

behavior of the complex. The wavelengths used for irradiation correspond (Figure 1) to ligand→metal electron-transfer bands (313 and 365 $m\mu$), to a singlet d-d band (443 $m\mu$), and to a triplet d-d band (530 $m\mu$).¹⁹ *In spite of the difference in energy and also in nature among the various excited states reached by irradiation, the same type of photochemical reaction occurs, and, moreover, it has the same quantum yield.* This result strongly suggests that the photoreaction does not take place directly in the various excited states, but it originates from the same chemically active state, independently of the wavelength of irradiation. Therefore, it appears that radiationless transitions having nearly unitary efficiency should lead the higher excited states to the lowest one (*i.e.*, to the triplet d-d state). Then, the following alternative possibilities could

occur: (a) The triplet state has a lifetime long enough to react. (b) An intersystem crossing process between the triplet d-d state and the electronic ground state leads to "hot" (*i.e.*, vibrationally excited) $PtBr_6^{2-}$ ions which can react during their relaxation periods. Both of these reaction paths agree with the proposed heterolytic mechanism (4). In fact, both the triplet d-d state (which has the same electronic distribution between the central ion and the ligands as the ground state) and the vibrationally excited levels of the ground state react with a heterolytic mechanism as $PtBr_6^{2-}$ ions do when they thermally decompose.

Acknowledgment.—The authors are indebted to Professor V. Carassiti for his interest in this work and for his helpful criticism.

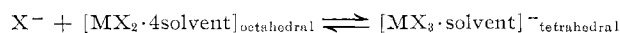
CONTRIBUTION FROM THE DIVISION OF MINERAL CHEMISTRY,
COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANIZATION,
PORT MELBOURNE, VICTORIA, AUSTRALIA

Influence of Temperature on Some Octahedral-Tetrahedral Equilibria in Solution

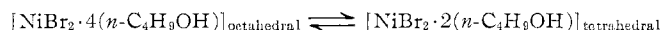
BY D. E. SCAIFE AND K. P. WOOD

Received July 20, 1966

The effect of temperature on the equilibria



has been studied for some cobalt and nickel halides in water and alcohols. High temperatures and high halide ion concentrations favor the tetrahedral species, and heats of reaction between 11.7 and 17.1 kcal/mole have been found. Considerations of these heats of reaction and the ligand field stabilization energies suggest that the curves of the negative heats of formation in solution (corrected for ligand field stabilization) of the octahedral and tetrahedral species intersect between Co and Ni, the slope of the curve for the tetrahedral species being greater. An equilibrium



with a heat of reaction of 17.0 kcal/mole is also reported.

Solution equilibria involving tetrahedrally coordinated complex halide species of the first-row transition series have been studied by many workers, but there has been little work on the influence of temperature on these equilibria. Furlani and co-workers have observed marked changes in spectra with temperature for nickel halides¹ and copper halides² in various solvents with added halide ion, while Katzin³ obtained ΔH values for the reaction



by observing changes in spectra with temperature. This paper reports work on the temperature effect for some nickel and cobalt halides in water and alcohols in the presence of large concentrations of added halide ion.

(1) C. Furlani and G. Morpurgo, *Z. Physik. Chim.*, **28**, 93 (1961).

(2) C. Furlani and G. Morpurgo, *Theoret. Chim. Acta* (Berlin), **1**, 102 (1963).

(3) L. I. Katzin *J. Chem. Phys.*, **35**, 467 (1961).

Experimental Section

For the studies in nonaqueous solvents, anhydrous salts of the type $[(C_2H_5)_4N]_2MX_4$ and $[(C_6H_5)_4As]_2MX_4$, prepared by the methods of Gill and Nyholm,⁴ were used as sources of the appropriate metal halide. The dissociation of these salts in the solvents gave solution species the same as those obtained from the anhydrous halides themselves. For the $CoCl_2-H_2O$ system, $CoCl_2 \cdot 6H_2O$ was used. In each case, the halide salt was dissolved in a solution of lithium halide in the required solvent of sufficient concentration to give the intense blue color of a tetrahedral species on heating. Under these conditions in the systems studied, the room-temperature spectra were generally of an octahedral species, with occasionally a small intensity of tetrahedral species also present. On heating, a progressively intensifying spectrum of a tetrahedral species became present, as shown in Figures 1-3.

A Beckman DK2A recording spectrophotometer was used to follow the spectra, with 1-cm stoppered cells. The temperatures were controlled by a Beckman temperature-regulated cell holder, calibrated by thermocouples and calibrated thermometers.

(4) N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1950).

