

creased much more than others. This provides a means of detecting the presence of poorly resolved components in favorable cases.

The CD curve of $(+)\text{[Co(en)}_2\text{pic]ClO}_4$ (Fig. 7) shows three peaks (+, -, +) in the region of the high-frequency absorption band. This further supports the assumption that the same splitting pattern applies to complexes of this general type, even if no optically active ligand is present. The CD curve in the low-frequency region is strikingly similar to that of the $(+)\text{[Co(en)}_2\text{glycine}]$ complex (Fig. 1).

The spiral pattern of the chelate rings in the complexes reported here is similar to that for $[\text{Co(en)}_3]^{3+}$. If one considers the symmetry to be lowered from $[\text{Co(NH}_3)_6]^{3+}$ (O_h) to $[\text{Co(en)}_3]^{3+}$ (D_3), the T_{1g} (O_h) level is split into the 1E and 1A_2 (D_3) levels. Further lowering of the symmetry to C_1 by replacing one nitrogen by an oxygen in $[\text{Co(en)}_2\text{aa}]^{2+}$ removes the degeneracy to give three A levels. Polarized absorption spectra¹² and CD studies¹³ of $[\text{Co(en)}_3]^{3+}$ showed that the A_2 peak is very close to the E peak. Mason's data for $(+)\text{[Co(en)}_3]^{3+}$ in solution and in the solid have shown that the positive CD peak is ${}^1A_1 \rightarrow {}^1E$

- (12) S. Yamada and R. Tsuchida, *Bull. Chem. Soc. Japan*, **33**, 98 (1960).
 (13) A. J. McCaffery and S. F. Mason, *Mol. Phys.*, **6**, 359 (1963).

and the negative peak is ${}^1A_1 \rightarrow {}^1A_2$. It is expected that for $[\text{Co(en)}_2\text{aa}]^{2+}$ the two components split out of the E level should have the same sign,¹⁴ which should be opposite to that of the third component. Since the 1A_2 and 1E components for D_3 symmetry are close together, it is reasonable to expect that lowering of the symmetry would give one of the components from the E level at higher energy and one at lower energy compared to the component related to 1A_2 . Therefore, the center component of the low-frequency band, which is opposite in sign to the other two, is related to the 1A_2 component for D_3 symmetry.

The $(+)\text{[Co(en)}_3]^{3+}$ ion has been shown to have a left spiral (Λ) configuration.¹⁵ For this isomer the 1A_2 CD peak is negative and hence the Λ configuration is assigned to all of the $(-)\text{[Co(en)}_2\text{aa}]I_2$ complexes reported here since their corresponding CD peaks are also negative. The solubilities of the diastereoisomers of $[\text{Co(en)}_3]^{3+}$, $[\text{Co(en)}_2\text{gly}]^{2+}$, and $[\text{Co(en)}_2\text{pic}]^{2+}$ are consistent with this assignment of configurations.

- (14) A. D. Liehr, private communication.

- (15) Y. Saito, K. Nakatsu, M. Shiro, and H. Kuroya, *Bull. Chem. Soc. Japan*, **30**, 795 (1957).

CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY,
 UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS

The Green Band of Crystalline Nickel Dimethylglyoxime. I. Mixed Crystals with Palladium, Platinum, and Copper and the Questions of Nonlocalized or d-p Transitions¹

BY G. BASU, GLENN M. COOK,² AND R. LINN BELFORD³

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Quantitative spectra of single crystals of Ni, Pt, and Pd dimethylglyoximates in polarized light show extinction coefficients much smaller than earlier values, which were obtained from polycrystalline specimens. This evidence, plus arguments based on band polarizations, cast serious doubt on a previous assignment of the visible band to a highly-allowed $p \leftarrow d$ transition. Preparation and visible salt pellet spectra of true binary mixed crystals of Ni, Pt, Pd, and Cu dimethylglyoximates are reported. The spectrum of a binary mixed crystal can be interpreted as containing bands belonging to each component. This interpretation is consistent with the solid-unique visible absorption's being caused by molecular transitions rather than by completely delocalized whole-crystal transitions. A new band is reported in the near-infrared spectrum of a single crystal of nickel dimethylglyoximate; it is probably a nickel d-like transition.

Introduction

Solid nickel bis(dimethylglyoxime) $[\text{Ni(DMG)}_2]$ has a strong green absorption⁴⁻⁸ that is not reported for

- (1) Partly abstracted from the Ph.D. thesis of G. M. Cook. This work was supported partly by National Science Foundation and U. S. Public Health Service (Division of General Medical Sciences) research grants.
 (2) National Science Foundation Fellow, summer 1960; supported by Illinois Drug and Chemical Industries Scholarship Award.
 (3) Alfred P. Sloan Research Fellow.
 (4) J. C. Zahner and H. G. Drickamer, *J. Chem. Phys.*, **33**, 1625 (1960); also J. C. Zahner, Ph.D. Thesis, University of Illinois, 1961.
 (5) S. Yamada and R. Tsuchida, *Bull. Chem. Soc. Japan*, **27**, 156 (1954); *J. Am. Chem. Soc.*, **75**, 6351 (1953); S. Yamada, *ibid.*, **73**, 1579 (1951).
 (6) K. Sone, *ibid.*, **75**, 5207 (1953).
 (7) R. L. Belford, University of California Radiation Laboratory Report UCRL 3051 (June, 1955).

the solutions. This absorption was seen in single crystals by Yamada and Tsuchida⁵ and Banks and Barnum⁹ as a rather featureless absorption edge. However, it was reported by Sone,⁶ Belford,⁷ and Banks and Barnum^{8,9} as a sharp, well-defined peak in the absorption spectra of powders, mulls, and suspensions. Zahner and Drickamer⁴ found that this sharp band, and the presumably analogous bands of the isomorphous

- (8) D. W. Barnum, Doctoral Dissertation, Iowa State College, 1957.
 (9) C. V. Banks and D. W. Barnum, *J. Am. Chem. Soc.*, **80**, 4767 (1958); C. V. Banks and D. W. Barnum, *ibid.*, **80**, 3579 (1958); C. V. Banks and S. Anderson, *ibid.*, **84**, 1486 (1962). Also see numerous other references cited in these works.

