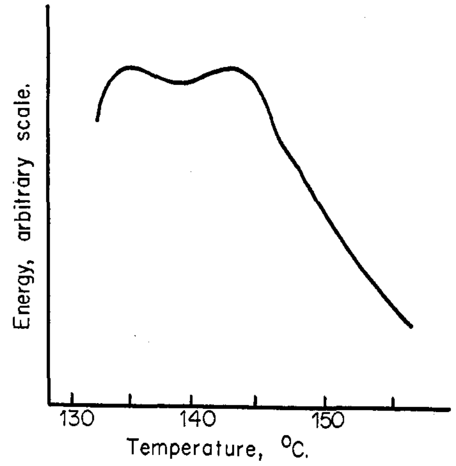

Figure 4.—Dta curve for $Ni\{(C_2H_5O)_2PS_2\}_2(py)_2$.

Table VII

Dta Data for $Ni\{(C_6F_5CH_3CHO)_2PS_2\}_2(py)_2$

Maxima, °C	Minima, °C
140	151
153–166	172
174	177
181	

leads to olefin formation. Dickert and Rowe[22] suggested that the dependence of thermal stability of metal dialkyldithiophosphates on variation of both the alkyl group structure and the size of the metal ion is related to an initial isomerization reaction, followed by an intramolecular (cis) elimination of olefin. The mass spectral data also show a ready elimination of olefin. It seems likely that isomerization and olefin elimination are responsible for the complex nature of the dta curves. This postulate is consistent with the NiS_4 chromophore being extremely stable.

Carcinostatic Activity.—Some of the metal chelates have been tested in the L-1210 lymphoid leukemia and the Walker carcinosarcoma 256 (intramuscular) tumor systems in mice. The complexes $M(dtp)_2$ (M = Ni, Pd, Pt; $R = CH_3$) are active in the Walker 256 tumor system; the palladium complex reduces the cancer to 6% relative to the control specimen under optimum conditions.

Larvicidal Activity.—Several of the metal chelates were tested for larvicidal activity against *Tineola bisselliella* with the objective of their being useful as agents for the mothproofing of wool. Of those tested only $Ni\{(ClCH_2CH_2O)_2PS_2\}_2$ has significant larvicidal activity.

Contribution from The Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-Ku, Tokyo, Japan, and The Institute of Physical and Chemical Research, Yamato Machi, Saitama, Japan

Spectroscopic Study of the Interaction between the Central Metal Ions in the Crystals of Bis(dimethylglyoximato)nickel(II) and Related Complexes

By YUKAKO OHASHI,[1a] ICHIRO HANAZAKI,[1b] and SABURO NAGAKURA*[1a]

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In the region of 160–700 nm, polarized absorption spectra were measured for single crystals of nickel and palladium dimethylglyoximes and of α- and β-nickel ethylmethylglyoximes, in addition to the visible and ultraviolet absorption spectra of the solutions. By comparing the observed transition energies and oscillator strengths in solution with the theoretical values, the 26.5- and 30.5-kK bands were ascribed to the metal-to-ligand charge-transfer transition and the 38.3-kK band was ascribed to the locally excited transition of the ligand. The crystal spectra polarized perpendicular to the c axis exhibit no remarkable change compared with those in solution. In the spectra polarized parallel to the c axis, however, two additional bands appear at 18.6 and 52.5 kK and at 20.5 and 53.6 kK for nickel dimethylglyoxime and β-nickel ethylmethylglyoxime, respectively. On the basis of the observed polarization and also of the theoretical consideration of the peak positions and oscillator strengths, the bands at ~53 and ~20 kK were interpreted to be the charge-transfer band between the neighboring nickel atoms and the $3d_{z^2} \rightarrow 4p_z$ transition band, respectively.

Introduction

According to the X-ray diffraction study,[2] the bisdimethylglyoximato complexes of nickel, palladium, and platinum (hereafter, abbreviated to $Ni(dmg)_2$, $Pd(dmg)_2$, and $Pt(dmg)_2$, respectively) have an isomorphous crystal structure in which the planar complex molecules are stacked face to face forming a column parallel to the c axis. In the crystalline state, they show sharp absorption bands polarized parallel to the column at 18.6, 21.5, and 15.1 kK for $Ni(dmg)_2$, $Pd(dmg)_2$, and $Pt(dmg)_2$, respectively. The appearance of these characteristic bands has been studied by several authors in connection with the intermolecular interactions in the crystal.[3–7]

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(1) (a) The Institute for Solid State Physics, The University of Tokyo. (b) The Institute of Physical and Chemical Research.

(2) (a) D. E. Williams, G. Wohlauer, and R. E. Rundle, *J. Amer. Chem. Soc.*, **81**, 755 (1959); L. E. Godycki and R. E. Rundle, *Acta Crystallogr.*, **6**, 487 (1953); (b) E. Frasson, C. Panattoni, and R. Zannertti, *ibid.*, **12**, 1029 (1959).