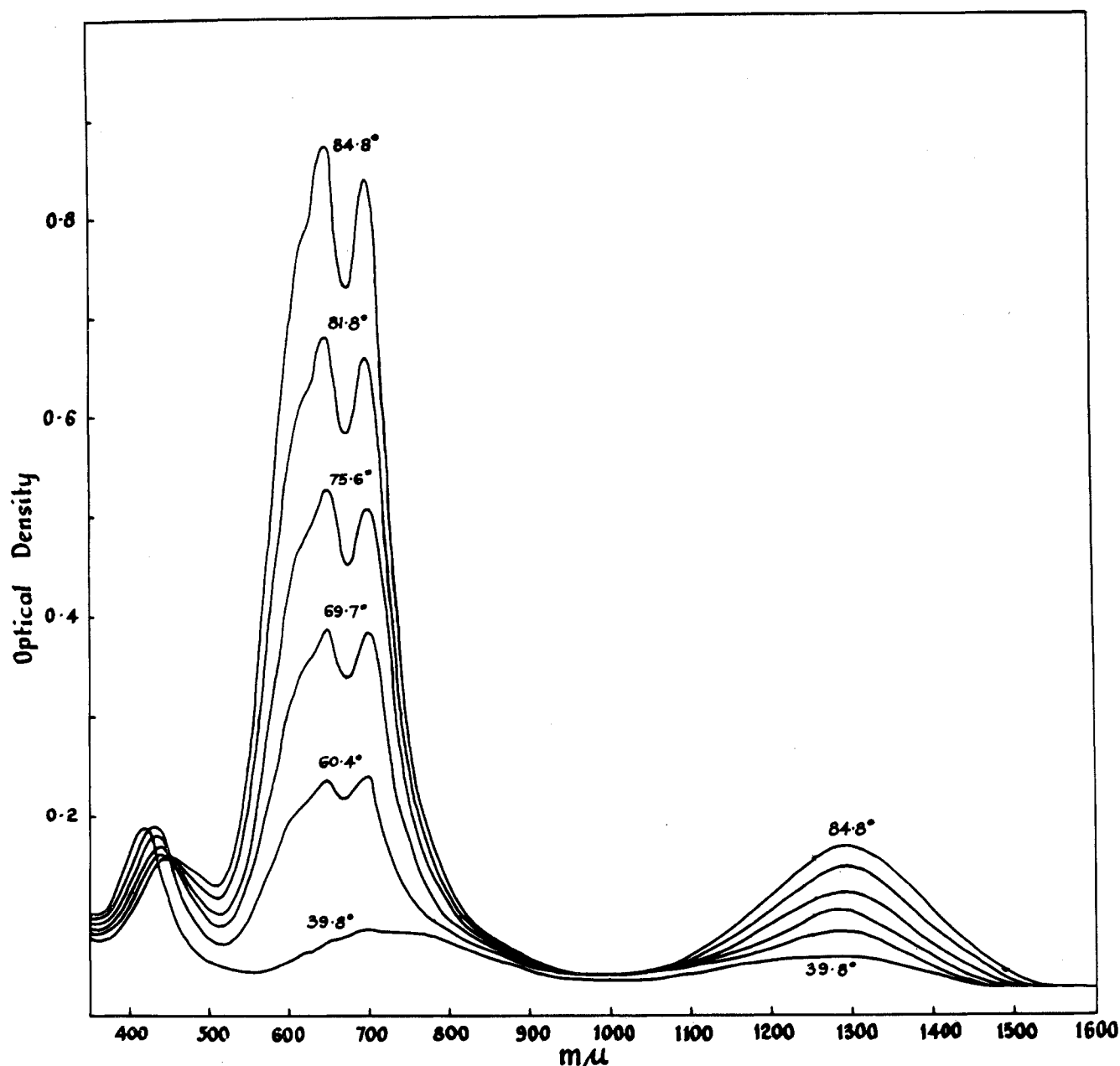


Figure 1.—Spectrum of $1.593 \times 10^{-2} M [(C_6H_5)_4As]_2NiCl_4 + 2.42 M LiCl$ in C_2H_5OH at various temperatures.

Temperatures were measured during a run and showed standard deviations of $0.3\text{--}0.5^\circ$ about the mean controlled temperature.

Results

The band positions of the octahedral species involved in the equilibria studied here are shown in Table I. These values were obtained directly from the room-temperature spectra either of solutions which gave tetrahedral species at high temperatures or of solutions slightly less concentrated in lithium halide to avoid interference from spectra of tetrahedral species. It was found that the spectra of the octahedral species remained unaltered on reducing the concentration of lithium halide by one-half or more.

On increasing the temperature, intense absorption bands attributable to tetrahedral species appear. The positions of the peaks on these complex bands, shown

in Table II, remain unchanged with temperature in all cases studied, as is shown clearly in Figures 1–3.

The relative intensities of the component peaks on the absorption bands of tetrahedral Ni(II) and Co(II) species are very sensitive to the ligand field strength of the species, as can be seen in the spectra shown by Buffagni and Dunn⁵ and Furlani and Morpurgo.¹ The constancy of band shape in our spectra is thus a good, but not unambiguous, test for constancy of species. Furthermore, there are indications of one or more isosbestic points in our spectra, although the accuracy of these points cannot be expected to be maintained over a temperature range. It would appear that one tetrahedral species predominates, but there is the possibility

(5) S. Buffagni and T. M. Dunn, *J. Chem. Soc.*, 5195 (1961).

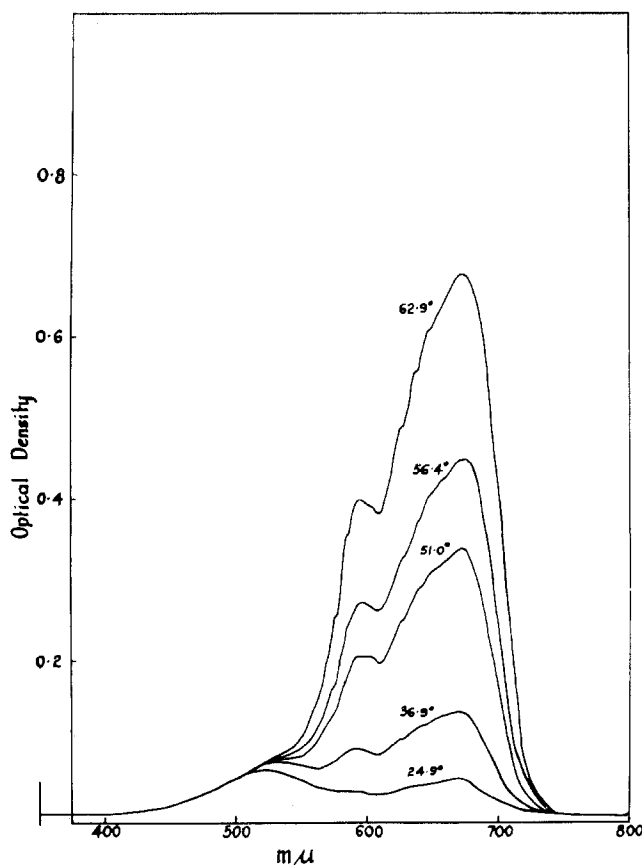


Figure 2.—Spectrum of $5.51 \times 10^{-3} M [(C_6H_5)_4As]_2CoCl_4 + 0.354 M LiCl$ in CH_3OH at various temperatures.

