

[CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY,^{1a} OAK RIDGE, TENNESSEE, AND THE POLYTECHNIC INSTITUTE OF BROOKLYN, BROOKLYN, NEW YORK]

Charge-Transfer and Ligand-Field Spectra of Tetrahedral Tetrahalonickel(II) Ions in Molten Dimethyl Sulfone and Molten Organic Halide Salts

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Ligand-field (LF) and charge-transfer (CT) spectra of tetrahedral tetrachloro-, tetrabromo-, and tetraiodonickelate(II) were measured in a number of media. The energy ranges investigated were 4000 to 47,000, 39,000, and 34,000 cm^{-1} for chloride, bromide, and iodide, respectively. The systems examined include crystalline tetra-*n*-butylammonium tetrabromonickelate(II) in a KBr disk, and dilute solutions of nickel(II) halides in molten dimethyl sulfone with excess lithium halides added, and in a number of molten substituted ammonium, phosphonium, and arsonium halides. Molten dimethyl sulfone proves to be an excellent solvent for studying transition metal ion complexes; it is transparent over wide energy ranges, and the solvent molecules coordinate only very weakly with these metal ions. The "organic" melts provide some of the most clear-cut examples of complex formation in molten salts. Assignments of spin-forbidden LF bands were attempted on the basis of a four-parameter model. The estimated LF parameters are (in cm^{-1}): for $[\text{NiCl}_4]^{2-}$, $Dq = 354 \pm 10$, $B = 734 \pm 6$, $C/B = 3.96 \pm 0.02$, and $\lambda = -275 \pm 50$ (limits fixed by the uncertainty in λ); for $[\text{NiBr}_4]^{2-}$, $Dq = \sim 330$, $B = \sim 680$, and $C/B = \sim 3.9$; and for $[\text{NiI}_4]^{2-}$, $Dq = \sim 330$, $B = \sim 540$, and $C/B = \sim 5.5$. The limits and uncertainties of these parameters were discussed. A few tentative assignments of the CT bands were made in terms of molecular orbital theory. The optical electronegativity of nickel(II), derived from the lowest-energy CT band, was 2.1 for all complexes.

Introduction

The ligand-field spectrum of a dilute solution of nickel(II) in an alkali halide melt has been shown²⁻⁷ to vary with the solvent cation. With alkali cations of large size, the spectrum approximates that of nickel(II) ions coordinated tetrahedrally in halide crystals, and this approximation becomes closer as the size of the cations increases. This trend is carried to the extreme in the present paper by the use of molten quaternary ammonium, phosphonium, and arsonium halides, including iodides. The ligand-field spectra in these organic halide salts agree in most details with what is expected for tetrahedral tetrahalonickelate(II) ions. Undoubtedly, this result is related to the common occurrence of crystalline tetrahalonickelate(II) salts with large organic cations.⁸⁻¹⁰

A second phase of the present paper deals with the spectroscopic identification of tetrahedral tetrahalonickelate(II) ions formed in molten dimethyl sulfone as solvent. Molten dimethyl sulfone possesses excellent properties as a solvent for spectroscopic investigations of transition metal complexes. It melts at a relatively low temperature (108°) to form a colorless liquid stable over the entire temperature range up to its boiling point (218°). A substantial number of inorganic salts dissolve readily in this medium without decomposition. In contrast to the behavior of water and many other common oxygen-containing solvents,

the oxygen atoms of dimethyl sulfone possess only weak coordinating capacity. Thus, in molten dimethyl sulfone the tendency toward metal ion-solvent complex formation in competition with dissolved ligands is minimized. This solvent is transparent over the wave length range 190-1100 $\text{m}\mu$ and has only a few relatively weak absorption bands between 1100 and 2500 $\text{m}\mu$. The background absorption due to these bands can be reduced to a tolerable level by the use of short path-length cells.

The spectra reported here cover much wider energy ranges than have previously been reported for these complex ions (4000-47,000 cm^{-1} for $[\text{NiCl}_4]^{2-}$, 4000-39,000 cm^{-1} for $[\text{NiBr}_4]^{2-}$, and 4000-34,000 cm^{-1} for $[\text{NiI}_4]^{2-}$). These ranges include most of the ligand-field bands, which serve to identify the ions, and a number of charge-transfer bands, all but one of which are reported for the first time. The ligand-field spectra, including some spin-forbidden bands, are analyzed in terms of the four-parameter model for cubic ligand fields¹¹ while the charge-transfer spectra are discussed in terms of Jørgensen's concept of optical electronegativities.¹²

Experimental

Chemicals.—Dimethyl sulfone is the commercial reagent recrystallized from methanol, water, and then 50% ethanol-water mixture.

Anhydrous nickel chloride, bromide, and iodide were prepared by sublimation of dehydrated salts.

Lithium Halides.—Lithium chloride and bromide were prepared by fusing the salts under an atmosphere of the respective hydrogen halide. After fusion, the gas was bubbled through the melt for 0.5 hr. The dissolved hydrogen halide in the melt was removed by repeated flushing with dry nitrogen and evacuation. The melt was filtered through a silica frit into a bulb which was then sealed. After cooling, the bulb was opened and its contents were ground in a drybox. Lithium iodide was prepared by thermally dehydrating the recrystallized trihydrate and subliming the product.

Organic Halide Salts.—Diethylamine hydrochloride, aniline hydrochloride, tri-*n*-butylbenzylphosphonium chloride, tri-*n*-

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butyl-2,4-dichlorobenzylphosphonium chloride, tetraphenylarsonium chloride, tetra-*n*-butylammonium bromide, tetra-*n*-pentylammonium bromide, tetra-*n*-butylammonium iodide, and tetra-*n*-hexylammonium iodide were reagent grade, recrystallized, and dried *in vacuo* at 75° for at least 24 hr.