(3) S. Yamada and R. Tsuchida, *Bull. Chem. Soc. Jap.*, **27**, 156 (1954).

(4) C. V. Banks and D. W. Barnum, *J. Amer. Chem. Soc.*, **80**, 4767 (1958).

(5) J. C. Zahner and H. G. Drickamer, *J. Chem. Phys.*, **33**, 1625 (1960).

(6) G. Basu, G. M. Cook, and R. L. Belford, *Inorg. Chem.*, **3**, 1361 (1964).

(7) B. G. Anex and F. K. Krist, *J. Amer. Chem. Soc.*, **89**, 6114 (1967).

Yamada and Tsuchida[3] measured the polarization of the band and suggested the existence of a specific metal–metal interaction for Ni(dmg)$_2$ and Pt(dmg)$_2$ in the crystal. Banks and Barnum[4] found a correlation between the peak position of the characteristic band and the metal–metal distance for some *vic*-dioxime complexes of nickel and palladium and concluded that the metal electrons delocalize along the metal–metal bonds.

Zahner and Drickamer[5] studied the effect of pressure upon the band for the dimethylglyoxime complexes of nickel, palladium, and platinum and observed a large red shift with pressure increase. In view of this result, they interpreted the band to be of intramolecular nature and ascribed the shift to an electrostatic interaction. Basu, Cook, and Belford[6] found that the mixed crystal of Ni(dmg)$_2$ and Pd(dmg)$_2$ exhibits a spectrum interpretable as the superposition of the spectra of the components and, therefore, that the electron delocalization between metal ions cannot be deduced from their experiment. Recently, Anex and Krist[7] carried out a detailed experimental study on Ni(dmg)$_2$ and the related compounds and concluded that the characteristic band in the visible region is of an intramolecular nature. They observed the remarkable intensity decrease of this band with increase in the intermolecular distance and explained this tendency by the difference of the mixing ratio between the $3d_{z^2} \rightarrow 4p_z$ and $3d_{z^2} \rightarrow \pi^*$ transitions.

Under these circumstances, we have undertaken to study the π-electron structures of the dimethylglyoxime complexes from both the theoretical and experimental points of view, paying special attention to the nature of the band pertinent to the interaction between the central metal ions of the neighboring complexes.

Experimental Section

Preparation of Materials.—Commercially available special grade dimethylglyoxime and synthesized ethylmethylglyoxime were used for the preparation of the metal complexes after purification by vacuum sublimation. Special grade nickel chloride, palladium chloride, and potassium chloroplatinite were used without further purification. The metal complexes were prepared by mixing the hot alcohol solutions containing the stoichiometric amounts of a metal salt and a ligand material. They were purified by repeated recrystallizations from chloroform or nitrobenzene. α-Nickel ethylmethylglyoxime (abbreviated hereafter to α-Ni(emg)$_2$) was obtained by very slow evaporation from the nitrobenzene solution of β-Ni(emg)$_2$ which was easily prepared from the reaction in chloroform. These two crystal forms were identified by the aid of the lattice constants determined by the X-ray diffraction technique. Thin crystals used for the microspectrophotometric measurements were prepared by evaporating the solvent from the chloroform solutions for Ni(dmg)$_2$, Pd(dmg)$_2$, and β-Ni(emg)$_2$ and from the nitrobenzene solution for α-Ni(dmg)$_2$. The thin film on a quartz plate was prepared by vacuum sublimation.

Measurements.—Ultraviolet and visible absorption spectra in solution were measured by a Cary recording spectrophotometer, Model 14 M. The visible absorption spectrum of the single crystal was measured by a microspectrophotometer constructed in our laboratory.[8] Recently, a new type microspectrophotometer was constructed in our laboratory[9] for absorption measurements of single crystals in the vacuum ultraviolet region (to 1500 Å). The polarized absorption measurements in the vacuum ultraviolet region were carried out by the use of this spectrophotometer. Single crystals of ~1 mm × 0.1 mm × 5 μ (thickness) were used for the measurements.

Theory

The π-Electron Structure of Free Ni(dmg)$_2$ Complex.—The theoretical calculation was made for free Ni(dmg)$_2$ based on the structure shown in Figure 1.[2a]

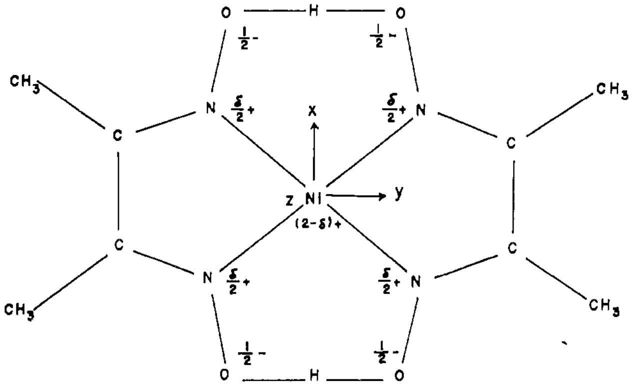

Figure 1.—The molecular structure of Ni(dmg)$_2$.