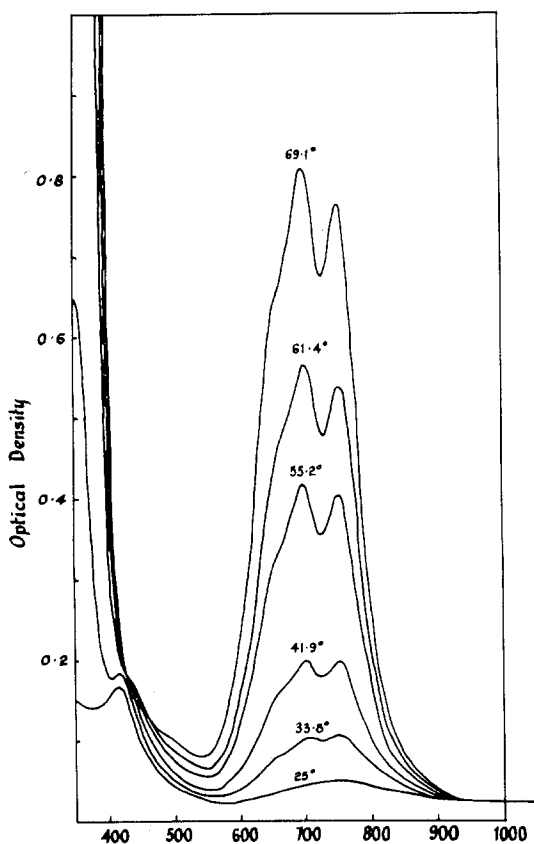


Figure 3.—Spectrum of $1.53 \times 10^{-2} M [(C_2H_5)_4N]_2NiBr_4 + 4.30 M LiBr$ in CH_3OH at various temperatures.

that a small amount of another tetrahedral species is present.

For each of these tetrahedral spectra, the change in optical density at a given wavelength may be plotted against reciprocal absolute temperature, and some of these plots are shown in Figures 4 and 5. Except for the data for Ni in LiBr- C_4H_9OH solutions, the graphs were fitted by least squares, and the slopes of the lines in kilocalories and the standard deviations of the slopes are shown in Figure 2, alongside the peak positions for which the data were obtained. These slopes are heats of reaction, ΔH_r , for the reaction under the conditions of the experiments. The plots for Ni in LiBr- $n-C_4H_9OH$ solutions, Figure 5, were roughly straight at lower temperatures with slopes of 14–15 kcal, but curved away at higher temperatures toward slopes of about 7 kcal.

For all these systems, the agreement between ΔH_r values for different peaks of the same band system is within the experimental error, and this is evidence that these band systems are predominantly those of a single tetrahedral species in each case.

In the case of Ni in LiBr- C_2H_5OH solutions, there is agreement between the sets of ΔH_r values at three widely different bromide concentrations. Together with the evidence that the spectra of the octahedral and tetrahedral species remain constant at these three concentrations, this suggests that the same equilibrium is involved and the species remain essentially unchanged. Similar constancy of band shape is found for two chloride concentrations in the aqueous cobalt chloride system, but the lower intensities found at the lower concentration gave only rough ΔH_r values, 12 ± 2 kcal, in approximate agreement with the accurate values at higher concentrations.

The final ΔH_r value for each of the tetrahedral species, shown in Table III, was taken as the weighted mean of the ΔH_r values for the individual peaks of the band, the weighting being in inverse proportion to the standard deviations of the individual ΔH_r values.

It was found that the extinction coefficients of the octahedral species in each system showed negligible change over the temperature ranged studied; no such information exists for the tetrahedral species, but small changes in extinction coefficients with temperature for these would be within the experimental error.

Discussion

Species such as $[M \cdot (6\text{solvent})]^{2+}$, $[MX \cdot 5\text{solvent}]^+$, $[MX_2 \cdot 4\text{solvent}]$, $[MX_2 \cdot 2\text{solvent}]$, $[MX_3 \cdot \text{solvent}]^-$, and $[MX_4]^{2-}$ have been reported in the extensive literature^{1,2,5-11} on Co^{2+} and Ni^{2+} in relatively weakly coordinating solvents. While there is little literature on the species in the more basic solvents of higher dielec-

(6) D. A. Fine, *Inorg. Chem.*, **4**, 345 (1965).

(7) D. A. Fine, *ibid.*, **5**, 197 (1966).

(8) L. I. Katzin, *J. Chem. Phys.*, **36**, 3034 (1962).

(9) L. I. Katzin and E. Gebert, *J. Am. Chem. Soc.*, **72**, 5464 (1950).

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

(11) F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *ibid.*, **83**, 4161 (1961).

TABLE I
SPECTRA OF OCTAHEDRAL SPECIES

Salt added	Solvent	Concn of Ni ²⁺ , M	Concn of lithium halide, M	X ⁻ /Ni ²⁺	Band position (cm ⁻¹) at 30°	Δ, cm ⁻¹	B, cm ⁻¹
[(C ₂ H ₅) ₄ N] ₂ NiBr ₄	CH ₃ OH	1.53 × 10 ⁻²	4.30	285	24,300, 13,300, 8080	8100	920
[(C ₂ H ₅) ₄ N] ₂ NiCl ₄	CH ₃ OH ^a	1.56 × 10 ⁻²	7.08	458	24,330, 14,330 sh, 13,260, 7980	7950	915
[(C ₂ H ₅) ₄ N] ₂ NiBr ₄	C ₂ H ₅ OH	7.69 × 10 ⁻³	2.30	303	23,920, 14,060 sh, 14,040, 7860	7860	903
		1.546 × 10 ⁻²	2.30	153			
		3.15 × 10 ⁻²	2.30	77			
[(C ₂ H ₅) ₄ N] ₂ NiCl ₄	C ₂ H ₅ OH	1.593 × 10 ⁻²	2.424	152	24,000, 13,120, 7790	7800	905
[(C ₂ H ₅) ₄ N] ₂ NiBr ₄	n-C ₄ H ₉ OH	3.23 × 10 ⁻²	0	4	24,100, 13,080, 7800	7800	917
		1.505 × 10 ⁻²	1.152	80			

^a No tetrahedral species found in this system.