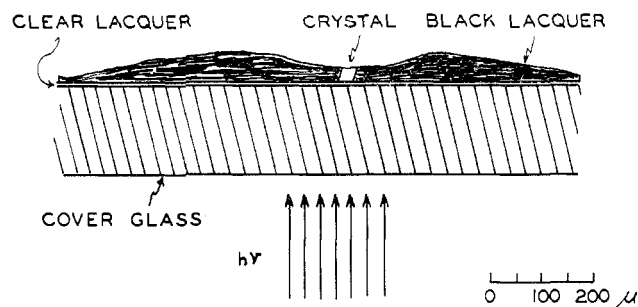


Fig. 1.—Single crystal mounting. (The top surface was prepared by wiping off the lacquer with a cloth dampened with dioxane.)

$\text{Pd}(\text{DMG})_2$ and $\text{Pt}(\text{DMG})_2$, of pressed salt pellets showed very strong red shifts with pressure and accordingly assigned the bands to $3d^{74p} \leftarrow 3d^8$ transitions. Because of the band's appearance only in the solid phase, which is characterized by an axial stacking of the $\text{Ni}(\text{DMG})_2$ molecules,^{10,11} most workers have supposed the transition to be among the levels of a nickel chain.

The main purposes of this paper are to present some previously neglected features—particularly absolute absorption intensities, temperature dependence, and infrared bands—in the crystal spectra of the metal-chain dimethylglyoximates, to present further studies (akin to previous work^{8,9}) of mixed-crystal spectra and band polarizations, and to compare these data with implications of various assignments.

Experimental

Preparations.— $\text{Ni}(\text{DMG})_2$ was prepared from NiCl_2 purified by passage through an anion-exchange resin. The NiCl_2 was made slightly basic, pH ~ 9 , with NaOH . A 50% $\text{C}_2\text{H}_5\text{OH}-\text{H}_2\text{O}$ solution of dimethylglyoxime was added to form the typical brick-red precipitate of $\text{Ni}(\text{DMG})_2$. $\text{Cu}(\text{DMG})_2$ was prepared by passing the alcoholic dimethylglyoxime over freshly prepared and washed precipitates of $\text{Cu}(\text{OH})_2$. $\text{Cu}(\text{DMG})_2$ is quite soluble; excess $\text{Cu}(\text{OH})_2$ was easily filtered off. The brown crystals of $\text{Cu}(\text{DMG})_2$ were obtained by allowing the dark brown solution to evaporate slowly. $\text{Pd}(\text{DMG})_2$ was prepared by making a 0.5 *M* solution of PdCl_2 slightly acidic with HCl , pH ~ 4 , to prevent any possible contamination by $\text{Ni}(\text{DMG})_2$. The yellow precipitate formed immediately upon the addition of the dimethylglyoxime solution. $\text{Pt}(\text{DMG})_2$ was prepared by adding stoichiometric amounts of Na_2SO_3 and NaOH to a 1 *M* solution of PtCl_4 to produce Pt^{+2} . This solution was buffered with NH_4OH and acetic acid to pH ~ 6.9 . The stock dimethylglyoxime solution was added, and the resulting solution was allowed to stand overnight. A grayish violet precipitate of $\text{Pt}(\text{DMG})_2$ was obtained.

Mixed Crystals.—Measured volumes of the saturated CHCl_3 solutions were allowed to evaporate slowly. With $\text{Pd}(\text{DMG})_2$ and $\text{Ni}(\text{DMG})_2$ a range of concentration ratios was used. With the other possible combinations of two solutions, one or two different ratios were used; the exception being $\text{Cu}(\text{DMG})_2$, which was combined only with $\text{Ni}(\text{DMG})_2$. A microscopic examination showed that *in any one batch the individual crystals were all of the same color and shape; thus, true mixed crystals were formed.* The only exception was the mixture of $\text{Cu}(\text{DMG})_2$ and $\text{Ni}(\text{DMG})_2$ in which variations were found in both color and crystalline form.

(10) L. E. Godyicki and R. E. Rundle, *Acta Cryst.*, **6**, 487 (1953).

(11) E. Frasson, C. Panattoni, and R. Zannetti, *ibid.*, **12**, 1027 (1959); J. Pech, M. Polster, and A. Rexabek, *Chem. Listy*, **43**, 180 (1949) [*Chem. Abstr.*, **44**, 9295c (1950)]; A. G. Sharpe and D. B. Wakefield, *J. Chem. Soc.*, 281 (1957).

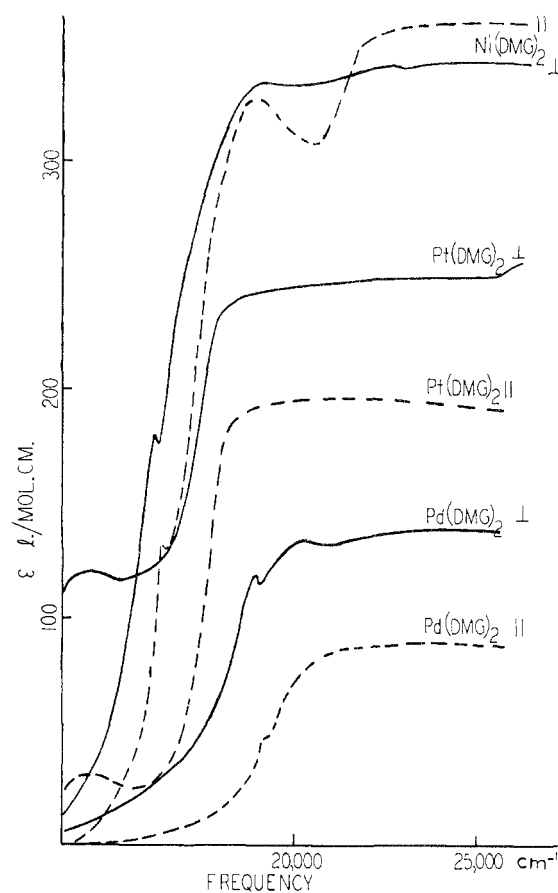


Fig. 2.—Single crystal spectra. The electric vector was parallel to the molecular plane (*i.e.*, perpendicular to the principal axis) for each spectrum marked ||. The small, sharp wiggles are not satisfactorily explained and are assumed to be caused by optical interference or other instrumental effects. The \perp spectrum is necessarily impure owing to convergence of the light in the Cassegrainian condenser, but the || spectrum is reliable.