At the outset the π-electron structure of the ligand anion was calculated by the SCF–MO–CI method, the electrostatic potential field of the central metal ion and the other ligand being taken into account.[10–12] By the use of these MO's, the π-electron structure of the complex was calculated by the composite molecule method described previously in detail.[10] The complex was divided into two ligand π-electron systems and a nickel atom with four $d\pi$ electrons. A configuration-interaction calculation was made among a ground configuration, four locally excited (LE) configurations for each ligand, and four metal-to-ligand charge-transfer (CT) configurations. The core resonance integral $\beta(3d\pi, 2p\pi)$ between the metal $3d\pi$ and nitrogen $2p\pi$ AO's was estimated to be −0.97 eV by the following general formula[13] based on the proportionality to the overlap integral $S(3d\pi, 2p\pi)$ and also to the ionization potentials I_{3d_π} and I_{2p_π} of appropriate valence states

$$\beta(3d\pi, 2p\pi) = k(3d\pi,2p\pi)S(3d\pi,2p\pi) = \frac{I_{3d_\pi} + I_{2p_\pi}}{2}S(3d\pi,2p\pi) \qquad (1)$$

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(8) J. Tanaka, *Bull. Chem. Soc. Jap.*, **36**, 8339 (1963).

(9) K. Kaya and S. Nagakura, Symposium on Molecular Structure, Tokyo, Nov 1968.

(10) I. Hanazaki, F. Hanazaki, and S. Nagakura, *J. Chem. Phys.*, **50**, 265 (1969).

(11) The π-electron structure of the free dimethylglyoxime anion in a trans form was first treated by the Pariser–Parr–Pople SCF–MO–CI calculation.[12] The one-center core integral of oxygen $2p\pi$ AO was taken as the negative of the second ionization potential, and the one-center Coulomb repulsion integral (pp|pp) for this AO was taken to be the difference between the second and first ionization potentials. The core resonance integrals were determined by the use of the proportionality to the overlap integral. The transition energy and oscillator strength for the lowest transition were calculated to be 5.383 eV and 0.9052, respectively. These values seem to be reasonable compared with the corresponding values observed for the free dimethylglyoxime anion in water, 5.51 eV and 0.34, although the calculated oscillator strength is several times as large as the theoretical one as usual. Hence we used the same set of integrals for the calculation of *cis*-dimethylglyoxime anion in the field of the metal and the other ligand.

(12) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953); J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

(13) R. S. Mulliken, *J. Phys. Chem.*, **56**, 295 (1952).

Oscillator strengths were calculated by the equation

$$f_{\text{calcd}} = 0.0875\sigma Q^2 \qquad (2)$$

where Q is a transition moment in ångströms and σ is a transition energy in electron volts.

The *c*-Axis Polarized Transitions.—In the crystalline state, the distance between the neighboring columns is large enough for neglecting the interaction between them. Furthermore, the symmetry consideration shows that the direct interaction between the ligands may be disregarded. Therefore we considered only the direct interaction of a nickel atom with the neighboring ones in a column, taking at the outset a model composed of the two atoms. We took the coordinates as shown in Figure 1 (the z axis is parallel with the c axis). The $3d_{z^2} \rightarrow 4p_z$, $3d_{yz} \rightarrow 4p_y$, and $3d_{zx} \rightarrow 4p_x$ transitions within the metal ion are polarized parallel to the c axis. Here the last two were disregarded since they have small transition moments and do not interact with the first which has a greater moment compared with theirs. In addition to the $3d_{z^2} \rightarrow 4p_z$ transition, we considered the interatomic CT transitions of the type $3d_{z^2}{}^a \rightarrow 4p_z{}^b$ (a and b denote the neighboring atoms).[14] Therefore the following configurations are taken into account in the present treatment: symmetry A_{1g}

$$G = |(d\bar{d})^a(d\bar{d})^b|$$

$$\text{LE}- = {}^1/_2[|(d\bar{p})^a(d\bar{d})^b| + |(p\bar{d})^a(d\bar{d})^b| - |(d\bar{d})^a(d\bar{p})^b| - |(d\bar{d})^a(p\bar{d}^b|]$$

$$\text{CT}- = {}^1/_2[|d^a\bar{p}^b(d\bar{d})^b| + |p^b\bar{d}^a(d\bar{d})^b| - |(d\bar{d})^a d^b\bar{p}^a| - |(d\bar{d})^a p^a\bar{d}^b|]$$

and symmetry B_{1u}

$$\text{LE}+ = {}^1/_2[|(d\bar{p})^a(d\bar{d})^b| + |(p\bar{d})^a(d\bar{d})^b| + |(d\bar{d})^a(d\bar{p})^b| + |(d\bar{d})^a(p\bar{d})^b|]$$

$$\text{CT}+ = {}^1/_2[|(d^a\bar{p}^b(d\bar{d})^b| + |p^b\bar{d}^a(d\bar{d})^b| + |(d\bar{d})^a d^b\bar{p}^a| + |(d\bar{d})^a p^a\bar{d}^b|]$$

where d and p denote the $3d_{z^2}$ and $4p_z$ atomic orbitals, respectively.

