

Cl→F charge-transfer state with ground electronic state in the magnetic field.¹⁹

It is somewhat surprising that no Pd-F coupling was detected in the nmr spectra. Using the parallelogram rules of Reeves²⁰ and the coupling constant for the PtF₆²⁻ ion, we would predict a $J_{\text{Pd-F}}$ value of ~100 Hz in PdF₆²⁻. It is unlikely that chemical exchange of the F⁻ ion would cause collapse of the spin-spin multiplets because the line width and chemical shift data show that all of the MF₆²⁻ ions studied here are nonlabile.

It is possible that the spin-spin interaction is "washed out" *via* the quadrupolar relaxation of the Pd nucleus by electric field gradients (due, for example, to ion-pair formation). The effectiveness of such relaxation depends not only on the field gradient but also on the size

of the electric quadrupole moment. For example, M-F spin-spin multiplets can be distinguished in the ¹⁹F nmr spectra of the NbF₆⁻ ion in HF where the ⁹³Nb resonance is also observable, but not in the spectra of the TaF₆⁻ ion where the ¹⁸¹Ta resonance is too broad to be detected.¹² Both ⁹³Nb and ¹⁸¹Ta are 100% abundant, but the electric quadrupole moment of ¹⁸¹Ta (~3 barns²¹) is more than an order of magnitude larger than that of ⁹³Nb (~-0.2 barns²²). The magnitude of the ¹⁰⁵Pd quadrupole moment apparently has not been measured. Roughly speaking, it must be at least as large as the ⁹³Nb quadrupole moment, if the quadrupolar interaction is responsible for the collapse of the multiplets. An experiment on Pd metal at low temperatures yielded an anomalously large spin-lattice relaxation rate.²³ This could be due to a large quadrupole moment of ¹⁰⁵Pd. An upper limit to the moment of ~4 barns was estimated in the latter experiments and it is not inconsistent with our provisional lower limit.

(19) It seems clear that a number of electronic states contribute to the chemical shifts of these systems. As noted by Dean and Evans,¹³ the ordering of the ¹⁹F shifts for the d⁹ and d¹⁰ M(IV) ions in Table IV is not that expected from simple electronegativity considerations. They suggest that the *low-field shift* for the d⁹ ions is due to the mixing of the fluorine p and the metal ion d orbitals in the magnetic field.

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The Electronic Spectrum of the Hexafluoronickelate(IV) Anion

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The electronic spectrum of the hexafluoronickelate(IV) anion has been studied by diffuse reflection in Na₂NiF₆ and K₂NiF₆ between 4 and 45 kK. The weak absorptions at 12.9 and 16.0 kK and the stronger bands at 19.0 and 25.3 kK are assigned, respectively, to d-d transitions from a ¹A_{1g}(t_{2g}⁶) ground state to ³T_{1g}, ³T_{2g}, ¹T_{1g}, and ¹T_{2g}(t_{2g}⁵e_g) states, and the intense bands at 30.8 and 38.9 kK, to π → e_g excitations. The broad band at 19.0 kK shows marked vibrational fine structure which is attributed to the superposition of a symmetric α_{1g} progression on the vibronically (τ_{1u}) allowed transition. Least-squares fitting of the d-d bands using the full Tanabe and Sugano strong-field matrices yields $Dq = 2010 \text{ cm}^{-1}$, $B = 515 \text{ cm}^{-1}$, and $\beta = 0.43$. The degree of covalency indicated, although exceptionally high for a fluoride complex, is not unexpected in view of the large formal charge on the metal.

Introduction

The fluoride complexes of transition metals exhibit several features of interest in their spectra. They are usually less nephelauxetic even than aquo ions (indicating a smaller tendency toward covalent bonding), and the Laporte-forbidden d-d transitions are not so often masked by allowed charge-transfer bands as in many other complexes. Furthermore, they frequently represent high and unusual oxidation states of the metals involved.

This latter feature is exemplified in potassium hexafluoronickelate(IV), K₂NiF₆, which was first obtained by Klemm and Huss¹ by the action of

fluorine on a 2:1 mixture of KCl and NiCl₂ at 275°. The rubidium salt was shown by Bodo and Voss² to have a regular cubic structure, and the potassium salt by Hoppe^{3a} (who also reported, without discussion, a rough spectrum^{3b}) to be diamagnetic and therefore to have a low-spin t_{2g}⁶ ground state. The measurement of the detailed electronic spectrum has hitherto been hindered by the extreme reactivity of the materials, but Professor R. Hoppe has kindly supplied us with samples of both Na₂NiF₆ and K₂NiF₆ sealed under vacuum in our silica cells, and their diffuse reflectance spectra are now reported.