In each batch, some needle-like crystals formed that were darker than those of pure $\text{Ni}(\text{DMG})_2$; these were presumably mixed crystals and were used in the work presented.

To use any information concerning changes in the spectra, one should know the relative concentrations of the two compounds in the crystal. The ratio of the concentrations of the two chelates composing any mixed crystal was estimated in each case by two methods. The first was simply to assume a crystal ratio equal to the mole ratio of the parent solutions. The second was to determine the ratio of the two chelates in a CHCl_3 extraction solution made by dissolving out the chelate compounds from the sample. This extraction was then spectroscopically examined to determine the ratio of the concentrations. The results of both methods were comparable.

Spectra.—Single crystals mounted as shown in Fig. 1 were examined with a modified Perkin-Elmer 99 monochromator outfitted with a tungsten light source, a Cassegrainian condenser at the exit (because of the small crystal area), a calcite polarizing prism, and a detector (PbS or photomultiplier). Precautions were observed to prevent light leakage past the crystal. After the spectra were taken, each crystal was carefully dissolved out of its mask and its thickness was determined from the depth of its impression in the mask; accuracy was about 1 μ .

Resulting spectra of $\text{Pt}(\text{DMG})_2$, $\text{Ni}(\text{DMG})_2$, and $\text{Pd}(\text{DMG})_2$ are shown in Fig. 2. (Spectra of single mixed crystals were run but were very disappointing and are not shown because the individual bands are poorly resolved owing to overlapping.)

Growth of larger single crystals of $\text{Ni}(\text{DMG})_2$ (from nitrobenzene) enabled us to determine more accurate polarization shapes

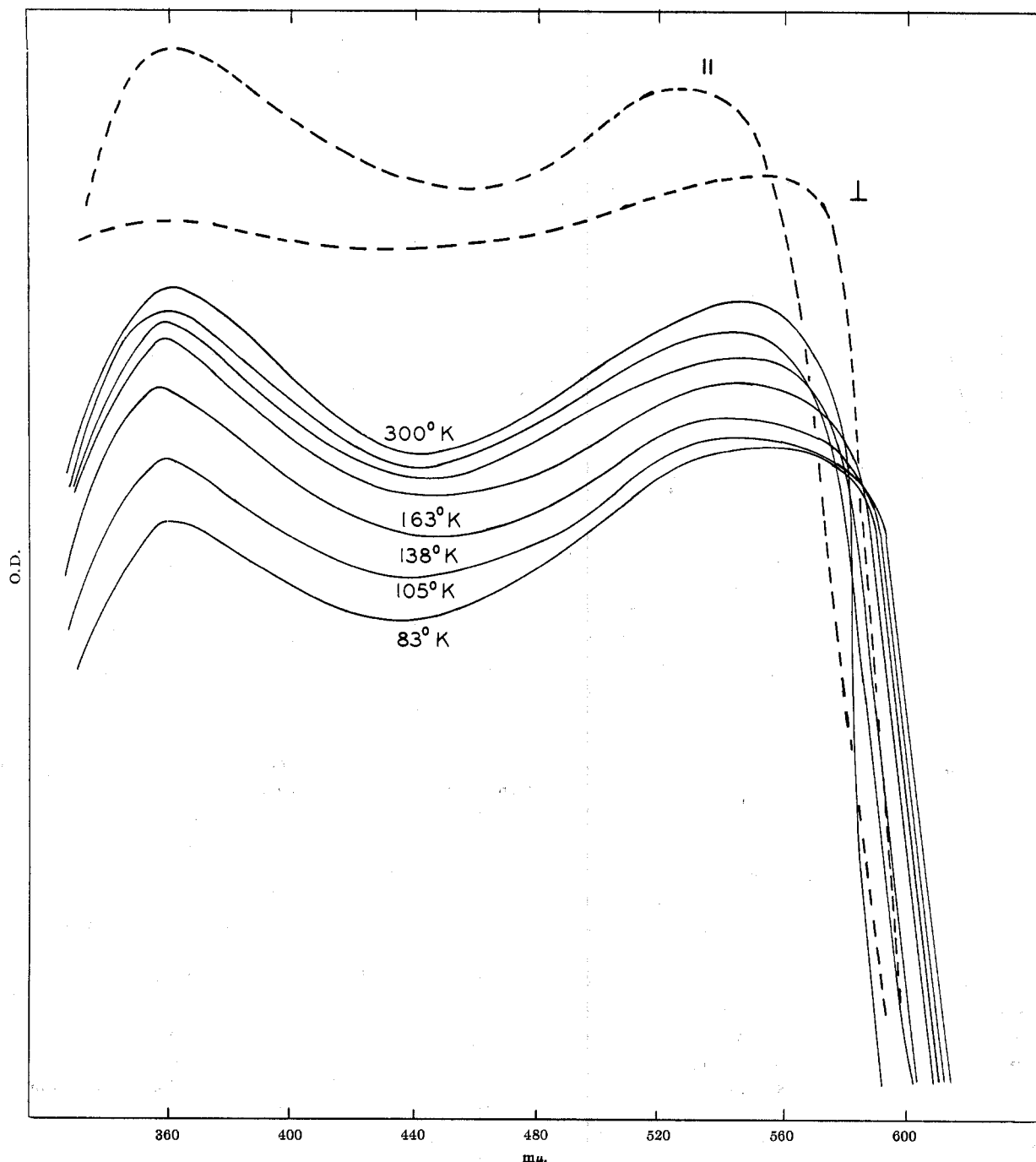


Fig. 3.—Large single crystal of $\text{Ni}(\text{DMG})_2$. The dashed curves are polarized spectra at liquid nitrogen temperature, parallel and perpendicular to the molecular plane. The solid curves are unpolarized spectra of the same crystal, taken at successive temperatures as the crystal warmed in the cell without disturbance. The base line is far below the bottom of this page; for clarity, the dashed curves are arbitrarily shifted up.

and the temperature effects for this crystal, as shown in Fig. 3.