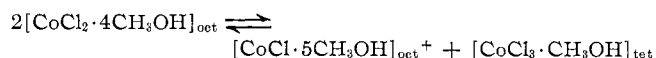
TABLE II
ABSORPTION PEAK POSITIONS AND ΔH VALUES

Metal	Halide	Solvent	Concn, M	X ⁻ /M	Peak positions, cm ⁻¹	ΔH _r values, kcal		
Ni	Br	CH ₃ OH	1.53 × 10 ⁻²	285	14,990 sh	11.98 ± 0.24		
					14,310	12.43 ± 0.43		
					13,330	12.13 ± 0.37		
					7,620			
Ni	Br	C ₂ H ₅ OH	(a) 7.70 × 10 ⁻³ (b) 1.546 × 10 ⁻³ (c) 3.16 × 10 ⁻²	303 153 77	16,670 sh	(a)	(b)	(c)
					15,120	17.08 ± 0.75	17.14 ± 1.44	16.52 ± 0.75
					14,380	17.22 ± 0.81	17.27 ± 1.44	17.47 ± 0.41
					13,500 sh	16.42 ± 0.72	17.26 ± 1.44	16.62 ± 2.01
					7,410			
Ni	Br	n-C ₄ H ₉ OH	3.23 × 10 ⁻²	4	15,870	17.03 ± 0.29		
					14,370 sh	17.03 ± 0.29		
					7,690			
Ni	Br	n-C ₄ H ₉ OH	1.505 × 10 ⁻²	80	16,920 sh			
					15,310			
					14,370	15		
					13,480	15		
					7,530	14		
Ni	Cl	C ₂ H ₅ OH	1.593 × 10 ⁻²	152	16,100 sh			
					15,480	13.05 ± 2.80		
					14,350	14.82 ± 0.53		
					7,690			
Co	Cl	H ₂ O	2.29 × 10 ⁻² 2.88 × 10 ⁻²	143 ^a 286	16,390 sh			
					16,080	11.57 ± 0.16		
					15,620 sh			
					15,170	11.78 ± 0.20		
					14,580	11.75 ± 0.20		
Co	Cl	CH ₃ OH	5.51 × 10 ⁻³	68.3	17,120 sh			
					16,920	13.64 ± 0.68		
					16,000 sh			
					15,600 sh			
					15,460 sh			
					14,930	13.50 ± 0.41		

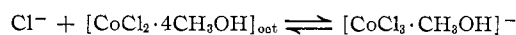
^a KCl solution.

tric constant such as those studied here, some tentative identification of the species concerned may be made.

Our spectra of the octahedral and tetrahedral species in the Co-Cl-CH₃OH system appear to be identical with those found by Katzin and Gebert⁹ in a study of this system up to Cl⁻/Co = 20 and identified by these authors by continuous variations as belonging to the species [CoCl₂·4CH₃OH] and [CoCl₃·CH₃OH]⁻. Katzin⁹ studied the temperature variation and found a value of ΔH = 13.4 kcal, close to our value, for the reaction which he identified as



We suggest that this disproportionation may be suppressed, in the presence of a large excess of chloride, in favor of



The heats of these two reactions would be expected to be very similar.

The spectra found by us for CoCl₂ in aqueous KCl and LiCl are the same as those found by Cotton, *et al.*,¹⁰