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Experimental Section

Sodium and Potassium Hexafluoronickelate(IV).—These were prepared by Dr. H. Henkel of the University of Giessen and supplied to us by courtesy of Professor R. Hoppe.

Diffuse Reflectance Measurements.—The diffuse reflectance spectra of the salts were measured at room temperature for the frequency range 4–45 kK using a Beckman DK-2A spectroreflectometer with magnesium oxide as reference. Microscopic examination showed the samples to have an average particle size of $20 \pm 5 \mu$. The intensities are expressed in terms of the Kubelka-Munk function, F_R , defined by $F_R = (1 - R_{diff})^2 / 2R_{diff} = k/s$, where $R_{diff} = I/I_{std}$ is the relative diffuse reflectance referred to a nonabsorbing standard, k is the absorption coefficient defined by $I = I_0 e^{-ks}$, and s is the scattering coefficient for the substance in question. Values of ϵ , the extinction coefficient, were obtained using the relationship $F_R = \epsilon c / 0.434s$, where c = density/molecular weight.

Results

The diffuse reflectance spectra of the hexafluoronickelate(IV) complexes are listed in Table I, and a typical spectrum is shown in Figure 1. As expected, the spectra of the sodium and potassium salts are virtually identical. In both compounds a broad band of medium intensity, showing pronounced vibrational fine structure, is observed at about 19 kK, and another peak of comparable strength appears at 25.3 kK as a shoulder to a higher energy charge-transfer transition. In addition, a very weak peak is found at 12.9 kK together with a shoulder on the low-energy side (ca. 16 kK) of the 19-kK band. These are assigned to Laporte-forbidden d-d transitions, and the intense broad bands at 30.8 and 38.9 kK are assigned to allowed charge-transfer excitations. Within the band at 19 kK, ten vibrational levels with a regular spacing of $490 \pm 50 \text{ cm}^{-1}$ can be distinguished.

Discussion

The occurrence of *two* fairly strong d-d transitions immediately provides confirmation of the low-spin t_{2g}^6 ground state deduced from magnetic data, since, for a high-spin d^6 complex only one spin-allowed transition is permitted. On the basis of the Tanabe and Sugano⁴ treatment, therefore, the bands at 19.0 and 25.3 kK are assigned to transitions from ${}^1A_{1g}(t_{2g}^6)$ to ${}^1T_{1g}$ and ${}^1T_{2g}(t_{2g}^5e_g)$, respectively. The much weaker band at 12.9 kK can thus be assigned to the ${}^3T_{1g}$ state, and the shoulder at 16 kK, to the ${}^3T_{2g}$ level.

The broad band at 19.0 kK has a half-height width of some 2.5 kK, but the extensive vibrational fine structure enables a rough estimate of the position of the 0-0 band to be made. As with all d-d transitions in complexes of O_h symmetry, the band owes its origin to vibronic coupling, most probably involving the ν_4 , τ_{1u} vibrational mode, which was found by Peacock and Sharpe⁵ at 654 cm^{-1} . However, the regular spacing of the fine structure is typical of a progression in the symmetric α_{1g} mode and can most readily be interpreted

TABLE I
THE DIFFUSE REFLECTANCE SPECTRA
OF Na_2NiF_6 AND K_2NiF_6

Band position, kK		Assignment	ϵ^b	f^b
Obsd	Calcd ^a			
12.9	13.0	${}^1A_{1g} \rightarrow {}^3T_{1g}$	1.1	3.5×10^{-6}
16.0	16.4	${}^1A_{1g} \rightarrow {}^3T_{2g}$	2.4	1.1×10^{-5}
19.0 ^c	18.4	${}^1A_{1g} \rightarrow {}^1T_{1g}$	107	1.1×10^{-3}
25.3	25.4	${}^1A_{1g} \rightarrow {}^1T_{2g}$	97	1.3×10^{-3}
30.8	...	$\pi \rightarrow e_g$	Strong	...
38.9	...	$\pi \rightarrow e_g$	Strong	...

^a Using $Dq = 2010 \text{ cm}^{-1}$ and $B = 515 \text{ cm}^{-1}$. ^b Obtained using curves derived by Gaussian analysis. ^c Vibrational fine structure: 17.09 (sh), 17.64 (sh), 18.18, 18.62, 19.08, 20.00, 20.47 (sh), 20.94 (sh), 21.41 (sh) kK.

