C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., New York, N. Y., 1962.

(10) A. B. Blake and F. A. Cotton, *Inorg. Chem.*, **2**, 906 (1963).

(11) F. Daniels, *et al.*, "Experimental Physical Chemistry," 4th Ed., McGraw-Hill Book Co., New York, N. Y., 1949, p. 50.

TABLE IV
 ASSESSMENTS OF $\Delta H_M - \Delta H_{Mn}$, WHERE ΔH_M IS THE ENTHALPY OF THE PROCESS

$$R_2MCl_4(s) + \infty H_2O = 2R^+(aq) + 4Cl^-(aq) + M^{2+}(aq)$$

Metal ion, M	$\Delta H_M - \Delta H_{Mn}$, kcal./mole			$-\Delta H_H$	Δ_0 , cm. ⁻¹	CFSE for $[M(H_2O)_6]^{2+}$
	(1)	(2)	(3)			
Mn	0	0	0	654
Fe	-2.5	-5.8	-1.0	680	10,400	9.1
Co	-0.5	-2.4	0.0	697	8,300	16.7
Ni	-11.0	-13.6	-18.6	716	8,500	29.2
Cu	2.5	-4.4	-7.8	717	11,200	19.0
Zn	...	+6.1	+6.1	701

The heats of solution of the ferrous compounds were determined using water through which nitrogen had been bubbled for several hours immediately before the experiment. In order to estimate the effect which slight oxidation might have on the results, one pair of measurements was made without attempting to remove oxygen from the water. The heats of solution in the latter case were appreciably (about 0.6 kcal./mole) greater than in the former, but the difference between the value for $FeCl_2 + 2(C_6H_5)_3CH_3AsCl$ and that for $[(C_6H_5)_3CH_3As]_2FeCl_4$ was practically unaffected, and the possibility of slight oxidation is thus not a serious hazard to the accuracy of the results.

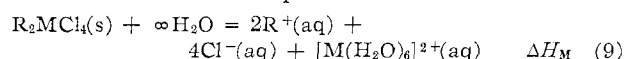
Calibration.—The heat of solution of KCl in 200H₂O was measured five times at 25° and the mean value obtained was 4.209 ± 0.005 kcal./mole. The mean of five measurements at 30° was 4.025 ± 0.003 kcal./mole. The heat of solution of KNO₃ in 400H₂O was also measured five times at 25°, the mean value being 8.267 ± 0.010 kcal./mole, and four times at 30°, with a mean value of 8.143 ± 0.009 kcal./mole. These may be compared with the values 4.201 kcal./mole for KCl + 200H₂O, and 8.28 kcal./mole for KNO₃ + 400H₂O, both at 25°, given in the National Bureau of Standards compilation.¹²

In addition to the standard deviations indicated, there is a total estimated uncertainty in the above results of about 0.6%, arising mainly in the measurement of current and resistance.

Discussion

There are many ways in which the thermodynamic data might be analyzed and interpreted. Those presented here seem to us to be the most meaningful ones we have considered, but this is somewhat a matter of opinion.

We first consider the process

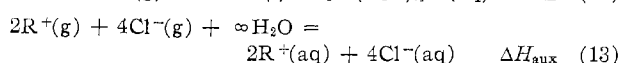
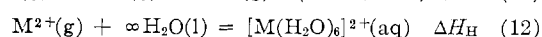
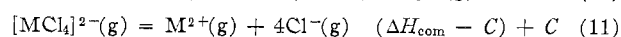
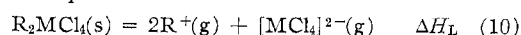


The subscript, M, denotes the particular transition metal concerned. Because we are dealing here only with the relative values of ΔH_M , we shall adopt ΔH_{Mn} as an arbitrary zero; in effect then, we shall wish to calculate and plot values of $\Delta H_M - \Delta H_{Mn}$. These can be computed in three different ways, each embodying different assumptions, approximations, or choices of supplementary data.

Method 1.—It will be noted that process 9 must be quite similar to, if not identical with, process 2, of which we have directly measured the enthalpies for various M. In order for processes 9 and 2 and hence ΔH_M and ΔH_S^A for the same M to be identical (within experimental error), it is necessary that (a) the actual solutions be dilute enough so that the ΔH_f values of all species in solution be equal to those at infinite dilution and (b)

there be no appreciable complexation of M^{2+} by Cl^- in the actual solutions. By referring to standard sources of data relating to each of these phenomena^{12,13} it has been established that these conditions are met in the measurements of ΔH_S^A . These ΔH_M ($\equiv \Delta H_S^A$) values are given in column 1 of Table IV.

Method 2.—Process 9 may be obtained as the sum of the set of eq. 10–13.