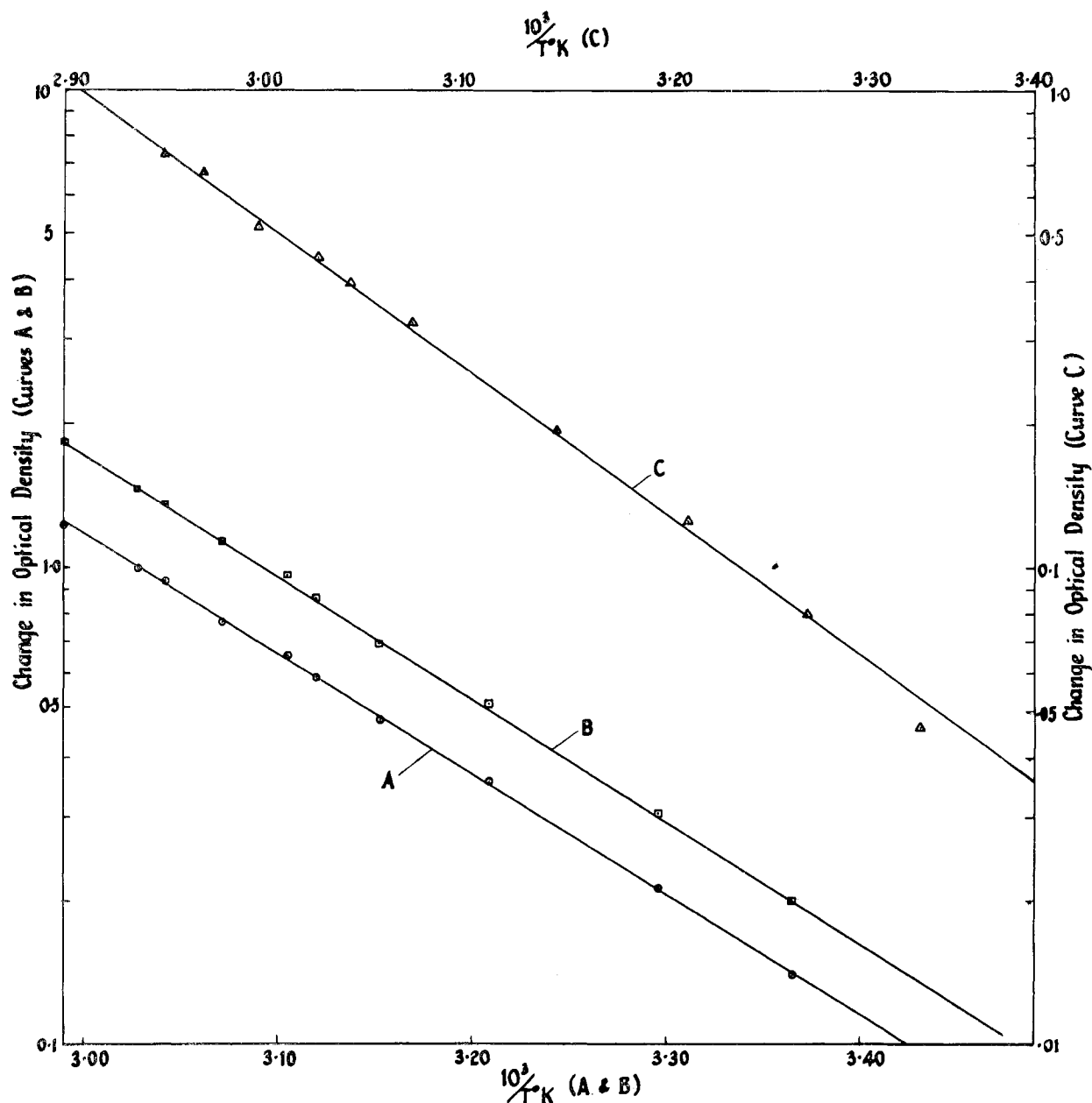


Figure 4.—Change in optical density against $10^3/T(^{\circ}\text{K})$ for $2.88 \times 10^{-2} M \text{CoCl}_2 \cdot 6\text{H}_2\text{O} + 8.47 M \text{LiCl}$ in H_2O (A) at $16,080 \text{ cm}^{-1}$ and (B) at $15,170 \text{ cm}^{-1}$ and for $5.51 \times 10^{-2} M [(\text{C}_6\text{H}_5)_4\text{As}]_2\text{CoCl}_4 + 0.354 M \text{LiCl}$ in CH_3OH (C) at $14,930 \text{ cm}^{-1}$.

TABLE III

Octahedral species	LFSE, kcal	Tetrahedral species	LFSE, kcal	ΔH_f , kcal	ΔH_f , kcal
$\text{NiBr}_2 \cdot 4\text{CH}_3\text{OH}$	-27.75	$\text{NiBr}_3 \cdot \text{CH}_3\text{OH}^-$	-7.80	+12.13	-7.82
$\text{NiBr}_2 \cdot 4\text{C}_2\text{H}_5\text{OH}$	-26.95	$\text{NiBr}_3 \cdot \text{C}_2\text{H}_5\text{OH}^-$	-7.43	+17.11	-2.41
$\text{NiCl}_2 \cdot 4\text{C}_2\text{H}_5\text{OH}$	-26.80	$\text{NiCl}_3 \cdot \text{C}_2\text{H}_5\text{OH}^-$	-7.88	+14.64	-4.28
$\text{NiBr}_2 \cdot 4n\text{-C}_4\text{H}_9\text{OH}$	-26.73	$\text{NiBr}_2 \cdot 2n\text{-C}_4\text{H}_9\text{OH}$	-7.83	+17.03	-1.93
$\text{NiBr}_2 \cdot 4n\text{-C}_4\text{H}_9\text{OH}$	-26.73	$\text{NiBr}_3 \cdot n\text{-C}_4\text{H}_9\text{OH}^-$	-7.63	+14.8	-4.3
$\text{CoCl}_2 \cdot 4\text{H}_2\text{O}$	-17.42	$\text{CoCl}_3 \cdot \text{H}_2\text{O}^-$	-11.70	+11.70	+5.98
$\text{CoCl}_2 \cdot 4\text{CH}_3\text{OH}$	-17.12	$\text{CoCl}_3 \cdot \text{CH}_3\text{OH}^-$	-11.65	+13.57	+8.10

for Co^{2+} in saturated LiCl and $12 M \text{KCl}$. The band positions and values of the ligand field parameter Δ and the Racah parameter B suggested to them that the species $[\text{CoCl}_3 \cdot \text{H}_2\text{O}]^-$ predominated under these conditions. Similar considerations of Δ and B support the proposed existence of $[\text{CoCl}_3 \cdot \text{CH}_3\text{OH}]^-$ in methanol.

Fine⁷ identified the species of Ni in bromide-methoxy methanol solutions as $[\text{NiBr}_4 \cdot \text{solvent}]^+$, up to Br^-/Ni

$= 10$. We suggest that the octahedral species in methanol, ethanol, and 1-butanol at the rather higher Br^-/Ni ratios used by us is more likely to be $[\text{NiBr}_2 \cdot 4\text{solvent}]$. This assumption is supported by the values of Δ and B , shown in Table I, calculated from the observed bands. The values of Δ are consistent with the species $[\text{NiX}_2 \cdot 4\text{ROH}]$, assuming values of Δ of about 7100 cm^{-1} for NiCl_6^{3-} and NiBr_6^{3-} , together with Δ for