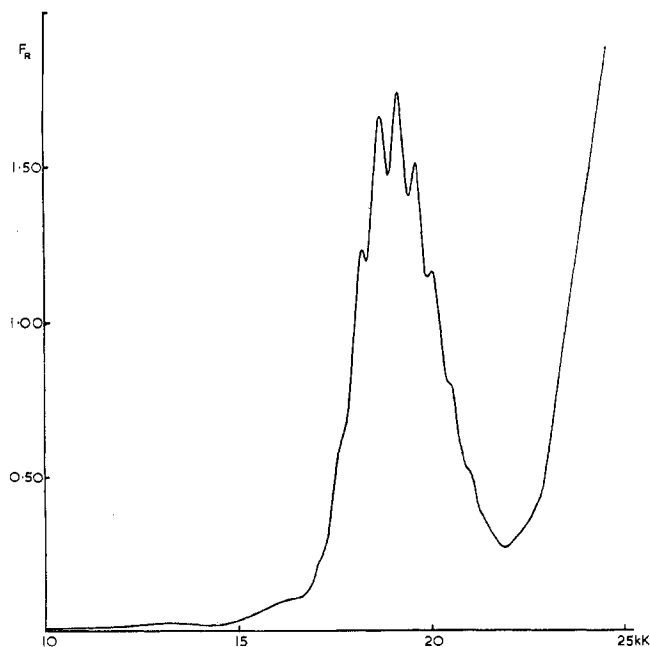


Figure 1.—The diffuse reflectance spectrum of potassium hexafluoronickelate(IV).

as being due to the superposition of this progression on the τ_{1u} vibronic transition. There can of course be no certainty as to the position of the origin of the progression, but this is unlikely to lie at higher energies than the maxima at 18.62 and 19.08 kK. If, as usual, the (1, 0) τ_{1u} vibronically excited state makes the major contribution to the band intensity, then the 0-0 transition must lie not higher than about 18.0–18.4 kK. An alternative explanation of the fine structure in terms of sequences based on the (1, 0) and (0, 1) τ_{1u} vibronic states is also possible, but leads to an unrealistically low value for $\nu_4(\text{ex})$, τ_{1u} , whereas the assumption of $\nu_1(\text{ex})$, $\alpha_{1g} = 490 \text{ cm}^{-1}$ is consistent with the observed⁵ value of $\nu_4(\text{g})$, τ_{1u} and accords well with the observation⁶ of the Raman-active $\nu_1(\text{g})$, α_{1g} mode at 560 cm^{-1} . The disparity between these ν_1 values arises from the reduction of the force constants in the excited state,

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due to the increased occupation of the e_g antibonding levels. It is also unlikely that Jahn-Teller distortion need be considered in interpreting the band: the ground state is a closed-shell ${}^1A_{1g}$ level, and in the excited $t_{2g}{}^5e_g$ states the hole in the t_{2g} shell and the electron in the e_g shell may well lead to compensating distortion tendencies.

It is, however, of interest to consider why vibrational fine structure should be found within the ${}^4T_{1g}$ band, since it is only rarely observed for transition metal complexes. Clearly all transitions from the ${}^1A_{1g}$, $t_{2g}{}^6$ ground state must involve the removal of electrons from t_{2g} orbitals, which are most often either non-bonding or weakly π bonding to the e_g antibonding level. This will be accompanied by a lowering of the force constants of the metal-ligand bonds, which should therefore lengthen, giving rise to progressions in the symmetric stretching frequency. Normally though, this structure will tend to be obscured, for a variety of reasons, for example, Jahn-Teller distortions, the superposition of sequences, spin-orbit coupling, the low vibrational frequencies involved, and so on, but it is noteworthy that the cases in which it is found are confined to high oxidation states of the metals concerned, when associated with strongly electronegative ligands. This is to be expected since the superposition of the α_{1g} progression will result in changes in polarizability which may lead to an increase in the transition moment of the τ_{1u} vibronic transition, and such an effect should be most marked in complexes of metals bearing high formal positive charges. Thus vibrational structure of this type is observed^{7,8} for PtF_6 and ReF_6 , and in $OsCl_6^{2-}$ and $ReCl_6^{2-}$, and our own preliminary results⁹ indicate it to be present for Co^{4+} in CoF_6^{2-} but absent for Ni^{3+} in NiF_6^{3-} . Likewise, no vibrational structure was found¹⁰ for CoF_6^{3-} or¹¹ for CrF_6^{3-} , although it has been found¹¹ for FeF_6^{3-} and reported absent¹² for MnF_6^{2-} .