The above configurations interact with one another as follows

$$\begin{array}{ll|lll} A_{1g}: & G & 0 & & \\ & \text{LE}- & 0 & E_1 & \\ & \text{CT}- & 2\beta(d^ap^b) & \beta(p^ap^b) & E_2 \end{array}$$

$$\begin{array}{ll|ll} B_{1u}: & \text{LE}+ & E_1 & \\ & \text{CT}+ & \beta(p^ap^b) & E_2 \end{array}$$

where $\beta(d^ap^b)$ and $\beta(p^ap^b)$ are the core resonance integrals between $3d_{z^2}{}^a$ and $4p_z{}^b$ and between $4p_z{}^a$ and $4p_z{}^b$, respectively, and E_1 and E_2 the energies necessary for the local excitation $3d_{z^2}{}^a \rightarrow 4p_z{}^a$ and for the CT excitation $3d_{z^2}{}^a \rightarrow 4p_z{}^b$, respectively.[15]

The E_1 and E_2 values can easily be obtained as a function of the interatomic distance R

$$E_1 = E^{\text{v}}{}_1 + \Delta_0 + \Delta(R) = E_1{}^0 + \Delta(R) \qquad (3)$$

$$E^{\text{v}}{}_1 = \begin{cases} \epsilon_p(d^{10}) - \epsilon_d(d^{10}) - (pp|dd) + 2(pd|pd) & \text{for Ni}^0 \\ \epsilon_p(d^9) - \epsilon_d(d^9) - (pp|dd) + 2(pd|pd) & \text{for Ni}^+ \end{cases}$$

$$E_2 = E_1 + (pp|dd) - 2(pd|pd) - (pp|dd)' \qquad (4)$$

Here $\epsilon_i(e)$, $(pp|dd)$, and $(pd|pd)$ are the orbital energy of the ith AO of the metal with electron configuration "e," the one-center Coulomb repulsion, and Coulomb exchange integrals, respectively. $E^{\text{v}}{}_1$ is the energy necessary for the transition from the $(3d_{z^2})^2$ valence state to the $(3d_{z^2}, 4p_z)$ one. These quantities were obtained from the analysis of the observed atomic spectra.[16] The two-center Coulomb repulsion integral $(pp|dd)'$ was evaluated by a quadratic equation determined in such a way as the value becomes equal to $1/R$ at a long distance and to the one-center value at $R = 0$.[17] Δ_0 is an electrostatic energy due to the formal charge on the atoms of the ligands in the same complex. $\Delta(R)$ is the electrostatic energy due to the positive charges on the central metal ion and the ligand nitrogen atoms of the neighboring complexes. The electrostatic energy terms were evaluated in the point-charge approximation, the interaction with the next nearest neighbors in addition to that with the nearest neighbors being taken into account.

The core resonance integrals $\beta(d^a, p^b)$ and $\beta(p^a, p^b)$ are estimated by the aid of eq 1, the overlap integral, $S(3d_{z^2}, 4p_z)$, being estimated by the following procedure. Since the intensity of the visible band at ~20 kK largely depends on R and therefore on the overlap integral $S(3d_{z^2}, 4p_z)$,[18] $S(3d_{z^2}, 4p_z)$ is evaluated by the aid of the following AO's (ψ_{3d} and ψ_{4p}) determined in such a way as the R dependence of the oscillator strength of the ~20-kK band observed for the nickel *vic*-dioxime complexes can be well explained

$$\psi_{3d} = 0.5817\phi_{3d}(5.75) + 0.5890\phi_{3d}(2.20) \qquad (5)$$

$$\psi_{4p} = 0.03924\phi_{2p}(11.50) - 0.13368\phi_{3p}(4.60) + 1.0080\phi_{4p}(1.34)$$

where ϕ_{nl}'s are the Slater-type AO's with the orbital exponents given in parentheses.[19] The k(p, p) or k(d,

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[14] The $3d_{yz}{}^a \rightarrow 4p_y{}^b$ and $3d_{zx}{}^a \rightarrow 4p_x{}^b$ transitions are insensitive to the change in the interatomic distance in view of the directions of these 4p orbitals and moreover they do not interact with the $3d_{z^2}{}^a \rightarrow 4p_z{}^b$ transition. This means that they have no predominant influence on this problem.

[15] E_1 and E_2 are the energies of the LE and CT configurations, respectively, evaluated by taking the ground configuration as the standard. Furthermore, in the present treatment the energy differences between LE+ and LE− and between CT+ and CT− are disregarded, because they are negligibly small.