Tetra-*n*-butylammonium tetrabromonickelate(II) was prepared by H. L. Holsopple of this laboratory by treating purified nickel bromide (2.928 g., 0.0134 mole) with tetra-*n*-butylammonium bromide (8.640 g., 0.268 mole) in 40 ml. of anhydrous ethyl alcohol. The product was crystallized upon partial evaporation of the alcohol on a water bath, and was dried *in vacuo*. The hygroscopic purple-blue compound melted at 82–84°.

Anal. Calcd.: C, 44.5; Br, 37.0; N, 3.25; Ni, 6.8. Found: C, 43.9; Br, 37.0; N, 3.19; Ni, 6.5.

Density of Dimethyl Sulfone.—The density at several temperatures between 120 and 150° was determined by the buoyancy method.¹³ During the measurement, milligram amounts of dimethyl sulfone condensed on the platinum wire connecting the platinum sinker to the balance and had to be corrected for in each weighing. The density measurements were considered to be better than 0.5%. The results are expressed by the equation $\rho = 1.258 - 1.16 \times 10^{-3}t$, where ρ is the density in g./ml. and t is the temperature in °C.

Densities of the Organic Halide Salts.—These densities have been reported.¹⁴

Spectroscopic Measurements.—The spectra were obtained on a Cary Model 14H spectrophotometer with a furnace that will be described elsewhere.¹⁵ Square silica absorption cells² with a 1-cm. path length were used and the path length was reduced to as little as a few microns by the use of closely fitting silica inserts. The absorption curves of the solvent and the solution of interest were run against air as reference, and the spectrum of the solute species was obtained by difference. Lithium halides are very soluble in dimethyl sulfone and yield transparent solutions except for the intense "cutoff" bands in the ultraviolet. With a 1-cm. path length, this "cutoff" occurs at about 210, 250, and 290 m μ for chloride, bromide, and iodide, respectively. Weighed portions of a nickel halide were added successively to a solution of the lithium salt of the same halide, and the spectrum was measured after each addition. The melts were kept under an atmosphere of high-purity nitrogen. Anhydrous nickel halides are practically insoluble in dimethyl sulfone but become readily soluble in the presence of even a small excess of halide ions. The soluble complexes that result have been shown to contain four halides per nickel(II) ion. This 4:1 ratio was established by a spectrophotometric study of the gradual conversion of the soluble, nitratonickel(II) complexes into the tetrahedral halo complexes by successive additions of lithium halide to the solution.¹⁶

In experiments involving molten organic halide salts, weighed amounts of nickel halides were added to weighed portions of the molten solvents and the spectra of the resultant solutions were measured under an atmosphere of high-purity nitrogen. A few of the spectra were measured on supercooled salt melts.

Results

Ligand-Field Spectra.—Typical ligand-field spectra of tetrahalonickelate(II) are presented in Fig. 1 and the spectroscopic results are summarized in Tables I and II. Beer's law was verified for the principal band maxima over the concentration ranges of nickel(II) listed in Table I. Additions of NiCl₂ to an organic bromide melt gave essentially the same spectrum as addition of NiBr₂. Likewise, addition of NiCl₂ to an organic iodide melt gave essentially the same spectrum as addition of NiI₂. These similarities are illustrated in Tables I and III.

These spectra are identified as absorptions of tetrahedral (or approximately tetrahedral) tetrahalonickelate(II) ions on the basis of a comparison of the stronger bands with previously measured spin-allowed absorptions of these ions in various media.^{4,5,9,17–19} Crystal

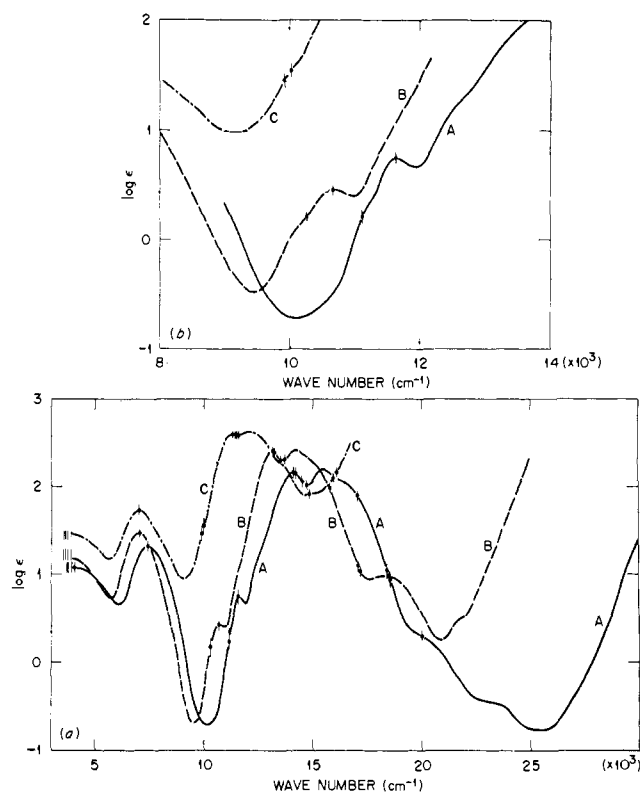


Fig. 1.—Ligand-field spectra of tetrahalonickelate(II) ions in molten dimethyl sulfone at 128° with excess lithium halide. Short vertical lines and dots mark computed energies listed in Table IV; (a) complete spectra, (b) region of ¹D transitions on an expanded wave number scale. Compositions for both (a) and (b) are: (A) [NiCl₄]²⁻ in solutions containing 0.002–0.5 M NiCl₂ + 1.6–2.6 M LiCl; (B) [NiBr₄]²⁻ in solutions containing 0.002–0.5 M NiBr₂ + 2.1 M LiBr; (C) [NiI₄]²⁻ in solutions containing 0.004–0.2 M NiI₂ + 2.1 M LiI.

spectra^{17,19} are particularly valuable for this comparison, and we augment these sparse data with a crystal spectrum of tetra-*n*-butylammonium tetrabromonickelate(II) measured in a KBr disk (see Table I). However, the solution spectra are essential for absolute intensity comparisons. The spin-allowed bands in the tables are designated according to their orbital excited states, which are triplets.

