

The Crystalline Perturbation of a Magnetic Dipole Transition in Tetracyanonickelates (II)

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The absorption spectra of a series of tetracyanonickelates have been recorded, in order to throw light upon the nature of the weak, polarized 22 500 cm^{-1} absorption band in $\text{BaNi}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$. A theoretical analysis is presented, which associates the band with a magnetic dipole transition in an isolated $\text{Ni}(\text{CN})_4^{2-}$ unit. Arguments based on perturbation theory indicate that the energy of this transition is very sensitive to the mutual arrangement of $\text{Ni}(\text{CN})_4^{2-}$ ions in the crystal, and an explanation is thus provided for the fact, that the 22 500 cm^{-1} band is observed only in compounds containing barium.

1. INTRODUCTION

In a previous paper from this laboratory the polarized absorption spectra of a number of crystals containing the tetracyano nickelate ion were reported and discussed.¹ The barium tetracyanonickelate remained a puzzle, however, in that it showed a weak, polarized absorption band at 22 500 cm^{-1} , in addition to the bands exhibited by the other crystals. The polarization of this special barium band is such that it cannot be explained as being due to an electric dipole transition. In the present communication we suggest that the band is due to a magnetic dipole transition, whose energy is very dependent upon the packing of the square planar $\text{Ni}(\text{CN})_4^{2-}$ ions in the crystal. For this reason the band is covered by more intense ones in crystals not containing barium.

More explicitly, it is suggested that the special band is connected with the in-plane transition $d_{xy} \rightarrow d_{x^2-y^2}$ of the $\text{Ni}(\text{CN})_4^{2-}$ unit. The unusual, strong variation of the energy associated with this transition in going from one compound to another is made possible by the fact that the planar $\text{Ni}(\text{CN})_4^{2-}$ ions in the crystal are stacked on top of each other in a card-deck like fashion. Two successive tetracyano-nickelate units are rotated with respect to each other, the angle of rotation, γ , being a parameter of the crystal cations (*i.e.* Ba^{2+} , K^+ , *etc.*). The $d_{xy} \rightarrow d_{x^2-y^2}$ transition energy is very dependent on γ through nearest neighbour interaction. This interaction is treated here by

perturbation theory, which also explains why the other $d \rightarrow d$ transitions in the tetracyano nickelates are rather insensitive to variations in γ .

The theoretical analysis of this paper makes use of the X-ray investigations of the two accompanying papers^{2,3} as well as new spectroscopic results to be presented here. A number of tetracyano nickelates, varying with respect to the cations, have been prepared and their absorption spectra measured in order to clarify the nature of the special barium band. The results of these measurements are presented in Section 2. Section 3 contains some remarks about the crystal structures of the cyanides of importance for the further discussion, and the theoretical considerations are given in Section 4.

2. SPECTROSCOPIC CHARACTERISTICS OF THE BARIUM BAND

A. *Experimental.* The following compounds have been studied:

BaNi(CN)₄·4H₂O, BaNi(CN)₄·4D₂O, BaPd(CN)₄·4H₂O, K₂Ba[Ni(CN)₄]₂·4H₂O, Cs₂Ni(CN)₄·3H₂O, CaNi(CN)₄·5H₂O, SrNi(CN)₄·5H₂O, and dilute mixed crystals of BaNi(CN)₄·4H₂O in BaPd(CN)₄·4H₂O. All crystals were grown by slow evaporation from aqueous solution; the K₂Ba[Ni(CN)₄]₂·4H₂O from an equimolar mixture of the potassium and the barium salts. Mixed crystals containing BaNi(CN)₄·4H₂O in BaPd(CN)₄·4H₂O form easily and a range of crystals has been grown. These crystals were analyzed for Ni/Pd ratio by dissolving in water and measuring the solution spectrum, since Ni(CN)₄²⁻ and Pd(CN)₄²⁻ absorb in quite different regions in aqueous solutions. Crystals were studied with a nickel content from 100 % to 2.7 %, at which point the absorption due to the Ni(CN)₄²⁻ becomes too weak to be seen.

Crystal spectra were obtained using methods described previously.¹ For the measurements made at liquid helium temperatures a commercially available dewar was used in conjunction with a Cary 14 and a 2-meter Zeiss grating spectrograph. Polarized spectra were taken on {110} and are reported $\parallel c(\pi)$ and $\perp c(\sigma)$. Sections of crystal exposing a non-principal face $\perp c$ were cut; spectra taken on these faces are termed axial (although we are not dealing with a uniaxial crystal).