[16] C. E. Moore, "Atomic Energy Levels," National Bureau of Standards Circular 467, U. S. Government Printing Office, Washington D. C., 1958.

[17] R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 767 (1953).

[18] The transition moment (R (Å)) between the CT− and CT+ configurations is larger than that (0.275 Å) between the G and LE+ configurations for the interatomic distance of ~3 Å. Therefore the intensity of the lowest transition largely depends on mixing ratio of CT− in the ground state. As is seen from the off-diagonal matrix elements for the CI calculation, the ratio is dependent on $\beta(d^ap^b)$ and, hence, on $S(3d_{z^2}, 4p_z)$.

[19] On the assumption that the terms with the greater orbital exponent are scarcely perturbed by the ligands, their values are fixed to those determined by Richardson, *et al.* (J. W. Richardson, W. C. Nieupoort, R. R. Powell, and W. F. Edgell, *J. Chem. Phys.*, **36**, 1057 (1962); J. W. Richardson, R. R. Powell, and W. C. Nieupoort, *ibid.*, **38**, 796 (1963)), and only one term of the smallest orbital exponent for each of ψ_{3d} and ψ_{4d} is parametrized to obtain the wave functions most suitable for the coordinated nickel ion. Consequently, we select the above functions, the coefficients, and orbital exponents of which are the same as those of the approximate Hartree–Fock AO's of free Ni^+ obtained by Richardson, *et al.*

p) value, another quantity necessary for the evaluation of $\beta(p^a, p^b)$ or $\beta(d^a, p^b)$, is varied as a parameter within a range reasonable from the consideration of the ionization potentials of the 3d and 4p orbitals and is determined in such a way as the transition energies and ocsillator strengths are best explained for the bands at ~20 and ~53 kK. Since we treat the transition bands polarized parallel to the *c* axis, the corresponding f_{calcd} is 3 times as large as that obtained by eq 2. The calculated values for these quantities are shown in Figure 2, together with the observed ones.[20]

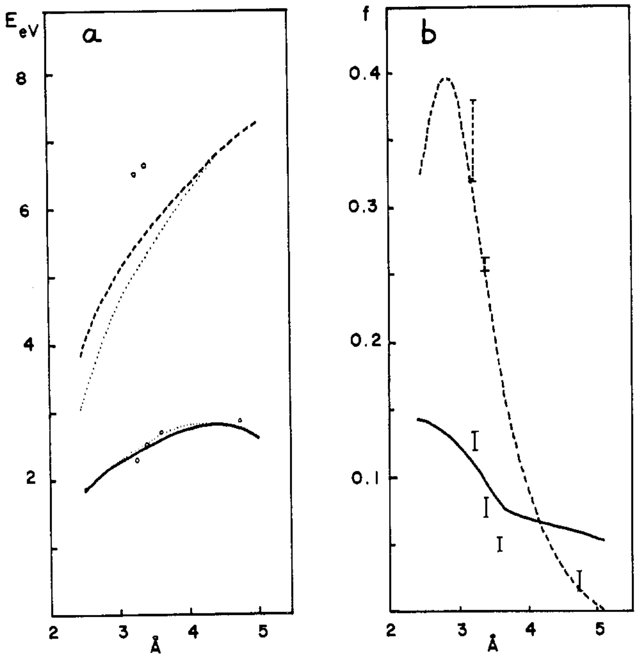

Figure 2.—The *R* dependence of the transition energy (a) and of the oscillator strength (b). The solid and broken lines represent the theoretical results for the bands at ~20 and ~53 kK, respectively, and the dotted line in a shows the configuration energy without CI. The points in a and the solid and broken vertical lines in b represent the observed values. The observed oscillator strength was obtained by the equation in Table I.

Results and Discussion

The Solution Spectra.—In Figure 3 are shown the absorption spectra of $Ni(dmg)_2$, $Pd(dmg)_2$, and $Pt(dmg)_2$ in the chloroform solution. Here we examine in detail the solution spectra taking $Ni(dmg)_2$ as an example. Its spectrum consists of four bands at 26.5, 30.5, 38.3, and 23.5 kK. The last band is weak (f = 0.01) and may be assigned to the $3d_{z^2} \rightarrow 4p_z$ transition. The other bands can be ascribed to the $\pi \rightarrow \pi^*$ transition as described below.