Empirical oscillator strengths, listed in Table II, were computed from the formula $f = 4.32 \times 10^{-9} \cdot \int \epsilon(\nu) d\nu$, where ν is in wave numbers. The values for chloro and bromo complexes are probably correct to within $\pm 10\%$ and those for the iodo complex to within $\pm 20\%$.

The energies and intensities of the ³T₁(F) → ³A₂(F) and ³T₁(P) bands of the chloro and bromo complexes have been studied and reported.^{9,18,19} There are small differences in band energies and, as expected, somewhat larger discrepancies in molar extinction coefficients, depending on the medium and the temperature. Our extinction coefficient data on these bands are in satisfactory agreement with the previous studies. The two previous measurements of oscillator strengths^{9,10} are in rough agreement with each other. Our oscillator strengths (Table II) agree well with those of Goodgame, Goodgame, and Cotton⁹ except for the ³T₁(F) →

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TABLE I: LIGAND-FIELD BANDS OF TETRAHALONICKEL(II) COMPLEXES

Chromophore	System	Band coordinates, cm. ⁻¹ over 1./mole-cm.									
		³ T ₂ (F)	¹ A ₂ (F)	D region			³ T ₁ (P)			G region	
[NiCl ₄] ²⁻	NiCl ₂ (0.002-0.5 M) + LiCl (1.6-2.6 M) in (CH ₃) ₂ SO ₂ , molten, 128°	~4080 (12)	7460 (21.2)	~11,200 (sh) ^a	11,600 (6.65)	~12,600 (sh)	14,160 (148)	15,510 (155)	~16,300 (sh)	~20,200 (sh)	23,500 (0.32)
[NiCl ₄] ²⁻	NiCl ₂ (0.0005-0.1 M) in (C ₆ H ₅ CH ₂)(C ₄ H ₉) ₃ PCl, molten, 165°		7440 (18)		11,650 (6.7)	~12,500 (sh)	14,140 (159)	15,370 (161)	~16,200 (sh)		
[NiCl ₄] ²⁻	NiCl ₂ (0.001-0.03 M) in (2,4-Cl ₂ C ₆ H ₃ CH ₂)(C ₄ H ₉) ₃ PCl, molten, 134°		7410 (20)		11,590 (6.8)	~12,500 (sh)	14,160 (164)	15,360 (165)	~16,200 (sh)		
[NiCl ₄] ²⁻	NiCl ₂ in (C ₆ H ₅ N)HCl, molten, 210°		7550		11,630		14,180	15,480	~16,700 (sh)		
[NiCl ₄] ²⁻	NiCl ₂ in (C ₂ H ₅) ₂ NH ₂ Cl, molten, 245°		7490		11,610		14,170	15,500	~16,700 (sh)		
[NiCl ₄] ²⁻	NiCl ₂ in (C ₆ H ₅) ₄ AsCl, molten, 247°		7410		11,590		14,140	15,410	~16,180 (sh)		
[NiBr ₄] ²⁻	NiBr ₂ (0.002-0.5 M) + LiBr (2.1 M) in (CH ₃) ₂ SO ₂ , molten, 128°	~4000 (~16)	7050 (30)	~10,100 (sh)	10,690 (2.85)		13,200 (252)	14,250 (255)	~14,900 (sh)	18,350 (9.2)	~21,800 (sh)
[NiBr ₄] ²⁻	[(C ₄ H ₉) ₄ N] ₂ (NiBr ₄) in KBr disk, solid		7070	~10,580 (sh)			13,260	14,230		18,350	~21,510 (sh)
[NiBr ₄] ²⁻	NiCl ₂ (0.01-0.08 M) in (C ₄ H ₉) ₄ NBr, molten, 124°		7050 (28)		10,720		13,290 (217)	14,340 (217)	~15,300 (sh)	18,650 (8.2)	~21,700 (sh)
[NiBr ₄] ²⁻	NiBr ₂ or NiCl ₂ in (C ₆ H ₁₁) ₄ NBr, molten, 117°		7140		10,720		13,030	14,180	~15,150 (sh)		
[NiI ₄] ²⁻	NiI ₂ (0.004-0.2 M) + LiI (2.1 M) in (CH ₃) ₂ SO ₂ , molten, 128°	<4000	7050 (53)	~10,000 (sh)			11,340 (385)	12,150 (423)	~13,510 (sh)	~14,900 (78)	
[NiI ₄] ²⁻	NiI ₂ (0.0003-0.01 M) in (C ₆ H ₁₃) ₄ NI, molten 122°		7030 (47)				11,350 (369)	12,120 (396)	~13,720 (sh)	~14,900 (65)	
[NiI ₄] ²⁻	NiCl ₂ (0.0005-0.008 M) in (C ₄ H ₉) ₄ NI, molten, 161°		6970 (45)				11,330 (364)	12,120 (413)			

^a (sh) means shoulder.

TABLE II

OSCILLATOR STRENGTHS OF SPIN-ALLOWED LIGAND-FIELD BANDS (BASED ON THE FORMULA $f = 4.32 \times 10^{-9} \int \epsilon(\nu) d\nu$)

Complex	Excited state	Medium (molten)	$f \times 10^4$
[NiCl ₄] ²⁻	T ₁ (P)	(CH ₃) ₂ SO ₂ + LiCl	24
		(C ₆ H ₅ CH ₂)(C ₄ H ₉) ₃ PCl	24
[NiBr ₄] ²⁻	A ₂ (F)	(CH ₃) ₂ SO ₂ + LiCl	1.5
		(C ₆ H ₅ CH ₂)(C ₄ H ₉) ₃ PCl	1.3
[NiBr ₄] ²⁻	T ₁ (P)	(CH ₃) ₂ SO ₂ + LiBr	32
		(C ₄ H ₉) ₄ NBr	32
[NiI ₄] ²⁻	A ₂ (F)	(CH ₃) ₂ SO ₂ + LiBr	1.9
		(C ₄ H ₉) ₄ NBr	1.8
[NiI ₄] ²⁻	T ₁ (P)	(CH ₃) ₂ SO ₂ + LiI	51
		(C ₆ H ₁₃) ₄ NI	44
[NiI ₄] ²⁻	A ₂ (F)	(CH ₃) ₂ SO ₂ + LiI	4.2
		(C ₆ H ₁₃) ₄ NI	3.3