B. *Results.* Among the "pure" crystals studied only BaNi(CN)₄·4H₂O, BaNi(CN)₄·4D₂O, and K₂Ba[Ni(CN)₄]₂·4H₂O showed the special band. The band was only seen in $\perp c(\sigma)$ polarization and not at all in the axial spectrum. For BaNi(CN)₄·4H₂O the characteristics of the band are at 300°K:

$\nu_{\max} = 22\,400 \pm 25 \text{ cm}^{-1}$, $\Delta\nu_{1/2} = 500 \text{ cm}^{-1}$, $\epsilon_{\max} = 2 \pm 0.3$. In Ref. 1 the deuterated compound was reported to behave differently from the undeuterated compound. A more thorough study has shown the two compounds to behave identically in all respects. For K₂Ba[Ni(CN)₄]₂·4H₂O the band has the following characteristics at 300°K:

$\nu_{\max} = 23\,980 \pm 25 \text{ cm}^{-1}$, $\Delta\nu_{1/2} = 300 \text{ cm}^{-1}$, $\epsilon_{\max} = 2$ per Ni(CN)₄²⁻ unit. These results are represented in Fig. 1. Upon cooling to liquid helium temperatures, the band showed a small decrease in intensity (~10 %) with no development of structure and only a very minor frequency shift.

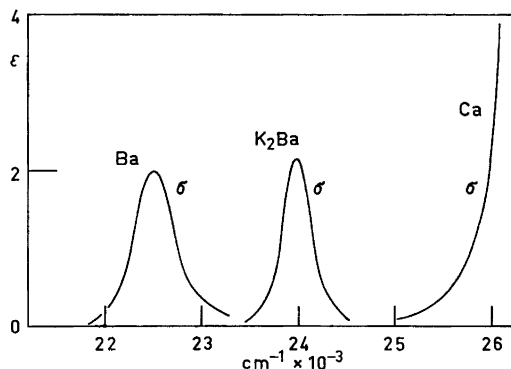


Fig. 1. $\sigma(\perp c)$ polarized absorption spectra on $\{110\}$ showing the special band for $\text{BaNi}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$ and $\text{K}_2\text{Ba}[\text{Ni}(\text{CN})_4]_2$ and the $27\,000\text{ cm}^{-1}$ band edge for $\text{CaNi}(\text{CN})_4 \cdot 5\text{H}_2\text{O}$.

The mixed crystals of $\text{BaNi}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$ in $\text{BaPd}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$ also exhibit the special band, but with the added property that the frequency of the band increases continuously with dilution of $\text{Ni}(\text{CN})_4^{2-}$ in $\text{Pd}(\text{CN})_4^{2-}$. This is shown in Fig. 2; the total range of the frequency shift is seen to be approximately 2000 cm^{-1} , although the results are uncertain for the very dilute crystal spectra due to the decreased intensity of the band and the nearness to the edge of the intense $27\,000\text{ cm}^{-1}$ band of the host.

Colin⁴ has recently observed a very small peak in the σ -spectrum of a number of tetracyanonickelates not containing barium. Thus $\text{CaNi}(\text{CN})_4 \cdot 5\text{H}_2\text{O}$ was reported to show a peak at $23\,200\text{ cm}^{-1}$, and $\text{SrNi}(\text{CN})_4 \cdot 5\text{H}_2\text{O}$ a peak at

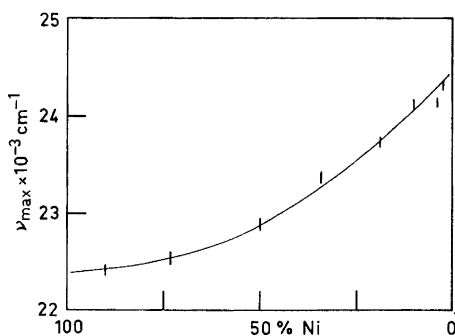


Fig. 2. Dependence of the special barium band frequency on Ni/Pd ratio for dilute mixed crystals of $\text{BaNi}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$ in $\text{BaPd}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$.

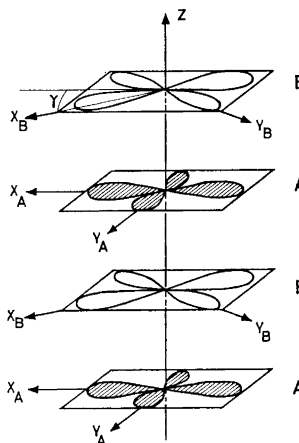


Fig. 3. Stacking of $\text{Ni}(\text{CN})_4^{2-}$ units in a "chain".

23 900 cm^{-1} . We have, however, not succeeded in finding the smallest indication of such peaks in our spectra, and it is possible, as pointed out by Colin,⁴ that the small peaks can be traced back to the π -spectrum. That the π -spectrum may, in fact, influence the form of the σ -spectrum in these crystals, was originally pointed out by Ballhausen *et al.*¹

3. CRYSTAL STRUCTURES OF SQUARE PLANAR CYANIDES

Complete crystal structure determinations are now known for a number of tetracyanonickelates,^{2,3} and a common feature for all the compounds is that the cyanide units are stacked on top of each other along the crystallographic c -direction. Thus we are dealing with parallel chains of these stacked units, the space between the chains being occupied by the cations and the water molecules of the compound. The packing of $\text{Ni}(\text{CN})_4^{2-}$ units in a given chain is of the type ABABAB. . . along the Ni—Ni axis (the crystallographic c -axis). All A-units occupy translationally equivalent sites as do the B-units, but the A and B units may be rotated through an angle γ with respect to each other about the common z (Ni—Ni) axis, as shown in Fig. 3. The A-unit planes are, to a good approximation (a few degrees) parallel with the B-unit planes. In the analysis to follow, we consider them exactly parallel.