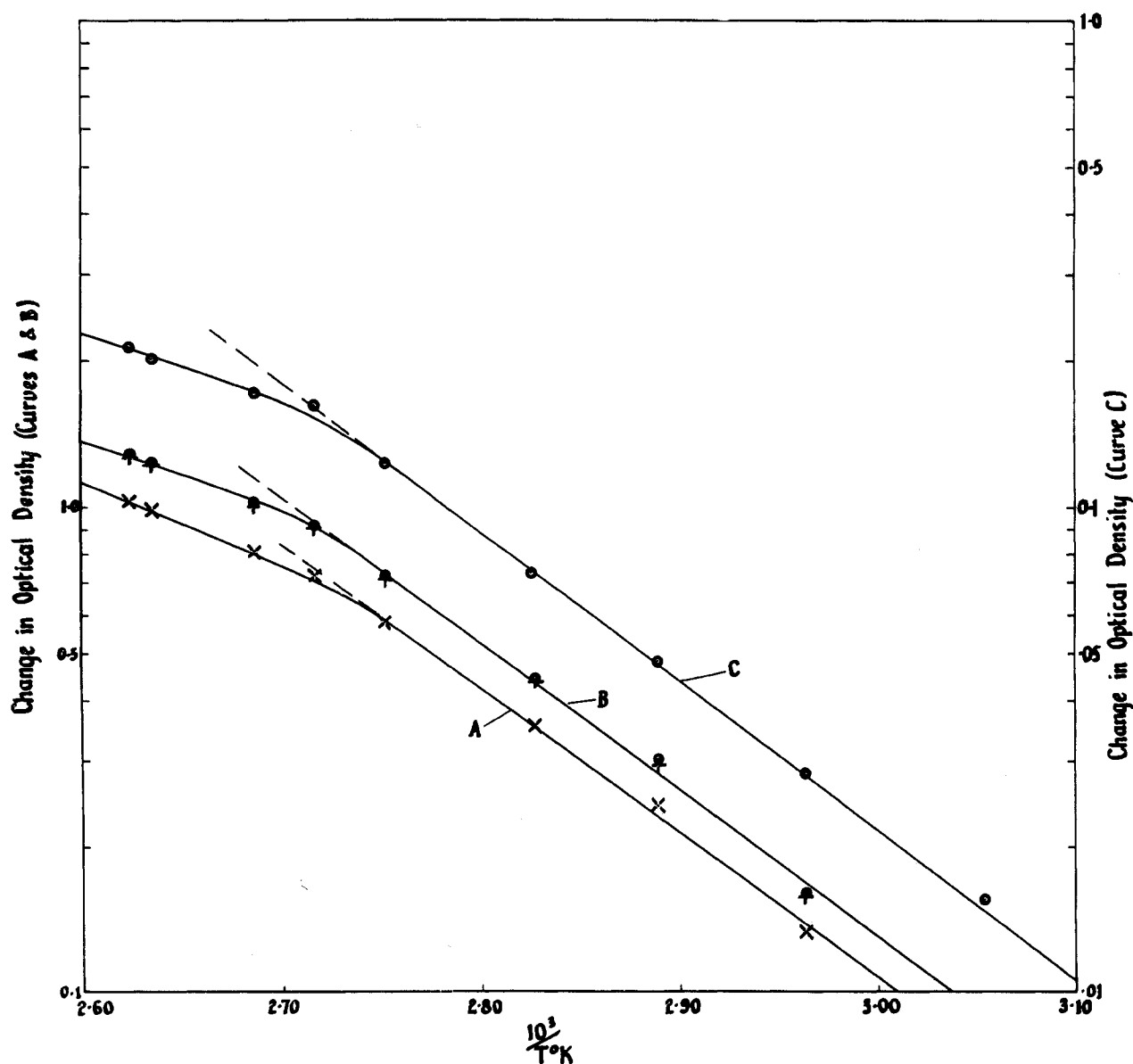


Figure 5.—Change in optical density against $10^3/T(^{\circ}\text{K})$ for $1.505 \times 10^{-2} M [(C_2H_5)_4N]_2NiBr_4 + 1.152 M LiBr$ in $n\text{-}C_4H_9OH$ (A) at $15,310\text{ cm}^{-1}$, (B) at $14,370$ and $13,480\text{ cm}^{-1}$, and (C) at 7530 cm^{-1} .

$[Ni(\text{ROH})_6]^{2+}$ of 8400 cm^{-1} for CH_3OH , 8100 cm^{-1} for $\text{C}_2\text{H}_5\text{OH}$, and 8000 cm^{-1} for $n\text{-}C_4H_9OH$, compared with 8600 cm^{-1} for H_2O . These values of Δ for ROH are in the order of the base strengths, dipole moments, and dielectric constants.

Furlani and Morpurgo¹ studied the effect of temperature on the spectra of a $0.1 M$ solution of $NiCl_2$ in $2.0 M LiCl\text{-}C_2H_5OH$ solution. The marked change in band shape of their spectra with temperature shows that, at these concentrations, more than one tetrahedral species is involved. Their spectrum at 70° resembles ours for this system, but is not identical. They infer that the species at this temperature is $NiCl_4^{2-}$, but comparison of the spectrum with the authentic $NiCl_4^{2-}$ spectra of Cotton, *et al.*,¹¹ suggests that the species is more likely $[NiCl_3 \cdot C_2H_5OH]^{-}$.

We have tentatively assumed that the species involved in all but one of the reactions studied are $[MX_2 \cdot 4\text{solvent}]_{\text{oct}}$ and $[MX_3 \cdot \text{solvent}]_{\text{tet}}$. In the case of

$[(C_2H_5)_4N]_2NiBr_4$ solutions in $n\text{-}C_4H_9OH$, the band positions indicate that the tetrahedral species is $[NiBr_2 \cdot 2C_4H_9OH]$. Similar species are suggested by Katzin⁸ for CoCl_2 solutions in higher alcohols.

The curvature of the plots for $Ni\text{-}Br\text{-}C_4H_9OH$ system suggests the participation of other species in this equilibrium. While involvement, to any large degree, of another tetrahedral species such as $[NiBr_2 \cdot 2C_4H_9OH]$ seems unlikely in view of the constancy of band shape, participation of an octahedral species other than $[NiBr_2 \cdot 4C_4H_9OH]$ at high temperatures cannot be ruled out, as the relatively low-intensity spectrum expected for such a species would have little effect on the band shape.

The values of ΔH_r obtained show small and apparently random changes from one system to another. The exact significance of comparison between the values for different systems is not clear, in view of the large changes of concentrations and activities of the lithium halide solutions. For the same reasons, there