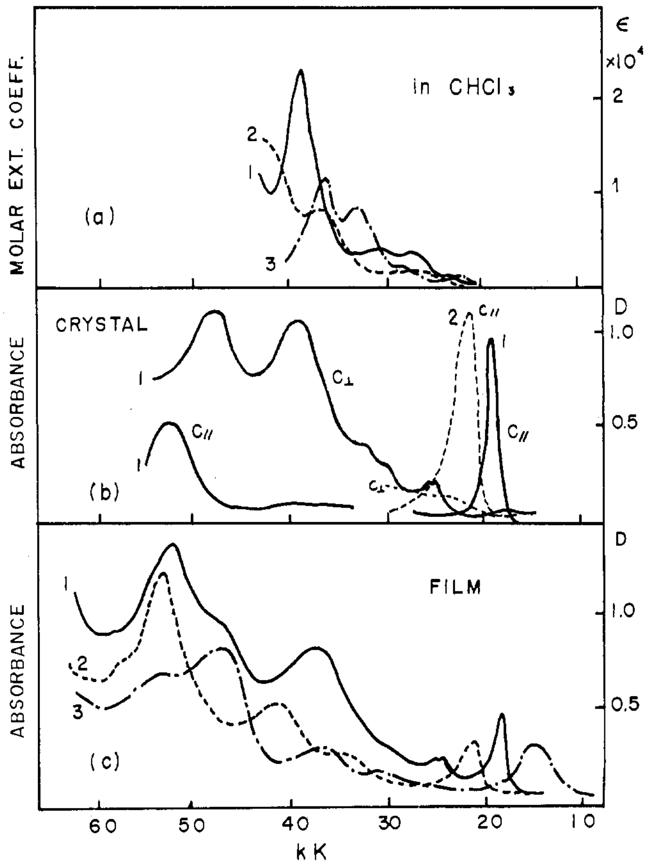

Figure 3.—The absorption spectra of (a) the chloroform solutions, (b) the single crystals, and (c) the thin films. Curves 1, 2, and 3 are for $Ni(dmg)_2$, $Pd(dmg)_2$ and $Pt(dmg)_2$, respectively.

TABLE I

THE THEORETICAL AND OBSERVED π-ELECTRON TRANSITION ENERGIES AND OSCILLATOR STRENGTHS OF FREE $Ni(dmg)_2$

Symmetry of the excited states	Character	E_{calcd}, kK	E_{obsd}, kK	f_{calcd}	$f_{\text{obsd}}{}^a$
B_{3u}	CT	28.89	26.5	0.03	0.13
B_{2u}	CT	30.26	30.5	0.22	
B_{3u}	LE	38.61	38.3	0.71	0.45
B_{2u}	LE	39.79		0.24	
B_{2u}	CT + LE	49.32		0.20	
B_{3u}	CT	52.36		0.09	

[a] f_{obsd} was obtained by inserting the observed molar extinction coefficient (ϵ in mol^{-1} l. cm^{-1}) and transition energy (σ in eV) into the equation $f_{\text{obsd}} = 3.49 \times 10^{-5} \int \epsilon d\sigma$

The transition energies and oscillator strengths calculated by the present method for the π-electron system of a free $Ni(dmg)_2$ are shown in Table I, together with the observed values obtained for the chloroform solution. In this calculation, the lowest metal-to-ligand CT configuration energy, E_1^{π}, is taken to be 3.1 eV in order to reproduce the observed spectrum. The energy (E_2^{π}) of the configuration caused by the electron transfer to the second lowest vacant MO of ligand is estimated by adding the theoretically calculated value of $E^{\pi} = E_2^{\pi} - E_1^{\pi}$ to the empirically determined E_1^{π} value. The theoretical value of E_1^{π} greatly depends on the degree of neutralization of the charge on the metal

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(20) The above calculation was carried out on the assumed model composed of the two atoms but in the actual complex crystal there exists a long column constructed by the stacked metal complexes. Therefore, the atom under consideration interacts equivalently with two atoms above and below it, and there exist two CT directions with different directions for each atom. Sakata and Nagakura treated this problem and derived the conclusion that the oscillator strength of the CT transition for the long-chain system is twice as large as that calculated by the two-atom model: T. Sakata and S. Nagakura, *Bull. Chem. Soc. Jap.*, in press. This correction was taken into account for the calculation of the oscillator strengths.

ion through the σ-dative bonding. The adopted value 3.1 eV seems to correspond to the charge between 0 and +1. This is consistent with the fact that ψ_{3d} and ψ_{4p} in eq 5 correspond to the AO's of Ni^+. According to our calculation, the LE energies and the core resonance integral between the metal ion and the $2p\pi$ orbital of ligand nitrogen are insensitive to the charge on the central metal ion in the range of 0–1. Hence, the result of Table I for the free $Ni(dmg)_2$ was obtained by the aid of the AO's of the neutral Ni atom and of the ligand MO's evaluated on the assumption of the complete neutralization of the charge on the central metal ion. Almost the same result was obtained for the case of Ni^+.

As clearly seen in Table I, the observed peaks at 26.5 and 30.5 kK are, respectively, assigned to the metal-to-ligand CT transition and the band at 38.3 kK is assigned to the two near-lying LE transitions of a ligand. The calculated oscillator strengths show a reasonable parallelism with the observed ones. Hence the bands in the solution spectrum except for the weakest band at 23.5 kK ($f = 0.01$) are well explained as due to the metal-to-ligand CT and LE transitions.