Despite a careful search, we were unable to find any evidence of fine structure in the ${}^1T_{2g}$ band at 25.3 kK. It is not entirely clear why this should be so, although the transition could well be blurred by intensity stealing from the allowed charge-transfer band at 30.8 kK which partially obscures it. The ${}^3T_{2g}$ transition appears only as a weak shoulder, and the ${}^3T_{1g}$ band at 12.9 kK is also so weak as to eliminate the possibility of detecting fine structure. Both the ${}^3T_{1g}$ and ${}^3T_{2g}$ bands should, however, be split by spin-orbit coupling, into $\Gamma_1, \Gamma_3, \Gamma_4, \Gamma_5$ and $\Gamma_2, \Gamma_3, \Gamma_4, \Gamma_5$, respectively, but it is readily shown, using the proportionality constants of Griffith,¹³ that the total splitting in the strong-field limit should be only $3/4\xi$. The value of ξ for Ni^{4+}

is not known, but a rough extrapolation from Griffith's¹³ data gives $\xi = 750 \text{ cm}^{-1}$, which predicts a splitting of about 560 cm^{-1} , which is consistent with the band width observed.

We determined the crystal field splitting parameter, Dq , the Racah interelectronic repulsion parameter, B , and the nephelauxetic ratio, β , by least-squares fitting of the bands using the full Tanabe-Sugano strong-field matrices. In principle, both β_{35} and β_{55} should be required to fit the bands since, although the energies of ${}^1T_{1g}$, ${}^1T_{2g}$, and ${}^3T_{2g}$ relative to that of ${}^3T_{1g}$ depend, in the strong-field limit, only on repulsions between $t_{2g}(\Gamma_5)$ and $e_g(\Gamma_5)$ electrons, the energy of ${}^3T_{1g}$ relative to the ground state depends on both $t_{2g}-e_g$ and $t_{2g}-t_{2g}$ interactions. However, we were able to obtain a very satisfactory fit of the experimental values using only a single value of B , and it can therefore be assumed that the parameters β_{35} and β_{55} are of very much the same magnitude. Unfortunately there are no experimental spectroscopic data for Ni^{4+} in the gas phase, but we were able to estimate the required B_{gas} value as 1200 cm^{-1} by extrapolation from the data of Tanabe and Sugano. (Extrapolation from the Slater-Condon parameters of Tondello, *et al.*,¹⁴ yields $B_{\text{gas}} = 1285 \text{ cm}^{-1}$, which would give a slightly lower β value.) In the calculations we varied the ratio of the Racah parameters, C/B , from 4.8 to 5.1, since Tanabe and Sugano obtained 4.71 and 4.89 for Ni^{2+} and Ni^{3+} , respectively. In fact, the C/B ratio has very little effect on the results: the values adopted are for $C/B = 5.0$, which gives $Dq = 2010 \text{ cm}^{-1}$, $B = 515 \text{ cm}^{-1}$, and $\beta = 0.43$.

The approximate equality of the parameters β_{35} and β_{55} suggests that the extent of delocalization of the e_g electrons by σ bonding is about the same as that of the t_{2g} electrons due to π bonding, and this is borne out by a calculation of the corresponding group overlap integrals $G, t_{2g}, d\pi-p\pi$, and $G, e_g, d\sigma-p\sigma$. Taking the crystallographic value² of 1.70 \AA for the Ni-F distance, and using the SCF radial functions of Richardson, *et al.*,¹⁵ for Ni and the double- ξ functions of Clementi¹⁶ for F, we find $G, t_{2g} = 0.204$ and $G, e_g = 0.227$. Possibly this implies that both the t_{2g} and e_g levels are about equally antibonding.

The actual value of β found is the lowest yet recorded for fluoride ligands and compares with $\beta_{35} = 0.77$ for Fe^{3+} and $\beta_{35} = 0.56$ for Mn^{4+} . Clearly, the larger the formal positive charge on the metal, the greater the tendency to covalency, even with such an ionic ligand as fluoride ion, and the greater the extent of the expansion of the radial function of the metal. Applying the method of Jørgensen¹⁷ for a rough quantitative estimation of the nephelauxetic effect and assuming equal contributions from central-field and symmetry-restricted covalency indicate a ligand contribution of