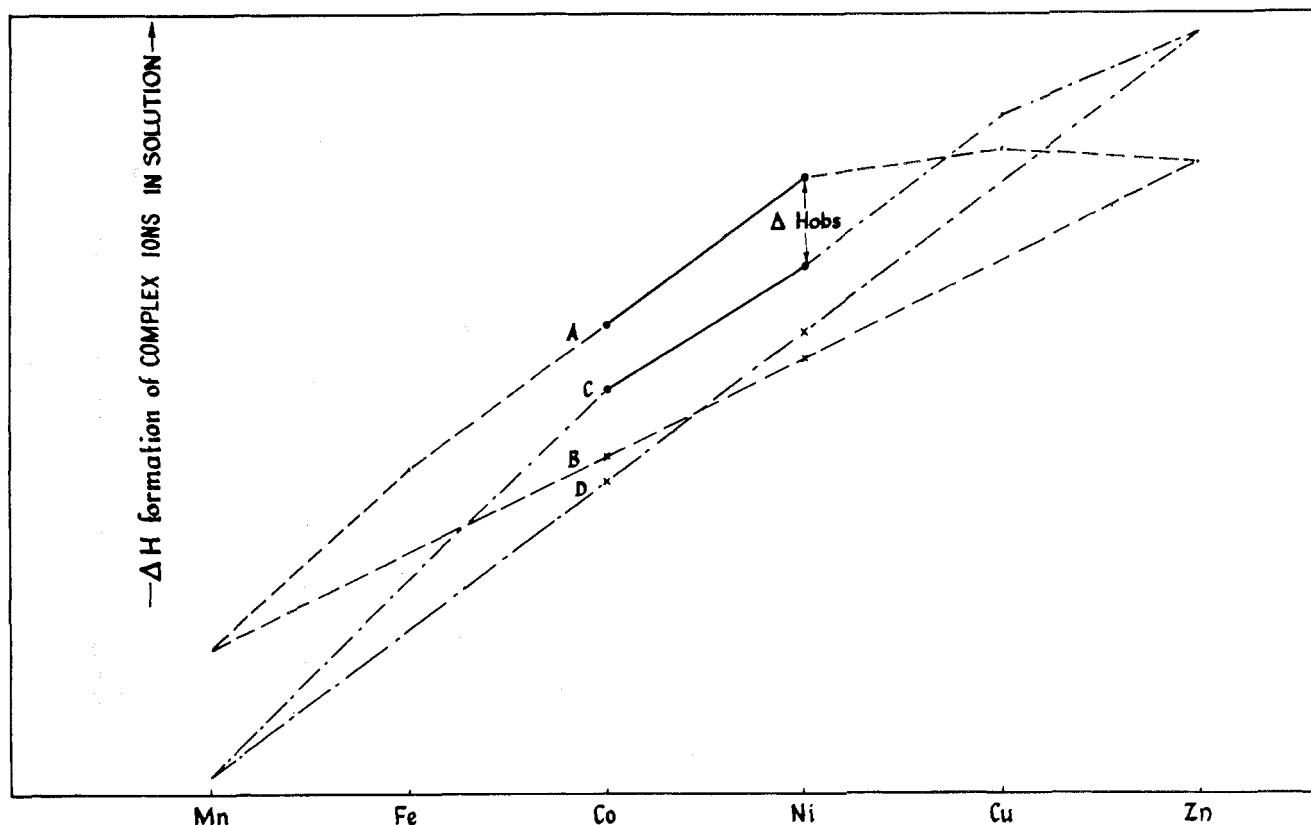


Figure 6.—Diagrammatic representation of negative heats of formation of complex ions in solution.

can be no clear correlation between the heats of reaction observed and the equilibrium constants. However, for the purposes of discussion, we assume that the ΔH_r values can be reasonably compared on the same basis and qualitatively account for the variations in the following discussion.

The heat of formation of the octahedral species is given by

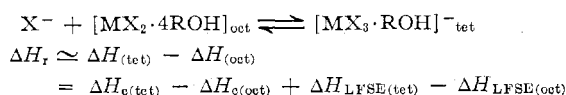
$$\Delta H_{\text{(oct)}} = \Delta H_{\text{e(oct)}} + \Delta H_{\text{LFSE(oct)}}$$

where $\Delta H_{\text{e(oct)}}$ is the energy of the center of gravity of the d levels; it is made up of large energy terms resulting from bonding and also includes the heats of solution. $\Delta H_{\text{LFSE(oct)}}$ is the ligand field stabilization energy resulting from the symmetry-dependent splitting of the d levels and is small compared to $\Delta H_{\text{e(oct)}}$.

Similarly, for the tetrahedral species

$$\Delta H_{\text{(tet)}} = \Delta H_{\text{e(tet)}} + \Delta H_{\text{LFSE(tet)}}$$

Then, for the reactions



Then

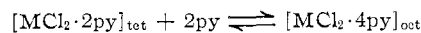
$$\Delta H_{\text{e(tet)}} - \Delta H_{\text{e(oct)}} = \Delta H_e = \Delta H_r - \Delta H_{\text{LFSE(tet)}} + \Delta H_{\text{LFSE(oct)}}$$

Values of ΔH_e , given in Table III, were determined from the ΔH_r values and the LFSE values, which were calculated from the observed spectra.

The values of ΔH_e for the Ni species were negative, while the Co values were positive. It was not possible to obtain direct comparisons between equivalent Co

and Ni species, as no tetrahedral species could be found for the Ni-Cl-CH₃OH system and the Ni-Cl-H₂O system, and the species $[\text{CoX}_2 \cdot 2\text{ROH}]$ seemed to predominate for cobalt bromide solutions in methanol and higher alcohols, and for cobalt chloride solutions in ethanol and higher alcohols. A rough comparison is therefore made between the ΔH_e values for the Ni-Br-CH₃OH and Co-Cl-CH₃OH systems.

Making this comparison, we use the calculated ΔH_e values to establish roughly the relative slopes and positions of the plots against atomic number of $\Delta H_{\text{e(oct)}}$ and $\Delta H_{\text{e(tet)}}$. For simplicity, we have assumed these plots are straight lines, although the thermodynamic data of Blake and Cotton¹² and Paoletti¹³ suggest they should be smooth curves. It can be seen that these plots of $\Delta H_{\text{e(oct)}}$ and $\Delta H_{\text{e(tet)}}$ apparently intersect between Co and Ni, the slope of the tetrahedral line being steeper. This is in accord with a similar suggestion made by Gill and Nyholm⁴ in comparing $[\text{M}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{MX}_4]^{2-}$, and by King, *et al.*,¹⁴ in comparing $[\text{MX}_2\text{L}_4]_{\text{oct}}$ and $[\text{MX}_2\text{L}_2]_{\text{tet}}$, where L may be pyridine or similar ligands. Similar effects have been noted by Libus and Uruska¹⁵ in the values of K for the reactions



The relative slopes and positions of the $\Delta H_{\text{e(oct)}}$ and $\Delta H_{\text{e(tet)}}$ curves will depend on the solvent, halide, and species considered, and this gives rise to the slightly

(12) A. B. Blake and F. A. Cotton, *Inorg. Chem.*, **3**, 5 (1964).

(13) P. Paoletti, *Trans. Faraday Soc.*, **61**, 219 (1965).

(14) H. C. A. King, E. Körös, and S. M. Nelson, *J. Chem. Soc.*, 5449 (1963).