NaCl pellets of parent and mixed crystals were made; the presses of Zahner and Drickamer⁴ were used at $\sim 17,000$ atm. The pellets were about 1 wt. % chelate, 0.25 in. in diameter, 0.3 mm. thick, and fairly clear in appearance. The spectroscopic apparatus described above was employed for some runs; it gave results comparable with those of the Cary Model 14 spectrophotometer, which was used for all the results shown in Fig. 3-9. Neither Beer's nor Lambert's law was obeyed by the salt pellets.¹

Spectra of mineral oil mulls of the chelates were taken on a Cary Model 14 spectrophotometer; effects of temperature, refractive index of the suspension medium, and particle size were investigated and are reported elsewhere.¹ We mention here that (1) the mull spectra are generally similar in appearance to the salt

pellet spectra, (2) both refractive index and particle size affect significantly the apparent absorption coefficients, and (3) the apparent absorption peak shifts to lower frequency at lower temperature.

For comparison with the solid-state spectra, Fig. 10 and 11 show corresponding spectra of solutions of the pertinent chelates in CHCl_3 .

Discussion

Single Crystal vs. Polycrystalline Spectra.—It has been thought that there are sharp absorption bands in the visible range for solid $\text{Ni}(\text{DMG})_2$, $\text{Pt}(\text{DMG})_2$, and $\text{Pd}(\text{DMG})_2$, as seen in their salt pellets (Fig. 5-9

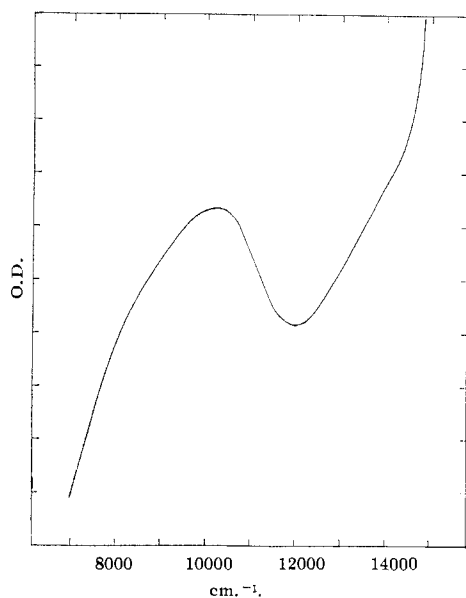


Fig. 4.—Unpolarized near-infrared spectrum of a large single crystal of $\text{Ni}(\text{DMG})_2$.

and ref. 4), powder films, or polycrystalline suspensions.^{1,6,7} However, our spectra of single crystals (Fig. 2 and 3) show that this is not the case. There is, in most cases, a fairly steep rise in absorption in the region of the sharp band which the polycrystalline specimens display; then there is a plateau (with or without a small maximum) which forms a shoulder on the side of the ultraviolet absorption. Before taking these spectra, we had supposed that the inability of earlier workers^{6,9} to observe sharp visible bands in small crystals was caused by poor optical resolving power. However, while our spectra do, indeed, show some improved detail, they generally do not have sharp visible peaks. We must conclude that the spectra of the polycrystalline samples, involving as they do a combination of absorption and reflection spectra (and the possibility of obscure effects caused by scattering, etc.), are not proper absorption spectra of the crystals.^{12a}

With this knowledge and reservation in mind, we shall nevertheless assume that the peak position in each salt pellet spectrum is a useful indication of the first transition frequency in the crystal. Since the salt pellet spectra are sharper than the true absorption spectra, it is possible to get more information from salt pellets of the mixed crystals than from their single crystals. Therefore, our discussion of the mixed crystal transitions is based on the salt pellet rather than the single crystal spectra.

Mixed Crystals.—In Fig. 5-9, one can see that the

(12) (a) Banks and Barnum⁹ also noticed differences between polycrystalline and single-crystal spectra of similar compounds. However, they did not measure apparent absorption intensities of the two. Thus it has not been previously known how greatly the polycrystalline results overshoot the extinction coefficients of these compounds. Some ordinary chelates, *e.g.*, copper acetylacetonate, have been examined in salt pellet, crystal, and solution forms in these laboratories, but the pellets showed the same spectra as the other states. (b) Some mixed-crystal colloidal suspension spectra of Ni, Pd, and Pt 4-methylglyoximes were reported by Banks and Barnum⁹ always to have only a single peak, in contradistinction to mechanical mixtures. This would seem to support the theory of a delocalized transition. However, we believe the data on mixed dimethylglyoximes point in the opposite direction.

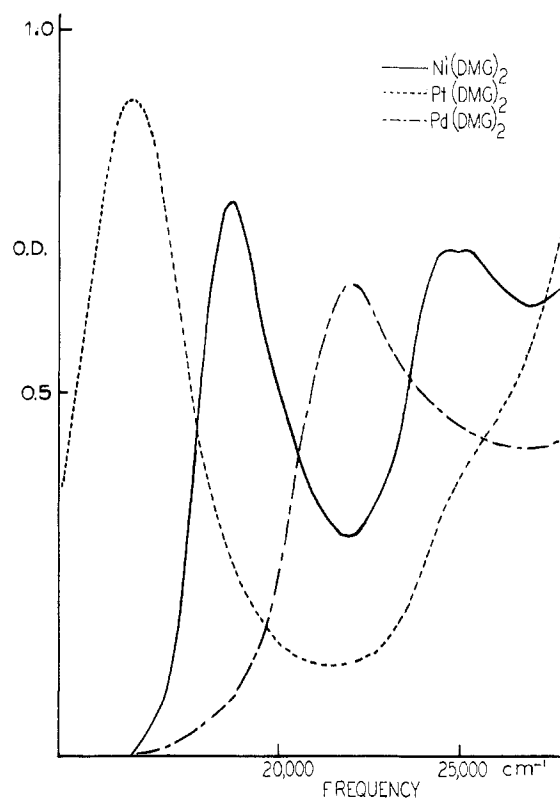


Fig. 5.—Transmission curves of NaCl pellets.

mixed crystals have truly different transmission curves than mechanical mixtures of the two separate component crystals. Thus the observed changes are caused by interactions in the mixed crystals rather than by any effects of pressing the pellets.