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about 20% and an effective charge on the metal of only +1.6. Thus even with fluoride ligands it is to be expected that low-spin configurations, with small values of β , will be found if the oxidation state of the metal is high enough. For the 4+ oxidation state, the decreasing stability of the higher valencies toward the end of the first transition series is consistent with the β values found for Mn^{4+} and Ni^{4+} , and further confirmation is provided by our data for CoF_6^{2-} (which also has a low-spin ground state⁹). From our results for Dq and β , Jørgensen's g and k parameters can be deduced: the values are 22.3 and 0.71, respectively, compared with 23.0 and 0.50 for Mn^{4+} . Our data also substantially confirm Jørgensen's predictions¹² of the positions of the ${}^1\text{T}_{1g}$ and ${}^1\text{T}_{2g}$ bands, which were based on the general behavior of Dq and β as functions of oxidation state: his figures of 20 and 28 kK, respectively, slightly overestimate Dq but are in good agreement with the experimental β value.

On the basis of their intensities, the strong bands at 30.8 and 38.9 kK may be assigned to allowed charge-transfer transitions. It seems most likely that these are $\pi \rightarrow e_g$ excitations, corresponding to $t_{1u} \rightarrow e_g$ and $t_{2u} \rightarrow e_g$ in a molecular orbital interpretation, and the predicted absence of other spin-allowed d-d transitions below about 40 kK supports this view.

In view of the uncertainties which are usually experienced in attaching quantitative significance to intensities measured by diffuse reflectance, we have attempted to obtain approximate extinction coefficients for the d-d bands from our F_R values. In order to derive ϵ from the Kubelka-Munk function it is necessary to know s , the scattering coefficient for the given sub-

stance, at any required wavelength. Although s does not appear to vary widely from one substance to another, its dependence on wavelength is very sensitive to particle size, especially above about 25 kK. The particle size of our samples is however sufficiently small ($20 \pm 5 \mu$) to eliminate any regular reflectance component below 25 kK, so that s is essentially constant in that region, and the observed spectrum is due only to diffuse reflectance. We were therefore able to use the data of Kortum¹⁸ for KMnO_4 ($s = 1.73$) to establish an approximate value for s , up to around 25 kK, and thence to derive the values of ϵ and the corresponding oscillator strengths shown in Table I.

It is seen that the intensities of the ${}^1\text{T}_{1g}$ and ${}^1\text{T}_{2g}$ bands are of reasonable magnitude for Laporte-forbidden transitions. Similarly the ${}^3\text{T}_{1g}$ band is about as weak as would be expected for a spin-forbidden transition, and an estimate of its strength relative to the ${}^1\text{T}_{1g}$ band can be made using the spin-orbit matrix elements of Griffith.¹³ From the matrix element of ${}^1\text{T}_1$ with the T_1 component of ${}^3\text{T}_1$ [$= (1/2\sqrt{2})\xi$], we estimate that the intensity stealing of ${}^3\text{T}_{1g}$ from the ${}^1\text{T}_{1g}$ band at about 19 kK should give an oscillator strength for the former of about $1/330$ of the spin-allowed transition. The experimental value is $1/315$, but the agreement can be improved if the origin of the ${}^1\text{T}_{1g}$ band lies below 18.4 kK. Similarly the matrix element of ${}^3\text{T}_2$ with the T_1 component of ${}^1\text{T}_1$ is $(1/4\sqrt{6})\xi$ which predicts the ${}^3\text{T}_{2g}:{}^1\text{T}_{1g}$ intensity ratio to be about $1/30$. The experimental value is $1/100$, but here the calculated value is extremely sensitive to the ${}^3\text{T}_{2g} - {}^1\text{T}_{1g}$ energy difference.

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Enthalpies of Formation of Some Tungstates, MWO_4

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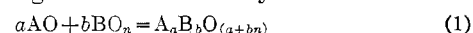
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The enthalpies of formation of the isostructural tungstates MWO_4 ($M = \text{Mg, Co, Ni, Cu, Zn, Cd}$) were determined by solution calorimetry in a $3\text{Na}_2\text{O} \cdot 4\text{MoO}_3$ melt at 970°K. Regularities in the heats of formation are compared with those observed for spinels, sulfates, and carbonates of the same cations.

Introduction

In previous communications,^{1,2} we have reported the enthalpies of formation of an extensive series of spinels. The spinel-forming reaction is but one example of the formation of a double oxide from the component acidic and basic oxides.

When one of the constituents is the oxide of a divalent cation, AO, this general reaction may be written



If the products are isostructural for a series of divalent cations and a given BO_n , regularities in the thermodynamics of reaction 1 may be related to specific properties of the divalent ions, *e.g.*, the ionic radius or the preference of the cation for a particular coordination.

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