The Crystal Spectra.—By extending the measurement for the single crystal of $Ni(dmg)_2$ to the vacuum ultraviolet region, we succeed in finding a new band polarized parallel to the c axis at 52.5 kK in addition to the 18.6-kK one observed hitherto. The experimental result is shown in Figure 3. The analogous spectrum with two peaks at 20.5 and 53.6 kK was observed for the single crystal of β-$Ni(emg)_2$ as shown in Figure 4. The crystals of these two complexes are isomorphous and have different metal–metal distances: $R = 3.25$ and 3.4 Å for $Ni(dmg)_2$ and β-$Ni(emg)_2$, respectively. Concerning nickel heptoxime, another isomorphous complex of $R = 3.6$ Å, the c axis polarized band was observed by Anex and Krist[7] at 21.9 kK. They also found the similar band at 23.0 kK for the α-$Ni(emg)_2$ crystal which has a different crystal structure with a considerably longer metal–metal distance, 4.75 Å. We measured a polarized vacuum ultraviolet absorption spectrum for this complex but could not find any band in the 50-kK region. The observed R dependences of the transition energy and oscillator strength[21] are summarized in Figure 2, together with the theoretical ones.

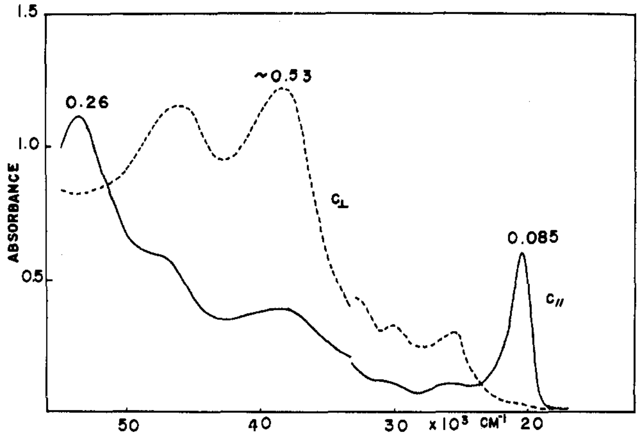

Figure 4.—The polarized absorption spectra of the single crystal of β-$Ni(emg)_2$. The figure attached to each band is the observed oscillator strength.

Anex and Krist[7] assigned the 23.5-kK band of $Ni(dmg)_2$ in solution to the weak $3d_{z^2} \rightarrow \pi^*$ transition and interpreted that the band was greatly intensified in the crystal by borrowing the intensity from the strong $3d_{z^2} \rightarrow 4p_z$ transition. According to our calculation by the use of the improved AO's,[19] however, the transition moment for $3d_{z^2} \rightarrow 4p_z$ becomes several times smaller than that calculated by the single Slater-type AO's and is too small to increase the intensity of a weak band by the mixing. Moreover, it is reasonable to assign the band at 23.5 kK in solution to the $3d_{z^2} \rightarrow 4p_z$ transition. This is because the band due to this transition may be expected theoretically to appear in the 20-kK region for the nickel ion considerably neutralized by the σ-electron migration from the ligands in the complex and also because this transition is stronger than the $3d_{z^2} \rightarrow \pi^*$ one.

In our opinion, the $3d_{z^2} \rightarrow 4p_z$ transition band at ~20 kK is intensified in the crystal by mixing with the CT transition. This is supported by the fact that the calculated moment for the interatomic CT transition is larger by a factor of 10 than that for the $3d_{z^2} \rightarrow 4p_z$ transition. In order to clarify further the nature of the bands at ~20 and ~53 kK, we discuss the R dependence of the transition energy and oscillator strength for these bands comparing the experimental results with the theoretical ones calculated on the basis of the interatomic CT model.

For the visible band at ~20 kK, the calculated R dependence of the transition energy shows a good coincidence with the observed values (Figure 2a), and the sharp intensity increase with the decrease of R in the region shorter than 3.5 Å appears also in the theoretical curve (Figure 2b). For the vacuum ultraviolet band at ~53 kK, the calculated R dependency can explain the observed tendency for both the transition energy and the oscillator strength, though we have only two observed points for each quantity. In this connection, it may be noticed that no c axis polarized absorption band could be found in the near-ultraviolet and vacuum ultraviolet region for the single crystal of α-$Ni(emg)_2$ with $R = 4.75$ Å. Since the intensity of the ~53-kK band is theoretically predicted to be very small at this distance as is clearly seen in Figure 2b, this result is reasonably interpreted on the basis of our viewpoint. Thus, the strong band at ~53 kK may be interpreted as the interatomic CT one.