Since ΔH_L occurs with a negative sign in C , it cancels out of the sum of these equations and the remaining two terms in C as well as the term ΔH_{aux} are strictly constant for all M. Thus $\Delta H_M - \Delta H_{Mn}$ is given by

$$\Delta H_M - \Delta H_{Mn} = (\Delta H_{com} - C)^M - (\Delta H_{com} - C)^{Mn} + \Delta H_H^M - \Delta H_H^{Mn} \quad (14)$$

Thus we need only a source of ΔH_H values in order to calculate $(\Delta H_M - \Delta H_{Mn})$ values using eq. 14. The required ΔH_H values shown in column 4 of Table IV were taken from George and McClure.¹⁴ It may be noted that as we are using only differences in these ΔH_H values, any question of the correctness of their absolute magnitudes is irrelevant.

Method 3.—We may also consider the approximation that all contributions to ΔH_M will vary smoothly (or be constant) as M changes from Mn to Zn, *except* for the difference in crystal field stabilization energies (CFSE) in the tetrahedral and octahedral environments. If, then, a straight line is drawn on Fig. 1 from the point for manganese to that for zinc and the change in crystal field stabilization energy on going from $[MCl_4]^{2-}$ to $[M(H_2O)_6]^{2+}$ for each of the intervening cases is subtracted, we obtain the figures listed in column 3 of Table IV. The Δ_0 values and the octahedral CFSE values obtained using these are listed in columns 5 and 6 of Table IV. In the two cases where the proportionality of CFSE to Δ_0 is not independent of Δ_0 because of configuration interaction, the CFSE has been calculated using the proportionality constant obtained in the limit $\Delta_0 \rightarrow 0$.

As may be seen in Fig. 1, the values of $\Delta H_M - \Delta H_{Mn}$ obtained by the three methods follow the same pattern

(12) "Selected Values of Chemical Thermodynamic Properties," Circular 500, Part I, U. S. Department of Commerce, National Bureau of Standards, Washington, D. C., 1961.

(13) J. Bjerrum, G. Schwarzenbach, and I. G. Sillén, "Stability Constants, Part II," Special Publ. No. 7, The Chemical Society, London, 1958.

(14) P. George and D. S. McClure, *Progr. Inorg. Chem.*, **1**, 381 (1959).

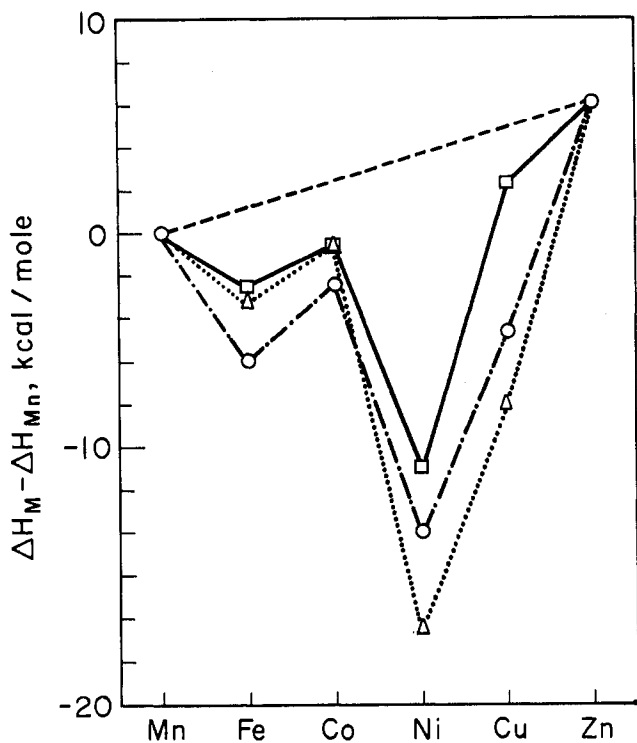


Fig. 1.— $\Delta H_M - \Delta H_{Mn}$ for $M = \text{Mn, Fe, Co, Ni, Cu, Zn}$: —, results from column 1 of Table IV; - - - -, results from column 2 of Table IV; · · · ·, results from column 3 of Table IV.

and in general agree within the probable limits of uncertainty in the data employed. There are, however, some discrepancies so large that we believe that they must be real; the significance of these therefore merits discussion. We consider first the sets of points obtained by methods 1 and 2. These are of essentially pure experimental origin. For Fe, Co, and Ni the discrepancies are probably not significant (≤ 3.5 kcal./mole). For Cu, the discrepancy (~ 7 kcal./mole) is unlikely to originate entirely in errors in calorimetric measurements. Certainly, we can see no possibility of an error exceeding about 0.5 kcal./mole in our ΔH_S^A values. Since we cannot see any reason for a genuine discrepancy either, we can only suggest that there is some sizable error (4–6 kcal./mole) in the auxiliary data used either by us or by McClure and George to obtain $\Delta H_{Cu} - \Delta H_{Mn}$ by method 2.