If the transitions are of a localized molecular variety, then we would expect to see the same bands as shown by the parent unmixed crystals, perhaps with incidental environmental shifts. If the transitions are non-localized, involving a long metal chain, then we might expect instead to see a different band, of intermediate position, for each new mixed crystal. This technique has been used in other problems—*e.g.*, to establish the participation of the entire ligand shell in the electron-transfer absorption of some bismuth halides.¹³

Some of the mixed-crystal pellet spectra obviously have the peaks characteristic of both components of the mixture^{12b}; in others, the separate peaks are not clearly seen. We are inclined to think that all the spectra are compatible with there being individual absorption frequencies for both constituents of each mixed crystal. Since this is not obvious, some explanation of our reading of the data is required.

The presence of a neighboring cation in the crystal appears to shift the peaks of a given ion to some extent. The following generalizations can be made from Fig. 3-7 (and from other such spectra taken in the course of this work¹): (1) In the Pt-Ni mixture, the lowest-energy peak of $\text{Pt}(\text{DMG})_2$ is shifted toward the blue while that of $\text{Ni}(\text{DMG})_2$ moves toward the red. (2)

(13) L. Newman and D. N. Hume, *J. Am. Chem. Soc.*, **79**, 4581 (1957); see also T. G. Spiro and D. N. Hume, *ibid.*, **83**, 4305 (1961).

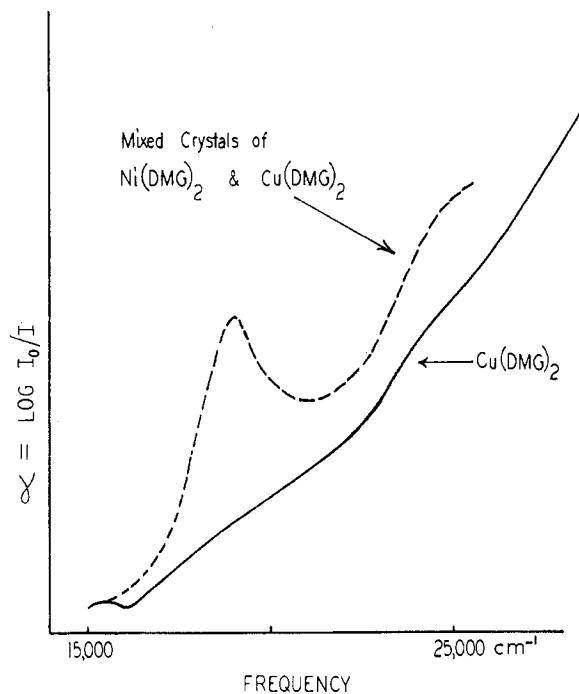


Fig. 6.—Transmission curves of NaCl pellets. The mixed crystals were not all identical; the ratio of Ni:Cu in them probably covers a large range.

In Pt-Pd mixtures, the lowest-energy peak of Pt-(DMG)₂ is shifted toward the blue while that of Pd-(DMG)₂ moves toward the red. (3) In Ni-Pd mixtures, the lowest-lying peak of Ni(DMG)₂ undergoes a blue shift, but it is difficult to determine the effect upon the Pd(DMG)₂ peak. (We also find the position of a Ni(DMG)₂ double peak—24.7 and 25.25 kK.—remaining essentially unchanged, but the components merge at high Pd concentrations. These will not be discussed.)

It is interesting to inquire whether the observed spectra could be explained using very simple ground rules. That which follows is a purely speculative and phenomenological attempt.

Suppose that each chelate molecule, *j*, shifts the lowest frequency of its neighbor by an amount $-v_j/2$, regardless of the identity of that neighbor. Suppose further that there is a solution peak corresponding to the salt-pellet peak. Then v_{Ni} is given as $v[\text{Ni}(\text{DMG})_2 \text{ solution}] - v[\text{Ni}(\text{DMG})_2]$; the corresponding expressions are used for Pt and Pd. Having simplified this far, let us further try correlating the lowest observed band in each solution spectrum with the corresponding band in the salt pellet. This yields $v_{Ni} = 4.95 \text{ kK.}$, $v_{Pd} = 4.50 \text{ kK.}$, $v_{Pt} = 7.70 \text{ kK.}$ Considering each mixed crystal to be randomly arranged, one would predict six lowest-lying absorption bands corresponding to sites having differing concentrations as shown in Table I.

The process just described is drastically oversimplified and naïve. Nevertheless, it describes the observed spectra amazingly well. For example, one can easily see how the Pd and Pt peaks, well-defined and well-separated in the mechanical mixture, can produce

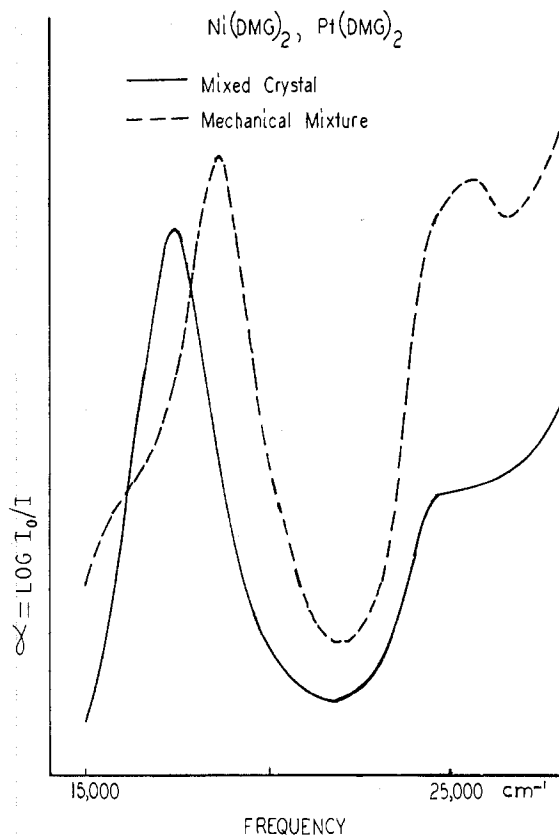


Fig. 7.—Transmission curves of NaCl pellets. The Ni:Pt ratio in the mechanical mixture is 1.3:1; in the mixed crystal, not well determined.