(15) W. Libus and I. Uruska, *Inorg. Chem.*, **5**, 256 (1966).

varying ΔH_f values for the same metal with different halide and solvent.

To the lines of $\Delta H_{e(\text{oct})}$ and $\Delta H_{e(\text{tet})}$ may be added the values of ΔH_{LFSE} estimated for each atomic number, to give values of ΔH_f against atomic number as the difference between the resulting lines, shown in Figure 6.

From the trends in these values, it can be predicted that the ΔH_f values for the analogous Mn and Fe reactions will be large and positive, while the value for Zn will be large and negative. The accuracy of this diagrammatic representation is insufficient to predict a value for the Cu reaction.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, NEW YORK, NEW YORK 10027, AND CONTRIBUTION NO. 3400 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, CALIFORNIA 91109

Molecular Orbital Theory for Square-Planar Metal Halide Complexes

By HAROLD BASCH AND HARRY B. GRAY

Received August 9, 1966

The electronic spectra of the square-planar chloride complexes are assigned using molecular orbital levels derived by the SCCC-MO method. The d-orbital ordering $x^2 - y^2 > xy > xz, yz > z^2$ is calculated for the planar tetrahalides, and values derived from observed spectral band energies are given for the ligand field parameters Δ_1 , Δ_2 , and Δ_3 . The apparent decrease in Δ_1 values with increasing oxidation numbers is discussed in terms of the high covalent character of these complexes.

Introduction

The ordering of the metal d orbitals in the d^8 tetrahalide square-planar complexes (D_{4h} symmetry) of Pd(II), Pt(II), and Au(III) has been the subject of numerous papers.¹⁻⁹ Interest has been focused on the absorption spectrum of the PtCl_4^{2-} ion, where attempts have been made to match the bands in the visible and near-ultraviolet regions of the spectrum to one-electron excitations from the occupied d-orbital MO's [$2b_{2g}(xy)$, $2e_g(xz, yz)$, and $3a_{1g}(z^2)$] to the empty $3b_{1g}(x^2 - y^2)$. The spectrum has been assigned variously depending on the authors' choice of ordering for the occupied d-orbital MO's and whether a low-intensity band found at $20,300 \text{ cm}^{-1}$ is considered a transition to a spin-singlet or spin-triplet excited state. However, the recent, elegant experimental studies by several investigators,^{4,5,8-11} particularly those of Martin and co-workers,^{4,8,9} have narrowed the assignment possibilities considerably, and it would seem an opportune moment to put forward a more quantitative molecular orbital model for the square-planar halides. In this paper we report SCCC-MO calculations^{12,13} and compare them

with detailed assignments for both the $d \rightarrow d$ and charge-transfer spectra of the PtCl_4^{2-} and PdCl_4^{2-} complexes.

Computational Details

Bond distances for PtCl_4^{2-} and PdCl_4^{2-} were taken from the literature¹⁴ as 2.32 Å. Analytic orbital functions for the valence nd , $(n+1)s$, and $(n+1)p$ orbitals for second- and third-row metals have been published.¹⁵ Initially, the orbital functions were taken for a charge of +1 on the metal. Subsequent SCCC-MO calculations revealed that the charges on the metals were all much closer to zero than +1. Wave functions for the d orbitals *only* were then recalculated for the neutral metal species¹⁶ and the SCCC-MO calculations were repeated. Analytic functions for the valence s and p orbitals of Cl were taken from the tabulations of Clementi.¹⁷

VOIP's for Pd, Pt, and Au were taken as the respective VOIP's of the corresponding first-row metal,^{13,16} minus $10,000 \text{ cm}^{-1}$. Recall that the first VOIP curve is for ionization of a d electron from the configuration d^n . For Au, this configuration does not exist, and thus, the configuration d^9s^2 was substituted¹⁶ and the requisite changes made in the programmed procedure for calculating the metal d VOIP's. Ligand VOIP's for the valence s and p orbitals of Cl,^{12,13} ligand symmetry orbitals,³ and relationships between group and diatomic overlaps³ have been given previously.

- (1) J. Chatt, G. A. Gamlen, and L. E. Orgel, *J. Chem. Soc.*, 486 (1958).
- (2) R. F. Fenske, D. S. Martin, Jr., and K. Ruedenberg, *Inorg. Chem.*, **1**, 441 (1962).
- (3) H. B. Gray and C. J. Ballhausen, *J. Am. Chem. Soc.*, **85**, 260 (1963).
- (4) D. S. Martin, Jr., and C. A. Lenhardt, *Inorg. Chem.*, **3**, 1368 (1964).
- (5) P. Day, A. F. Orchard, A. J. Thomson, and R. J. P. Williams, *J. Chem. Phys.*, **42**, 1973 (1965).
- (6) J. R. Miller, *J. Chem. Soc.*, 713 (1965).
- (7) H. B. Gray, *Transition Metal Chemistry*, **1**, 240 (1965).
- (8) D. S. Martin, Jr., M. A. Tucker, and A. J. Kassman, *Inorg. Chem.*, **4**, 1682 (1965), as amended in **5**, 1298 (1966).
- (9) D. S. Martin, Jr., J. G. Foss, M. E. McGarville, M. A. Tucker, and A. J. Kassman, *ibid.*, **5**, 491 (1966).
- (10) O. S. Mortensen, *Acta Chem. Scand.*, **19**, 1500 (1965).
- (11) B. Bosnick, *J. Am. Chem. Soc.*, **88**, 2606 (1966).
- (12) H. Basch, A. Viste, and H. B. Gray, *J. Chem. Phys.*, **44**, 10 (1966).
- (13) H. Basch, A. Viste, and H. B. Gray, *Theoret. Chim. Acta*, **3**, 458 (1965).

- (14) "Tables of Interatomic Distances and Configurations in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958.
- (15) H. Basch and H. B. Gray, *Theoret. Chim. Acta*, **4**, 367 (1966).
- (16) H. Basch, Ph.D. Thesis, Columbia University, 1966.
- (17) E. Clementi, *J. Chem. Phys.*, **40**, 1944 (1964); IBM Research RJ-256.