Now, comparing the “experimental” results, as given by methods 1 and 2, with those obtained by method 3, in which a theoretical assumption is made, we see that the agreement is qualitatively good throughout and even quantitatively satisfactory in two of the four instances. For Fe and Co, all three points are in adequate agreement; those obtained by method 1, which are probably more reliable than those from method 2, agree almost perfectly with the ones based on the difference in CFSE values. For Cu, the difference between the energy predicted by the difference in CFSE values and that directly measured (method 1) is quite large. At least a part of this difference may be attributed to (a) the unreliability of the CFSE values because of the severe distortions of both the $[\text{CuCl}_4]^{2-}$ tetrahedron and the $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ octahedron and (b)

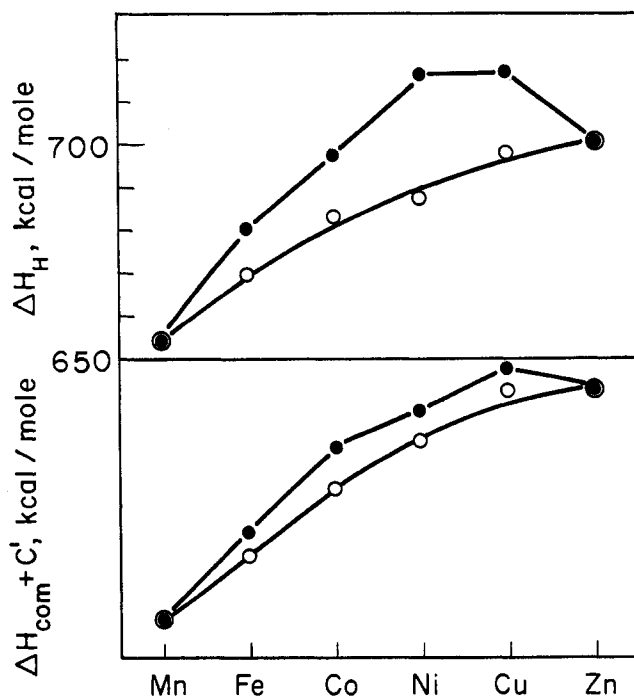


Fig. 2.—Solid points represent the ΔH_H values (Table IV) for the divalent ions (upper curve) and the ΔH_{com} values (lower curve) for MX_4^{2-} species, the latter being plotted on a completely arbitrary absolute scale. The curves defined by open circles are those obtained from each of the others after correction for the CFSE values.

the possible difference in the actual lattice energy of $[\text{As}(\text{C}_6\text{H}_5)_3\text{CH}_3]_2[\text{CuCl}_4]$ from that which has, implicitly, been interpolated for it by treating it as though it were isomorphous with all the other $[\text{MX}_4]^{2-}$ salts of the same cation, even though it is not. The first of these effects seems very likely to be operating in the right direction, since the relatively loose attachment of two of the six water molecules probably decreases the CFSE for $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ appreciably from that estimated. The effect of the different structure of the $[\text{CuCl}_4]^{2-}$ salt is not inferable. In the case of Ni, the difference between the result obtained by method 3 and that by method 1, or the average of those by methods 1 and 2, is such that method 3 overestimates the instability of $[\text{NiCl}_4]^{2-}$ relative to $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ by 5.5–7.0 kcal./mole.

We believe that the discrepancy in the case of nickel probably represents a genuine inadequacy in the approach based purely on CFSE values. This can probably be traced to the implicit assumption in this approach that the “cubic part of the ligand field” or, more realistically, the metal–ligand polar–covalent bond energy is a smoothly—nearly linearly—varying function of atomic number through a series of homologous complexes. This should indeed be approximately true, but deviations of the order of 5–10 kcal./mole might easily arise in particular metal ions as a result of higher order effects, such as configuration interaction, which are ignored in the usual forms of either the crystal field or the molecular orbital theories of the bonding in complexes.

The important conclusion to be drawn from Fig. 1,

however, is that the simple argument based on CFSE values gives an impressively good account of the thermodynamic data. Thus, while granting, freely, the point that CFSE values make up only a tiny fraction of the total enthalpies of forming complex ions from the gaseous metal ion and ligands, and cannot therefore be taken as useful measures of the absolute stability of complexes, the relative CFSE values in properly chosen homologous series of compounds appear capable, *in themselves*, of providing a semiquantitative guide to the relative stabilities of the members of the series. An early and now classic example of this sort of use of CFSE values is the correlation of the site preferences of various metal ions in mixed oxides (*e.g.*, spinels).^{15,16} The present results for process 9, which is not unrelated to the site preference problem, strongly support the fundamental validity of the theory proposed for the latter.