TABLE I			
Pt-Pd Mixtures (Pd fraction <i>f</i>)			
Pt(DMG) ₂ bands, kK.	Concn.	Pd(DMG) ₂ bands, kK.	Concn.
16.0	(1 - <i>f</i>) ³	18.8	<i>f</i> (1 - <i>f</i>) ²
17.6	2(1 - <i>f</i>) ² <i>f</i>	20.4	2 <i>f</i> ² (1 - <i>f</i>)
19.2	(1 - <i>f</i>) <i>f</i> ²	22.0	<i>f</i> ³
Pt-Ni Mixtures (Ni fraction <i>f</i>)			
Pt(DMG) ₂ bands, kK.	Concn.	Ni(DMG) ₂ bands, kK.	Concn.
16.0	(1 - <i>f</i>) ³	16.0	<i>f</i> (1 - <i>f</i>) ²
17.375	2(1 - <i>f</i>) ² <i>f</i>	17.375	2 <i>f</i> ² (1 - <i>f</i>)
18.750	(1 - <i>f</i>) <i>f</i> ²	18.750	<i>f</i> ³
Pd-Ni Mixtures (Ni fraction <i>f</i>)			
Pd(DMG) ₂ bands, kK.	Concn.	Ni(DMG) ₂ bands, kK.	Concn.
21.55	<i>f</i> ² (1 - <i>f</i>)	18.750	<i>f</i> ³
21.775	2 <i>f</i> (1 - <i>f</i>) ²	18.975	2 <i>f</i> ² (1 - <i>f</i>)
22.00	(1 - <i>f</i>) ³	19.200	<i>f</i> (1 - <i>f</i>) ²

a broad intermediate peak in the corresponding mixed crystal (Fig. 9). Also, one can see how the Ni and Pd peaks (Fig. 8), while much less separated and no better defined than the Pt and Pd peaks, still are separately recognizable in mixed Pd, Ni crystals.

In fairness, we must point out that considerable delocalization of the transition is consistent with observation of peaks corresponding to both ion types in a mixed crystal. For example, if the transition involves electron transfer from one molecule to a

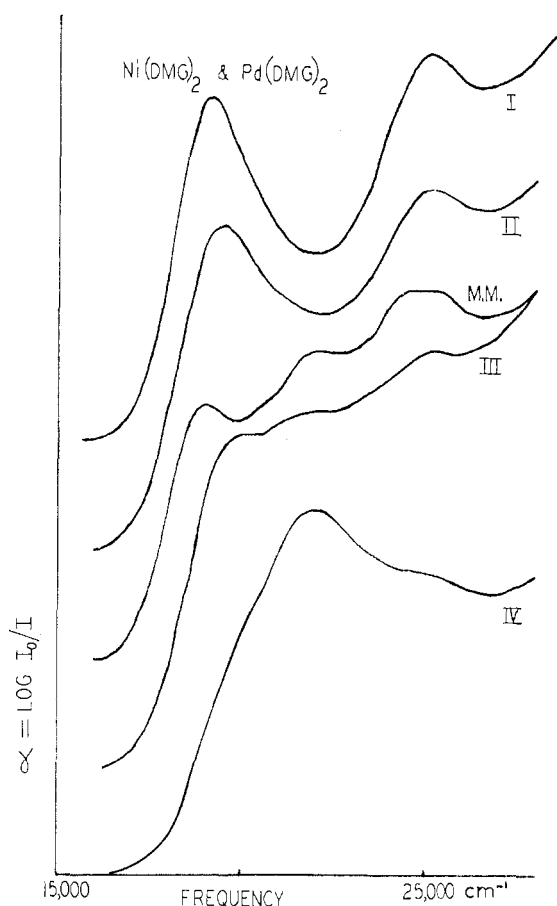


Fig. 8.—Transmission curves of NaCl pellets. M.M. is a mechanical mixture, Ni:Pd::0.635:1. The others are true, uniform mixed crystals, the Ni:Pd ratio being (by two different methods of determination) as follows: I 3.0, 2.09; II 1.0, 0.89; III 0.33, 0.33; IV 0.11, 0.14.

neighboring molecule or molecules, then behavior similar to our phenomenological analysis of the mixed-crystal spectra might well be expected. For example, this kind of transition has been postulated by Robin¹⁴ to explain some bands in the spectrum of Prussian blue; he supposes an electron transfer from one iron ion to another. Here, too, we might have crystal transitions involving electron transfers such as the following: $-\text{Ni}^{+2}-\text{Ni}^{+2}-\text{Ni}^{+2} \xrightarrow{1} -\text{Ni}^{+2}-\text{Ni}^{+3}-\text{Ni}^{+1}$, $-\text{Ni}^{+2}-\text{Ni}^{+2}-\text{Ni}^{+2} \xrightarrow{2} -\text{Ni}^{+1.5}-\text{Ni}^{+3}-\text{Ni}^{+1.5}$, etc. For example, suppose the process involved electron transfer of kind 2; then in a mixed crystal of molecules *a* and *b* there would be six excited states: $a^{-1/2}-a^{+}$, $a^{-1/2}-a^{+}-b^{-1/2}$, $b^{-1/2}-a^{+}-b^{-1/2}$, $b^{-1/2}-b^{+}-b^{-1/2}$, $b^{-1/2}-b^{+}-a^{-1/2}$. The six transitions would be expected to follow a pattern such as that given in our naïve analysis if a fixed ionization energy and "electron affinity" were assigned to each atom. (Here there might be some difficulty in correlating solution with crystal transitions, but this is not really a vital feature of the analysis.) The example just given is but one of many possible assignments which would involve some electron delocalization and yet be compatible with the experimental observations. However, we believe

(14) M. B. Robin, *Inorg. Chem.*, **1**, 337 (1962).

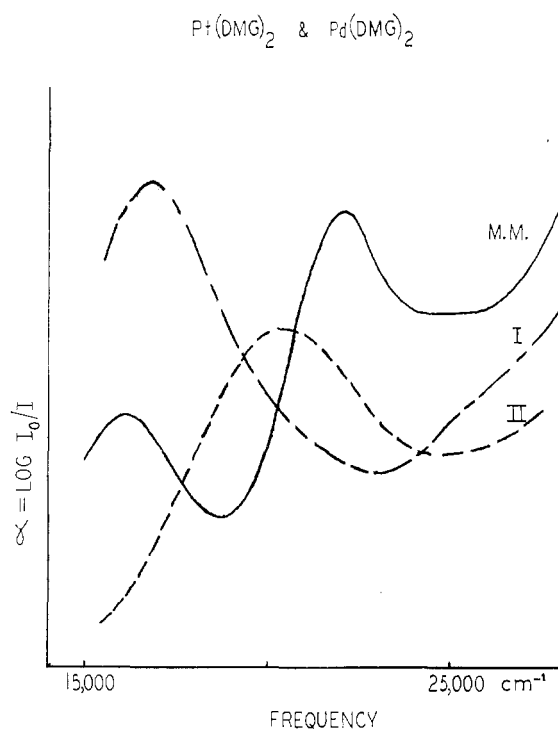


Fig. 9.—Transmission curves for NaCl pellets of mechanical mixture (M.M.) and two batches of true mixed crystals (I and II). The ratio of Pd to Pt is as follows: M.M., 1.96; II, ~1.93; I, ~0.75.