TABLE III

CHARGE-TRANSFER BANDS OF TETRAHALONICKEL(II) COMPLEXES

Chromophore	System	Band coordinates, cm. ⁻¹ over 1./mole-cm.				
[NiCl ₄] ²⁻	NiCl ₂ (0.002-0.03 M) + LiCl (1.6 M) in (CH ₃) ₂ SO ₂ , molten, 128°	35,840 (2980)	38,760 (2730)	~42,100 (sh) ^a	43,100 (3650)	
[NiBr ₄] ²⁻	NiBr ₂ (0.002-0.008 M) + LiBr (2.1 M) in (CH ₃) ₂ SO ₂ , molten, 128°	28,650 (2530)	30,580 (2300)	34,360 (3060)	37,590 (3550)	
[NiBr ₄] ²⁻	[(C ₄ H ₉) ₄ N] ₂ NiBr ₄ in KBr disk, solid	28,410	30,490	34,360	38,200	
[NiBr ₄] ²⁻	NiCl ₂ (0.01-0.08 M) in (C ₄ H ₉) ₄ NBr, molten, 124°	28,450 (2520)	30,300 (2450)	34,250 (3200)		
[NiI ₄] ²⁻	NiI ₂ (0.004-0.04 M) + LiI (2.1 M) in (CH ₃) ₂ SO ₂ , molten, 128°	~19,200 (sh)	19,800 (2790)	~24,270 (sh)	25,770 (3450)	26,600 (3500)
[NiI ₄] ²⁻	NiI ₂ (0.0003-0.01 M) in (C ₆ H ₁₃) ₄ NI, molten, 122°	~18,700 (sh)	19,450 (2570)	~23,600 (sh)	25,800 (3100)	26,600 (3100)

^a (sh) means shoulder.

${}^3A_2(F)$ band of $[NiBr_4]^{2-}$, for which we get a significantly smaller value despite excellent agreement for the extinction coefficient at the band peak.

The ${}^3T_1(F) \rightarrow {}^3T_2(F)$ bands are difficult to measure although their general location is well established.^{5,17,19} These bands cross the lower wave number limit of our measurements, 4000 cm^{-1} , so that their coordinates are not accurately established but their location near 4000 cm^{-1} agrees with previous work.

Very little information has been published on $[NiI_4]^{2-}$. The positions of the ${}^3T_1(F) \rightarrow {}^3A_2(F)$ and ${}^3T_1(P)$ bands, reported by Goodgame, *et al.*,⁹ for crystalline $(n-Bu_4N)_2[NiI_4]$, and a solution of this compound in nitromethane with excess iodide ions, agree well with our data, but the band intensities obtained from nitromethane solutions are much lower. However, as these authors pointed out, complexation of nickel(II) by iodide in nitromethane was probably incomplete as evidenced by the presence of a spurious band near 8300 cm^{-1} that was probably associated with a solvated species. This spurious band is absent in our spectra. Oscillator strengths for the iodo complex have not been reported previously.

A number of weak bands and shoulders are given in Table I. Most of these are attributed to spin-forbidden absorptions and will be discussed later. A number of these bands have also been reported by Goodgame, *et al.*,⁹ to occur in the spectra of crystalline tetrahalonickelate(II) salts.

Charge-Transfer Spectra.—Table III and Fig. 2 give the charge-transfer spectra of tetrahedral tetrahalonickelate(II) ions over substantial energy ranges. Beer's law was verified over the listed concentration ranges of nickel(II) halides in Table III for those peaks whose molar extinction coefficients are given. The spectrum of crystalline tetra-*n*-butylammonium tetrabromonickelate(II) is given to provide a check on the corresponding solution spectra.

The only previous datum on the charge-transfer bands of the tetrahedral tetrahalonickelate(II) ions is for the lowest-energy band in the spectrum of the iodo complex. Goodgame, *et al.*,⁹ reported this band for crystalline tetra-*n*-butylammonium tetraiodonickelate(II) to be at 19,230 or 19,420 cm^{-1} , depending on the method of measurement. This agrees well with our measurements. Previous attempts^{8,9} to measure the intensity of this band in nitromethane as the solvent gave values that are much too low compared to our results. As evidenced by the ligand-field spectra presented previously, formation of the iodo complex in this solvent was not complete.

Discussion

Ligand-Field Spectra.—The spectra reported here prove to be good examples for exploring the utility and limitations of four-parameter ligand-field theory¹¹ as a basis for rationalizing the band energies of complexes of approximately cubic symmetry in liquid media. A complete test requires explicit account of spin-forbidden transitions, which will be attempted for the first time for tetrahalonickelate(II) ions in this paper. Two- or three-parameter models are generally used to analyze the spectra of complexes in liquid media but, as pointed out by Goodgame, *et al.*,⁹ are inadequate for the quantitative treatment of tetrahedral nickel(II) complexes. In the following discus-