- (15) D. S. McClure, *J. Phys. Chem. Solids*, **3**, 311 (1957).
 (16) J. D. Dunitz and L. E. Orgel, *ibid.*, **3**, 318 (1957).

Finally, the results reported here permit us to evaluate a suggestion made by Gill and Nyholm^{2c} that there would be a difference in the mean slopes of the curves for H_{com} of octahedral and tetrahedral complexes sufficient to play an important role in the energetics of process 9. Figure 2 shows a plot similar to theirs except that we have used the actual rather than hypothetical results for the tetrahedral complexes. Qualitatively, the predicted effect is present: the gap between tetrahedral and octahedral curves closes by about 7 kcal./mole in going from Mn to Zn. However, this is too small an effect, only ~ 1 kcal./mole per element, to have any significant impact on the over-all results. The conclusion proposed above, *viz.*, that the CFSE values, *in themselves*, can pretty well account for the over-all thermochemical results, may thus be reiterated.

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A Molecular Orbital Treatment of the Bonding in Certain Metal Atom Clusters^{1a}

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The structures of the $[M_6X_8]^{4+}$, $M = \text{Mo, W (?)}$; $[M_6Cl_{12}]^{2+}$, $M = \text{Nb, Ta}$; and $[M_3X_{12}]^{3-}$, $M = \text{Re}$, species, which contain clusters of heavy transition metal atoms, are compared and the occurrence of approximately square MX_4 units is noted as a common feature. The metal-to-metal bonding within the clusters is treated by a simple molecular orbital method and it is shown that in this way all the general aspects of the electronic structures can be straightforwardly accounted for. Clues provided as to other possible metal ion cluster compounds are discussed.

Introduction

There exist three classes of compounds of the transition elements, aside from polynuclear metal carbonyls, in which the principal structural feature is a cluster of metal atoms in some symmetrical array at internuclear distances indicative of strong metal-metal interactions. These are (1) the $[M_6X_{12}]^{2+}$ systems in which M is Nb or Ta, (2) the $[M_6X_8]^{4+}$ systems in which M is Mo and, probably, though this is not entirely certain, W, and (3) the recently discovered $[\text{Re}_3\text{Cl}_{12}]^{3-}$ anion. The first two systems have been recognized for a long time and various attempts have been made to treat the bonding therein. Thus, for both the $[M_6Cl_8]^{4+}$ and the $[M_6Cl_{12}]^{2+}$ types, molecular orbital treatment has been carried so far as to produce some parametric equations for orbital energies.² On the other hand, it has also been proposed that in addition to the molybdenum-chlorine bonding in $[\text{Mo}_6\text{Cl}_8]^{4+}$, the Mo-Mo bonds be considered as discrete, two-center bonds, thus affording a valence bond formulation of the bonding in which the

molybdenum is considered to have a valence of six.³ This valence bond approach has been elaborated, leading to the suggestion that the molybdenum atoms use sets of square antiprismatic hybrid orbitals with the Mo-Cl bonds then being extraordinarily bent.⁴

The present attempt at a molecular orbital treatment, embracing all three types of compound, has been undertaken for several reasons.

(1) We believe that a valence bond approach, based on formation of two-center metal-metal bonds by use of certain limiting, generally quite symmetrical, hybridization schemes (or even more general, less symmetrical ones), is not a useful *general* approach, although it may be sufficient in some instances.⁵ In most cases, the $[\text{Mo}_6\text{Cl}_8]^{4+}$ ion as depicted in Fig. 4 of ref. 4 being a cogent example, one must use bonds which are so bent or so

(3) J. C. Sheldon, *J. Chem. Soc.*, 1007, 3106 (1960).

(4) R. J. Gillespie, "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, p. 34.

(5) For example, in $\text{Os}_3(\text{CO})_{12}$ and analogous molecules, one may assume approximate octahedral hybridization at each metal atom, so that each one forms four Os-C two-center bonds and two, somewhat bent, $\text{Os}_2\text{-Os}_2$ two-center bonds and thus account for the diamagnetism of such compounds in a satisfactorily facile manner.

(1) (a) Supported by the United States Atomic Energy Commission; (b) Fellow of the Alfred P. Sloan Foundation; (c) N.S.F. Predoctoral Fellow.

(2) L. D. Crossman, D. P. Olsen, and G. H. Duffey, *J. Chem. Phys.*, **38**, 73 (1963).