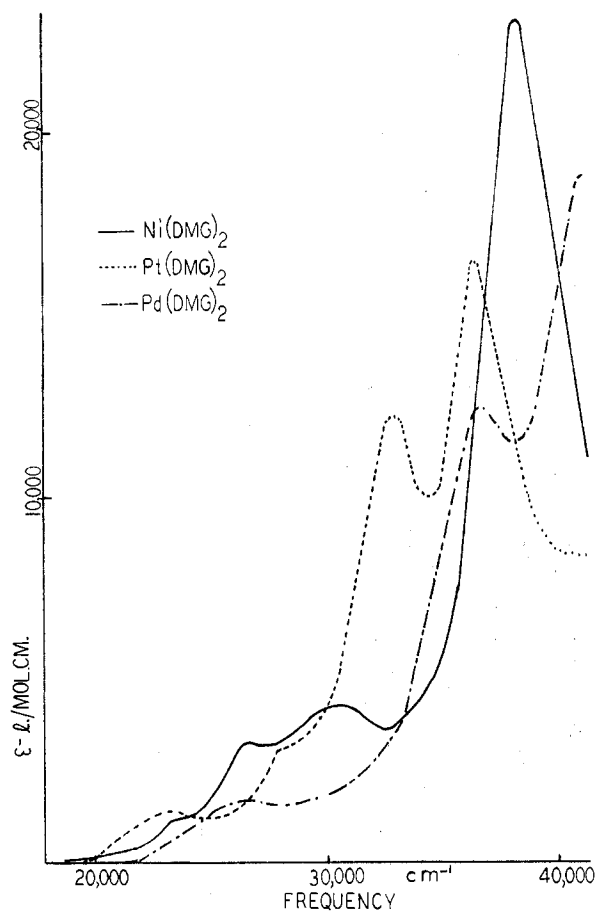
that all such assignments should take at least one (probably the ground) state to be largely localized.

Single Crystal Spectra and Absolute Intensities.—

The extinction coefficients reported in Fig. 2 have the right order of magnitude ($\epsilon \sim 10^2$ l./mole cm.) for usual ligand field d-electron spectra of strongly bound chelates. They also have the right magnitude for several other partially-forbidden types of transition including some charge transfers. It seems rather unlikely that their magnitude is compatible with the suggestion⁴ that they are d-to-p electron promotions, which are highly allowed and should display enormous extinction coefficients.

Observed Polarization vs. d-p Predictions.—The d-p assignment seems not to fit the observed polarization of the red tail, which is stronger in the direction perpendicular to the molecular planes. If the loosest electrons reside in the π d-like molecular orbitals xz and yz , then in group D_{2h} the transitions to the p_z -orbital would be in-plane polarized, while the transitions to p_x and p_y would be z -polarized. Now, the arguments for a drastic lowering of the energy of a p-orbital on account of stabilization by neighboring metal ions would require that the p-orbital in question be p_z . Therefore, the observed polarization (always z for the lowest energy portion of the visible absorption) is in disagreement with the $d_{\pi} \rightarrow p_z$ assignment. On the other hand, if the electron jumped from the A_{1g} orbital resembling $3z^2 - r^2$, then strong z -polarization would be indicated, but the experimental fact that the in-plane component is also fairly strong would be unexplained.

Infrared Spectrum.—As shown in Fig. 4, we observed

Fig. 10.—CHCl₃ solution spectra.

a broad, asymmetric, low-intensity infrared absorption in a large single crystal of Ni(DMG)₂ peaking at about 10.3 kK. The asymmetry is quite pronounced and hints at a structure. However, we could resolve no structure by cooling the crystal to 80°K. It is reasonable to suppose that this band, stretching between 7 and 11.5 kK., contains one or more of the expected d-like nickel ion transitions, which have been hitherto undetected in the nickel bisdioximates. The visible absorption, then, probably consists of the higher-energy d-like transitions and some of the partially-allowed charge-transfer bands; since there are probably several π and π ligand orbitals crowded into a fairly small energy range, the broad nearly featureless character of the visible absorption would be easy to understand.

The Metal-Metal Bond.—There does not seem to be any spectroscopic feature of crystalline Ni(DMG)₂, Pd(DMG)₂, or Pt(DMG)₂ which requires the existence of an actual metal-metal bond (as opposed to the obvious electrostatic interaction), though there has been some controversy about the possibility that the low solubility of Ni(DMG)₂ is caused by such a bond.⁹ Such bonding can perhaps occur incidental to an accident of crystal packing, but evidence for its being an important primary effect is as yet very sparse. For example, the so-called “abnormal” dichroism^{5,15}

(15) C. M. Harris and S. E. Livingstone, *Rev. Pure Appl. Chem.* **12**, 27 (1962).

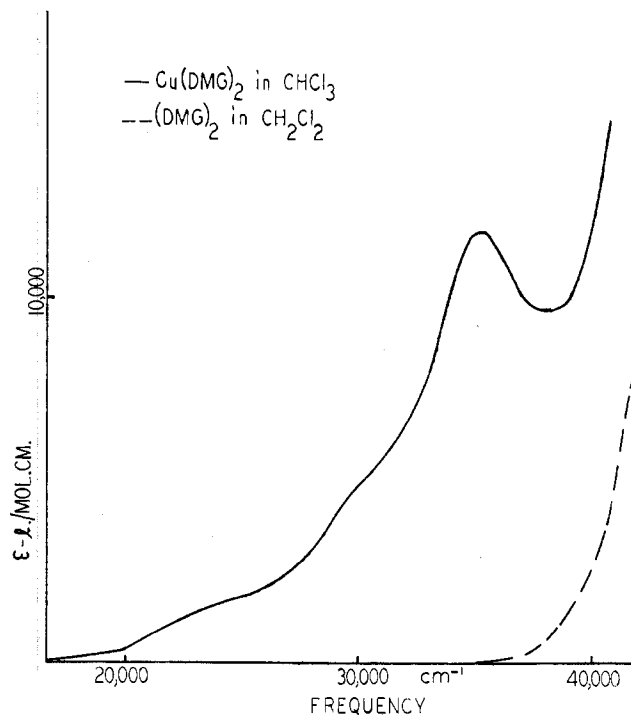


Fig. 11.—Solution spectra.