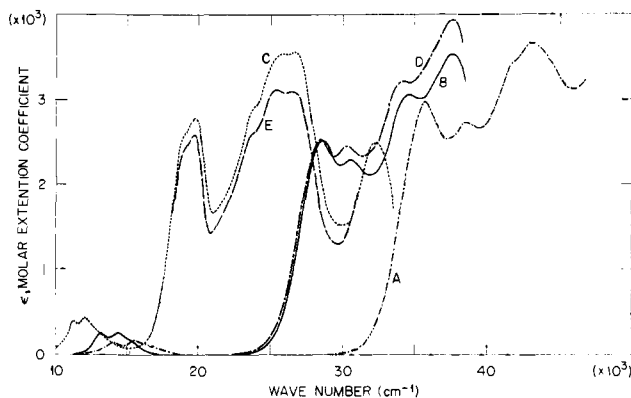


Fig. 2.—Charge-transfer spectra of tetrahalonickel(II) complexes in molten organic solvents. The weak bands in the 10,000–16,000 cm^{-1} range are the most intense ligand-field absorptions; (A) $[NiCl_4]^{2-}$ in molten dimethyl sulfone at 128° containing 0.002–0.03 M $NiCl_2$ + 1.6 M $LiCl$; (B) $[NiBr_4]^{2-}$ in molten dimethyl sulfone at 128° containing 0.002–0.008 M $NiBr_2$ + 2.1 M $LiBr$; (C) $[NiI_4]^{2-}$ in molten dimethyl sulfone at 128° containing 0.004–0.04 M NiI_2 + 2.1 M LiI ; (D) $[NiBr_4]^{2-}$ in molten tetra-*n*-butylammonium bromide at 124° containing 0.01–0.08 M $NiCl_2$; (E) $[NiI_4]^{2-}$ in molten tetra-*n*-hexylammonium iodide at 122° containing 0.0003–0.01 M NiI_2 .

sion on the four-parameter model, λ is chosen to specify spin-orbit coupling, Racah's B and C parameters to specify electron correlation, and Dq to specify the cubic field.

From the outset we can recognize several limitations in the application of four-parameter theory to the reported spectra. First, as Liehr has pointed out,²⁰ there are inherent limitations in ligand-field theory. One manifestation of these inherent limitations deserves special attention. The 1G_4 level in the spectrum of free nickel(II) is incorrectly predicted by the Slater-Condon-Shortly theory to lie about 1400 cm^{-1} below its measured position. Consequently, errors of similar magnitude may be expected in the prediction of levels derived from this component in weak ligand fields. Thus, there is unavoidable uncertainty in the assignment of these bands, and they are not suitable for fixing ligand-field parameters.

Second, the broad absorption in or near the visible region, associated with the ${}^3T_1(F) \rightarrow {}^3T_1(P)$ orbital transition, is split into component bands either by ground-state distortions from regular cubic geometry or by Jahn-Teller instability in the excited states.²¹ The four-parameter model cannot cope with such behavior, and this band will have to be treated as though it were not split.

Third, fine structure associated with spin-orbit splitting is unobserved so that λ is known primarily through its effect on the separation of the E and T_2 components of the 1D term and secondarily through its effect on the position of the ${}^3T_1(F)$ levels. It turns out that only one component of 1D is accurately fixed by experiment. Identification of the other component from the spectra involves uncertainties so that λ can be specified only in a very approximate way. Consequently, the other three ligand-field parameters, which are mildly coupled to λ , can be specified only within ranges of values. The calculations described below will show that this limitation is not serious

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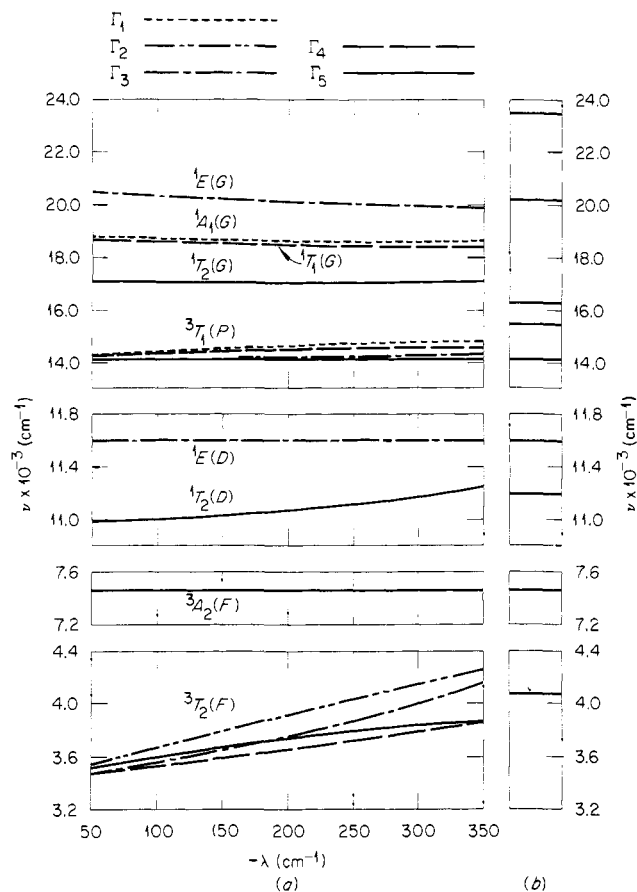


Fig. 3.—(a) Computed energy levels of the d^8 -configuration in a tetrahedral field as functions of the spin-orbit parameter when the $\Gamma_5: {}^3A_2(F)$, $\Gamma_3: {}^1E(D)$, and $\Gamma_5: {}^3T_1(P)$ levels are constrained to have the energies 7460, 11,600, and 14,160 cm^{-1} , respectively, relative to $\Gamma_1: {}^3T_1(F)$ at zero. Calculations are based on the Liehr-Ballhausen secular determinants. (b) Observed bands for $[\text{NiCl}_4]^{2-}$ in molten dimethyl sulfone. A weak shoulder near 12,600 cm^{-1} is not shown.

as long as one is comparing parameters for quite different complexes [tetrachloronickelate(II) *vs.* tetrabromonickelate(II), for example]. However, it does limit very seriously the validity of evaluating small effects, such as solvent effects, in terms of ligand-field theory.

In a previous analysis of tetrahalonickelate(II) spectra, Goodgame, *et al.*,⁹ fitted two transitions to obtain Dq and B by using plausible values of λ and the C/B ratio. As will be shown, their choices of λ and C/B for the chloro and bromo complexes prove to be quite good.