Figure 5 shows the ground-state stabilization energy due to the interatomic CT interaction and the character of each state. The mixing of the CT configuration increases with the decreasing R in both the ground

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[21] The transition energy and oscillator strength for the nickel heptoxime crystal and the oscillator strengths of the visible bands of the other complex crystals are quoted from the value observed by Anex and Krist.[7] The oscillator strength of the vacuum ultraviolet band was determined with reference to that of the visible band obtained by them.

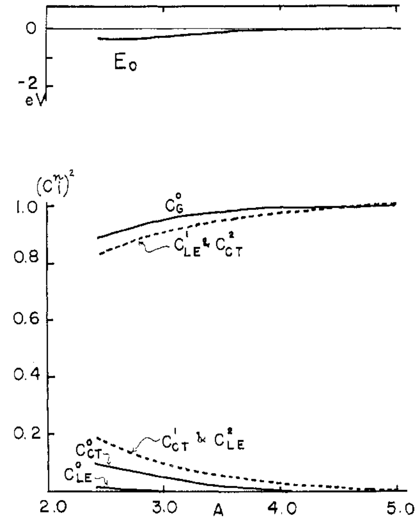

Figure 5.—The R dependence of the wave function of each state and the ground-state stabilization energy due to the interatomic CT interaction: $\psi_0 = C^0{}_{G}G + C^0{}_{LE}LE_- + C^0{}_{CT}CT_-$ for the ground state; $\psi_1 = C^1{}_{LE}LE_+ + C^1{}_{CT}CT_+$ for the excited state of the band at ~20 kK; $\psi_2 = C^2{}_{LE}LE_+ + C^2{}_{CT}CT_+$ for the excited state of the band at ~53 kK.

state and the first excited state. This causes the rapid increase of the transition probability for the visible band with the decreasing R, because the moment is large for the transition between the CT− and CT+ configurations. The stabilization energy of the ground state amounts to 5 kcal/mol for Ni(dmg)$_2$. This seems to be one of the reasons for the low solubility of Ni(dmg)$_2$ and also for its particular crystal structure.

From the above-mentioned discussion for the crystal spectra polarized parallel to the c axis, we can conclude that the sharp band at ~20 kK is mainly due to the $3d_{z^2} \rightarrow 4p_z$ transition within a nickel ion and is intensified in the crystal by borrowing the intensity from the interatomic CT excitation. Furthermore, the strong absorption peak in the vacuum ultraviolet region was found to be mainly due to the interatomic CT transition. That is to say, we succeeded in observing the new band characteristic of the interatomic CT interaction in the Ni(dmg)$_2$ and β-Ni(emg)$_2$ crystals. Since the present theoretical results on the crystal spectra depend to some extent on the adopted parameters, too much importance should not be attached to them from the quantitative point of view. Qualitatively, however, the present treatment gives a reasonable interpretation of the observed crystal spectra.

As is seen in Figure 3, the films of Pd(dmg)$_2$ and Pt(dmg)$_2$ show spectra analogous to that of Ni(dmg)$_2$. In the visible region, they have strong bands at 21.5 and 15.1 kK, respectively, which correspond to that at 18.6 kK of Ni(dmg)$_2$. Furthermore, another peak was observed for each complex in the region above 50 kK, corresponding to the 52.5-kK band of Ni(dmg)$_2$, though it is altered to some extent by the central metal ion. The conclusions obtained by the present theoretical calculation for the nickel *vic*-dioximes are considered to be also applicable qualitatively to the crystals of Pd(dmg)$_2$ and Pt(dmg)$_2$.

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The Preparation and Hydrogen-1 and Fluorine-19 Nuclear Magnetic Resonance Spectra of Fluoroalkylplatinum(II) and -platinum(IV) Compounds

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Fluoroalkyl halides of the types RI or RCH$_2$I (R = perfluoroalkyl) react with several methylplatinum(II) complexes containing the ligands P(CH$_3$)$_2$C$_6$H$_5$ or As(CH$_3$)$_2$C$_6$H$_5$ to give platinum(IV) complexes whose stereochemistry has been determined by ^{1}H nmr spectroscopy. Long-range H-F coupling has been observed in many of the proton spectra. Fluorine-19 nmr data are given: there is a wide variation in Pt-F coupling constants. Complexes of the type *trans*-PtIR{P(CH$_3$)$_2$C$_6$H$_5$}$_2$ (R = CF$_3$, C$_2$F$_5$, or C$_3$F$_7$) result from the decomposition of some of the platinum(IV) complexes.

Introduction

Alkylplatinum(II) and -platinum(IV) complexes can be prepared using Grignard or lithium reagents,[1,2] but the corresponding fluoroalkyl complexes are not accessible by these routes. Fluoroalkylplatinum(II) complexes have been prepared by oxidative addition of fluoroalkyl iodides to platinum(0) species,[3] and we now report the preparation of some platinum(IV) complexes containing fluoroalkyl groups by oxidative addition of fluoroalkyl iodides to methylplatinum(II) complexes. Some of these compounds can be degraded readily to give fluoroalkylplatinum(II) complexes.

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