(cf. Fig. 2) can be a result of the normal vibronic selection rules in a centric molecule and does not—at our current stage of knowledge¹⁶—tell us anything about metal-metal bonding. Yet this seems to have been considered a principal piece of evidence in support of the metal-metal bond theory.¹⁵ Rundle's¹⁷ and Miller's¹⁸ qualitative suggestions involve (in essence) metal chain orbitals formed from the metal 3d(3z² - r²) and 4p(z) orbitals—Rundle favoring a net bonding, Miller, a net antibonding. Certainly, orbitals of this kind can be presumed to form. The question is whether there is very much resulting delocalization of the electrons. It seems just as probable that the crystal structure of these solid compounds is determined more by packing than by covalent intermolecular bonding and that their peculiarities might be explained by largely electrostatic interactions between neighboring molecules. (Such an approach was favored by Zahner and Drickamer,⁴ who assumed the Ni(DMG)₂ molecule to have its usual description modified in the crystal by a differential movement of all the energy levels owing to the presence of neighboring charges along the molecular axis, and who assumed the visible band to be a Ni(DMG)₂ molecular transition from the ground state to an excited state that is lowered greatly in energy by the electrostatic interaction.)

Until recently, the only clear-cut cases of stacking of neighboring metal ions have also been crystals in which the lowest-energy visible band showed polarization perpendicular to the molecular planes. This has been cited as evidence both that a special kind of

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metal-metal bond exists and that the lowest-energy visible band is a special transition associated with the metal chain.¹⁵ However, the case of orthorhombic nickel bis(N-methylsalicylaldimine) [Ni(Me salim)₂] demonstrates the failure of this assumption. In Ni(Me salim)₂, the Ni atoms are lined up in exactly the same way as in Ni(DMG)₂, with almost identical spacing.¹⁹ However, the single crystal spectra taken by Ferguson²⁰ and more recently by us (unpublished) show that the lowest-energy visible band is in-plane polarized, unlike that of Ni(DMG)₂. Thus, so-called "abnormal" dichroism is not a necessary companion to the nickel ion chain structure found in Ni(DMG)₂. Also, inspection of the single-crystal spectra of Ni(DMG)₂ shows that the out-of-plane dichroism is really very slight, being caused merely by a slightly broader red tail of the visible absorption in the out-of-plane direction. Therefore, the *apparent* striking dichroism is not much more than a consequence of the fact that the eye is responding only to light in the fre-

quency region of the red tail, as the absorption of light by the crystal is practically total in the regions of the shoulder or maximum. Finally, there is nothing abnormal in out-of-plane band polarization for a planar molecule. The "abnormal" designation arises from the fact that π - π transitions of planar organic molecules are, to a good approximation, symmetry forbidden in out-of-plane polarization. However, when other types of transitions can occur (particularly where a transition metal ion is involved) many will be out-of-plane permitted.

The temperature effect on the single-crystal absorption spectrum of Ni(DMG)₂ (Fig. 3) is very small. This fact hints at one of two alternatives: (1) the transition probability is not caused by the vibronic mechanism and (2) the transition probability is produced by vibronic coupling to very high-frequency modes. One cannot yet choose between these alternatives. There is a small red shift as the temperature is decreased; it is evident both in the single crystal (Fig. 3) and in polycrystalline samples.¹ We presume that this shift is caused by sample contraction and is merely another manifestation of the red pressure shift.⁴

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CONTRIBUTION FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY,
IOWA STATE UNIVERSITY, AMES, IOWA

The Vibronic Absorption Spectrum and Dichroism of Potassium Tetrachloroplatinate(II)¹

BY DON S. MARTIN, JR., AND CHARLES A. LENHARDT

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The absorption spectrum from 550 to 270 m μ for a single crystal of K₂PtCl₄, with light polarized parallel and normal to the symmetry axis of the PtCl₄⁻² ion, is reported. Absorption peaks are well resolved so that a shift in maxima between alternative polarizations is apparent. A consideration of the vibronic interactions permits the assignment of the ¹A_{1g} → ¹A_{2g} transition. An assignment of other transitions is proposed on the basis of the shift of maxima which orders the d-orbitals d_{z²} > d_{xy} > d_{xz}, d_{yz}. The influence of Jahn-Teller splitting of the excited E_g state is discussed.

Introduction

The absorption spectrum of the square-planar ion, PtCl₄⁻², in aqueous solution contains four peaks which can be attributed to transitions between d-electron states. However, various authors have proposed different transition assignments for these observed peaks.²⁻⁴

The spectrum of a freshly prepared K₂PtCl₄ solution in dilute HCl is shown in Fig. 1. The intense absorption above 36,000 cm.⁻¹ is presumably due to a charge-transfer process.⁴ Below 36,000 cm.⁻¹, two strong peaks, labeled 3 and 4, and a weaker peak, 2, are clearly evident. The ν_{\max} , ϵ_{\max} , and oscillator strengths

from a Gaussian analysis for the spectrum are in Table I. As a consequence of the Gaussian analysis a very weak absorption (1), of perhaps questionable existence, appears at about 17,000 cm.⁻¹. As shown in Fig. 1, the sum of the Gaussian components deviates by a similar amount in the region of 23,000 cm.⁻¹.

Crystals of K₂PtCl₄ are ideally suited for the study of polarized spectra for this ion since each PtCl₄⁻² occupies a site in the unit cell with the full D_{4h} symmetry and with one ion per unit cell.⁵ Therefore the fourfold symmetry axis (z-axis) is aligned with the crystallographic c-axis. The ions lie directly over one another with an eclipsed arrangement of chlorides and with platinum atoms separated along the z-axis by 4.13 Å. With the inversion symmetry and the exact alignment of the symmetry axes in the crystals, their polarized

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