The four-parameter model for nd^2 - and nd^8 -configuration shells has been derived by Liehr and Ballhausen.¹¹ It consists of five secular equations that yield eigenvalues and eigenvectors of twenty electronic states as functions of the four ligand-field parameters. The F_2 and F_4 parameters used in these equations are related to the parameters B and C through the expressions $B = F_2 - 5F_4$ and $C = 35F_4$.

In principle, the joining of theory with experimental data could be accomplished in many ways. The procedure followed here is particularly suitable for dealing with the special problems presented by solution spectra. Three bands are selected as experimentally reliable and assigned to three of the nineteen transitions from the ground state predicted by theory.

At a fixed value of λ the Liehr-Ballhausen secular equations are solved subject to the condition that the computed energies of the three assigned transitions equal the measured energies of the three bands. The solution yields values of the other three ligand-field parameters, Dq , B , and C , and energies of the sixteen unassigned transitions. This procedure is carried through over a range of λ -values and plots are made of the sixteen transition energies as functions of λ . The unassigned bands are matched against these plots to give the most plausible assignments and, for the chloro complex, an approximate value of λ .

In discussing these band assignments, Bethe's symbols, Γ_i , will be used to give the spin-orbit representation and will be followed by Mulliken's notation for the orbital representation. The free-ion term from which a state is derived in the weak-field limit is given in parentheses. Thus, the ground electronic state of nickel(II) in a tetrahedral field will be denoted $\Gamma_1: {}^3T_1(F)$. The three fixed assignments used with the present spectra are the following: The band labeled ${}^3A_2(F)$ in Table I is assigned to $\Gamma_1: {}^3T_1(F) \rightarrow \Gamma_5: {}^3A_2(F)$; the lowest-energy component of the band group labeled ${}^3T_1(P)$ in Table I is assigned to $\Gamma_1: {}^3T_1(F) \rightarrow \Gamma_5: {}^3T_1(P)$; and one of the bands in the 1D region is assigned to one of the two transitions $\Gamma_1: {}^3T_1(F) \rightarrow \Gamma_5: {}^1T_1(D)$ or $\Gamma_3: {}^1E(D)$. For this third assignment, that of a 1D band, there are several choices for tetrachloronickelate(II) spectra, but calculations showed that the assignment described by Fig. 3, and discussed below, gave by far the best fit between theory and experiment.

Calculations using the Liehr-Ballhausen secular equations were carried out on a CDC 1604 computer. Eigenvalues and transition energies were derived by a standard matrix-diagonalization procedure. The more difficult task of adjusting parameters so that computed energy levels fitted measured spectral bands was coded for us by H. W. Joy of this laboratory.

All of the numerical values cited below for tetrahalonickelate(II) apply to dimethyl sulfone solutions unless otherwise stated.

Results of the best assignment of the tetrachloronickelate(II) spectrum are presented in Fig. 3. On the whole the theory rationalizes the spectrum quite well. The ${}^3T_1(F) \rightarrow {}^3T_2(F)$ transitions occur at the right place, and the weak bands at about 11,200 and 11,600 cm^{-1} are quantitatively accounted for as the $\Gamma_1: {}^3T_1(F) \rightarrow \Gamma_5: {}^1T_2(D)$, and $\Gamma_3: {}^1E(D)$ transitions, respectively. The shoulder centered near 20,300 cm^{-1} is clearly a transition to a 1G state. It lies close to the predicted $\Gamma_3: {}^1E(G)$ level but, as noted above, theory is expected to underestimate the positions of the 1G bands by a sizable amount. The absence of any observable weak bands below 20,300 cm^{-1} provides no evidence because intense absorption from the very broad ${}^3T_1(F) \rightarrow {}^3T_1(P)$ band prevails in this region. Two very weak bands, at 12,600 and 23,500 cm^{-1} , are unaccounted for, and we shall discuss them after presenting the analyses of the spectra of the bromo and iodo complexes.

The dependence of Dq and B on λ , given in Fig. 4, is substantial and illustrates an inadequacy in the standard two- and three-parameter models when applied to the tetrahalonickelate(II) ions. (In the latter models, λ is set equal to zero.) For the chloro complex, λ is estimated to be $-275 \pm 50 \text{ cm}^{-1}$ by fitting

the observed bands to the λ -dependent energy levels in Fig. 3. This may be compared with the value of about -305 to -320 cm^{-1} previously²² determined for $[\text{NiF}_6]^{4-}$ in crystals at low temperatures. With this estimate of λ , corresponding values of the other parameters for the chloro complex may be deduced: $Dq = 354 \pm 10$ cm^{-1} , $B = 734 \pm 6$ cm^{-1} , and $C/B = 3.96 \pm 0.02$ where the uncertainty limits are defined by the uncertainty in λ . The C/B ratio is not far from the free-ion value of 3.896.²⁰ The set of transition energies listed in Table IV is computed by substituting these values of ligand-field parameters for the chloro complex into the Liehr-Ballhausen secular equations.

TABLE IV
CALCULATED ELECTRONIC ENERGY LEVELS OF
TETRAHALONICKEL(II) COMPLEXES^a

Orbital level	Γ	Energy (cm^{-1})		
		NiCl_4^{2-} ($\lambda = -275$, $Dq = 354$, $B = 734$, $C/B = 3.96$)	NiBr_4^{2-} ($\lambda = -275$, $Dq = 332$, $B = 680$, $C/B = 3.88$)	NiI_4^{2-} ($\lambda = -275$, $Dq = 331$, $B = 537$, $C/B = 5.51$)
${}^3T_1(F)$	1	0	0	0
	4	330	320	320
	3	890	870	870
	5	1110	1100	1090
	4	3760	3570	3590
${}^3T_2(F)$	5	3820	3620	3630
	3	3940	3760	3770
	2	4090	3900	3920
${}^3A_2(F)$	5	7460*	7050*	7050*
${}^1T_2(D)$	5	11,140	10,290	9880
${}^1E(D)$	3	11,600*	10,690*	10,000*
${}^3T_1(P)$	5	14,160*	13,200*	11,350*
	3	14,230	13,270	11,550
	4	14,540	13,570	11,480
	1	14,730	13,760	11,660
	5	17,050	15,780	14,860
${}^1T_1(G)$	4	18,460	17,080	16,030
${}^1A_1(G)$	1	18,600	17,210	16,160
${}^1E(G)$	3	19,990	18,540	17,750
${}^1A_1(S)$	1	40,250	37,020	36,150

^a The complexes were treated as rigorously T_d ; Dq , B , and C/B were chosen by fixing λ and adjusting the starred levels to fit bands observed in spectra obtained with dimethyl sulfone as solvent.

Results for tetrabromonickelate(II) are given in Fig. 4b and Table IV and are quite similar to the results for the chloro analog. All observed absorptions are well accounted for except the weak shoulder near 21,700 cm^{-1} , which will be commented on later. As before, C/B is almost independent of λ and quite close to the free-ion value.

Results for tetraiodonickel(II) complex ion are set forth in Fig. 4c and Table IV. Only a single indistinct band is observed in the 1D region, but the two transitions expected in this region are computed to have almost identical energies as indicated in Table IV. (The slight discrepancy between computed and observed energies for the $\Gamma_1: {}^3T_1(F) \rightarrow \Gamma_5: {}^3T_1(P)$ transition is of no physical consequence, and resulted from making a short cut in what otherwise would have been a very expensive calculation.) The band near 14,900 cm^{-1} fits the calculated energy of the $\Gamma_1: {}^3T_1(F) \rightarrow \Gamma_5: {}^1T_2(G)$ transition, while the three higher-energy transitions to states derived from 1G are enveloped by the strong

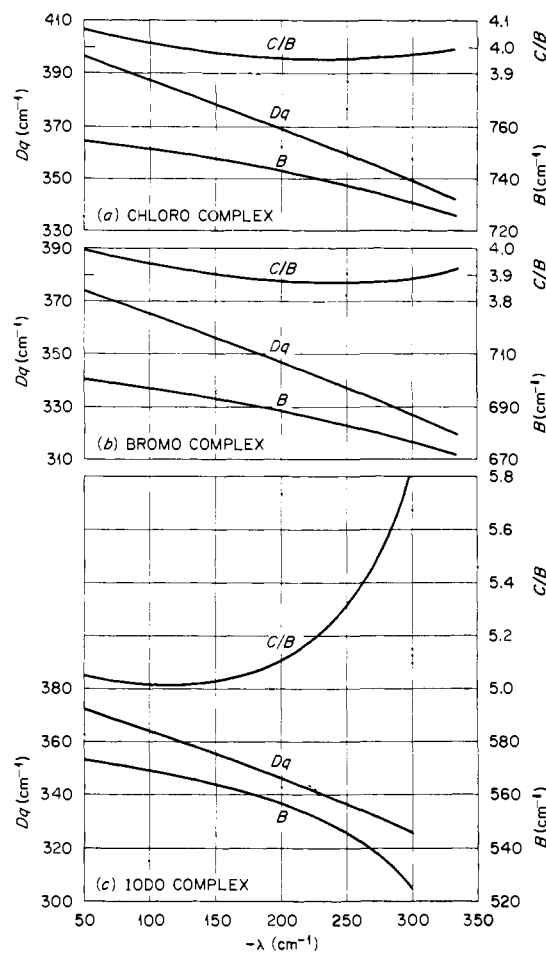


Fig. 4.— Dq , B , and C/B as functions of the spin-orbit coupling parameter when the $\Gamma_5: {}^3A_2(F)$, $\Gamma_3: {}^1E(D)$, and $\Gamma_5: {}^3T_1(P)$ levels, respectively, are constrained to fit observed bands as follows: (a) 7460, 11,600, and 14,160 cm^{-1} for $[\text{NiCl}_4]^{2-}$; 7050, 10,690, and 13,200 cm^{-1} for $[\text{NiBr}_4]^{2-}$; and 7060, 10,000, and 11,340 cm^{-1} for $[\text{NiI}_4]^{2-}$.

charge-transfer absorption edge. The iodo and bromo complexes have essentially the same value of Dq . To some extent this is a consequence of the fact that the ${}^3T_1(F) \rightarrow {}^3A_2(F)$ transitions for both complexes were found to have the same energy.

The only simple trend observed for the ligand-field parameters is an increasing nephelauxetic displacement over the series of ligands from chloride through iodide. This trend is largely responsible for the progressive shift of the prominent ${}^3T_1(F) \rightarrow {}^3T_1(P)$ band groups.

As previously mentioned, three weak bands are unaccounted for by the above analysis. They are at about 12,600 and 23,500 cm^{-1} for $[\text{NiCl}_4]^{2-}$, and 21,500 to 21,800 cm^{-1} (depending on the medium) for $[\text{NiBr}_4]^{2-}$. The latter band was observed in our crystal spectrum as well as solution spectra and has also been reported by Goodgame, *et al.*,⁹ to be at 21,000 cm^{-1} for a crystal spectrum. The 23,500 cm^{-1} band in $[\text{NiCl}_4]^{2-}$ is extremely weak.

Possibly these are bands of equilibrium "contaminant" nickel(II) species. For example, the bands above 20,000 cm^{-1} could be the ${}^3A_2(F) \rightarrow {}^3T_1(P)$ transitions of trace amounts of octahedral hexahalonickelate(II) ions, and the 12,600 cm^{-1} shoulder could be a ${}^3A_2(F) \rightarrow {}^3T_1(F)$ band of this same "impurity." This would be in keeping with the supposi-

tion that $|Dq_{\text{octa}}|$ is somewhat more than twice as large as $|Dq_{\text{tetra}}|$. Opposed to this explanation, although not definitively opposed, are the occurrence of the 21,500 cm^{-1} band in crystals of tetrabromonickelate(II) and the observation⁶ that the ${}^3A_2(F) \rightarrow {}^3T_1(F)$ and ${}^3T_1(P)$ bands of nickel(II)-doped, hexagonal CsCdCl_3 occur substantially below the positions of the unidentified bands in the $[\text{NiCl}_4]^{2-}$ spectrum. Note, however, that interpretation of the $\text{CsCdCl}_3\text{-Ni(II)}$ spectrum is complicated by an unexpected splitting of the ${}^3A_2(F) \rightarrow {}^3T_1(P)$ band.

It is also possible that the bands above 20,000 cm^{-1} are transitions to the ${}^1E(G)$ levels of $[\text{NiX}_4]^{2-}$ and that theory makes an extremely poor prediction of their positions. Clearly, there is a need for very careful experiments and additional theoretical analysis of the high-energy part of the ligand-field spectrum. The chloro complex is particularly suitable for this purpose because the lowest-energy charge-transfer band lies far above the highest-energy spin-allowed ligand-field band.

Attempts to assign the 12,600 cm^{-1} band to ${}^3T_1(F) \rightarrow {}^1E(D)$ lead to poor agreement between theory and experiment and a large value of the C/B ratio.

Charge-Transfer Spectra.—The intense ultraviolet bands of simple complexes are of special chemical interest because of the anticipation that they will become a basic source of information on bonding electrons. Present understanding of these absorptions is quite primitive, and the available data on simple complexes, while growing rapidly, are still sparse.

Group-theoretical analysis of one-electron transitions, based on the linear combination of atomic orbitals—molecular orbital (LCAO—MO) model, does not lead to an unambiguous assignment of the spectra reported here except for the lowest-energy transition. It proves reasonable to attribute this transition to an electron jump from a filled orbital of symmetry species t_1 into the partly filled t_2 orbital. The t_1 -orbital has π -type two-center symmetry and is nonbonding in ligand-metal directions in the LCAO—MO model that does not use orbitals of the central atom above 4p.

Jørgensen¹² proposed the concept of optical electronegativities as a basis for relating charge-transfer spectra to one-electron energy levels. When the optical electronegativity of nickel(II) relative to the t_1 -orbital is estimated from the lowest-energy charge-transfer bands as reported here, the value obtained fits well with Jørgensen's correlations.²³

The basic relation in the optical-electronegativity concept is given by

$$\nu_{\text{cor}} = 3 \times 10^4(x_{\text{opt}}[\text{X}] - x_{\text{opt}}[\text{M}]) \quad (1)$$

where $x_{\text{opt}}[\text{X}]$ and $x_{\text{opt}}[\text{M}]$ are optical electronegativities of the ligands, X, and the central atom, M, respectively (the conversion factor from the Pauling electronegativity scale to the wave number scale is 3×10^4) and ν_{cor} is a transition energy obtained by correcting the observed transition energy, ν_{obsd} , for energetic effects in the d-shell.

The relation between ν_{obsd} and ν_{cor} , when the electron jumps into the higher of the two d-subshells, is given by

$$\nu_{\text{cor}} = \nu_{\text{obsd}} - 10Dq + D[\langle S(S+1) \rangle - S(S+1)] \quad (2)$$

where Dq is the ligand-field parameter; D is the spin-pairing energy parameter, obtained from ligand-field spectra with the aid of eq. 3; and S is the total spin quantum number for the central atom. The term $-10Dq$ corrects for the orbital energy difference between the two d-subshells, t_2 and e , and is used in this relation only when the jump is into the higher subshell. For electrons in the d-shell, the spin-pairing energy parameter, D , is given by

$$D = (7/6)[(5/2)B + C] \quad (3)$$

where B and C are Racah's electron-correlation parameters, which were evaluated for tetrahalonickelate(II) ions in a preceding section. Jørgensen¹² has tabulated values of $[\langle S(S+1) \rangle - S(S+1)]$. In the present case the value is -0.66 .

For ν_{obsd} , we use the band maxima of the lowest-energy charge-transfer transitions in the case of $[\text{NiCl}_4]^{2-}$ and $[\text{NiBr}_4]^{2-}$ and the average of the two components of the lowest-energy band in the case of $[\text{NiI}_4]^{2-}$. To compute ν_{cor} , values of Dq , B , and C are taken from Table IV. The computation of optical electronegativities is summarized in Table V. In order to show more clearly the relative importance of the various terms, energy values are given in Pauling units ($3 \times 10^4 \text{ cm}^{-1}$).

TABLE V
OPTICAL ELECTRONEGATIVITIES OBTAINED FROM CHARGE-TRANSFER SPECTRA (ALL QUANTITIES ARE IN PAULING UNITS OF $3 \times 10^4 \text{ CM}^{-1}$)

Complex	ν_{obsd}	$10Dq$	$(7/3)D$	ν_{cor}	$x_{\text{opt}}[\text{X}]^a$	$x_{\text{opt}}[\text{Ni(II)}]$
$[\text{NiCl}_4]^{2-}$	1.19	-0.12	-0.12	0.95	3.0	2.1
$[\text{NiBr}_4]^{2-}$	0.95	-0.11	-0.11	0.73	2.8	2.1
$[\text{NiI}_4]^{2-}$	0.65	-0.11	-0.11	0.43	2.5	2.1

^a Ref. 23.

The value of $x_{\text{opt}}[\text{Ni(II)}]$ is independent of the complex to within the low precision that must be expected with this approximate concept. The value 2.1 fits well with Jørgensen's correlations.²³

Assignment of the higher-energy charge-transfer bands should be aided greatly by a search for empirical regularities in the spectra of a variety of related halo complexes. This approach has been adopted by Jørgensen²⁴ in his study of the charge-transfer spectra of hexahalo complexes of elements in the fifth and sixth periods. Such a search is necessarily beyond the bounds of the present paper and will be reserved for future reports.

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