Table 1 lists the angle γ and shortest Ni—Ni distance for some crystals whose exact structures are known. From the analysis of Section 4 it follows that the value $\gamma=0$ corresponds to the lowest energy of the chain, but the value of γ is presumably to a higher degree determined by the packing of cations and water molecules between the chains.

4. THEORETICAL PART

A. *Electronic structure of an isolated $\text{Ni}(\text{CN})_4^{2-}$ unit.* In order to throw into relief the special crystal effects in the tetracyanonickelate spectra, we summarize the electronic properties of an isolated square planar $\text{Ni}(\text{CN})_4^{2-}$ unit. Square planar complexes have been treated by ligand field theory⁷ and by molecular orbital theory.⁸ Molecular orbital theory predicts the level

Table 1. The rotation angle γ and shortest Ni—Ni distance in various crystals.

Crystal	γ	Ni—Ni distance	Reference
$\text{BaNi}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$	45°	3.36 Å	3
$\text{CaNi}(\text{CN})_4 \cdot 5\text{H}_2\text{O}$	$26^\circ 56'$	3.39 Å	2
$\text{SrNi}(\text{CN})_4 \cdot 5\text{H}_2\text{O}$	0°	3.64 Å	5

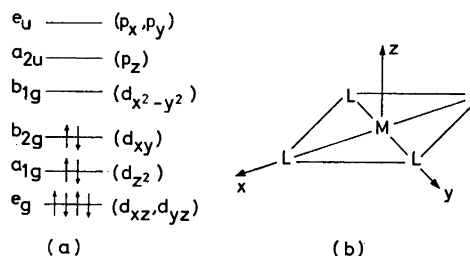


Fig. 4. a. Qualitative molecular orbital level scheme for a square planar complex ML_4 . b. Coordinate system used to classify orbitals in D_{4h} symmetry.

scheme of Fig. 4,* in which the highest occupied orbitals (b_{2g} , a_{1g} , e_g in D_{4h} symmetry) and the lowest empty orbital (b_{1g}) are antibonding and essentially made up of metal d -orbitals. The empty a_{2u} and e_u orbitals are linear combinations of metal p -orbitals and ligand π -orbitals. Ligand field theory predicts the same level scheme in a strong tetragonal field; in a weak tetragonal field the a_{1g} and b_{2g} orbitals become interchanged.

The solution spectrum of $Ni(CN)_4^{2-}$ is composed mainly of charge transfer transitions and has been interpreted by Gray and Ballhausen⁸ using the level scheme of Fig. 4. Their assignments are given in Table 2. In all the crystal spectra transitions at 23 000 cm^{-1} and 27 000 cm^{-1} are observed. These have been interpreted as ligand field transitions by Ballhausen *et al.*¹ The proposed assignments are also given in Table 2.

It is suggested here that the special barium band described in Section 2B is due to the magnetic dipole allowed transition ${}^1A_{1g} \rightarrow {}^1A_{2g}$ ($b_{2g} \rightarrow b_{1g}$). This suggestion is in complete accordance with the spectral data of section 2B: From $\Delta\nu_{1/2}$ and ϵ_{max} one finds the oscillator strength 5×10^{-6} for $BaNi(CN)_4 \cdot 4H_2O$, characteristic for a magnetic dipole transition. Furthermore, a magnetic dipole transition is governed by the matrix element

Table 2. Transitions and assignments in $Ni(CN)_4^{2-}$.

Frequency, cm^{-1}	ϵ	Assignment
32 300	700	${}^1A_{1g} \rightarrow {}^1B_{1u}$ ($b_{2g} \rightarrow a_{2u}$)
35 200	4 200	${}^1A_{1g} \rightarrow {}^1A_{2u}$ ($a_{1g} \rightarrow a_{2u}$)
37 600	10 600	${}^1A_{1g} \rightarrow {}^1E_u$ ($e_g \rightarrow a_{2u}$)
> 22 400	2	${}^1A_{1g} \rightarrow {}^1A_{2g}$ ($b_{2g} \rightarrow b_{1g}$)
23 000	~ 50	${}^1A_{1g} \rightarrow {}^1B_{1g}$ ($a_{1g} \rightarrow b_{1g}$)
27 000	~ 100	${}^1A_{1g} \rightarrow {}^1E_g$ ($e_g \rightarrow b_{1g}$)

* The coordinate axes in Fig. 4 are here chosen as in Refs. 7 and 8. In Ref. 1 a different choice of axes was preferred for practical reasons ($D_{4h} \rightarrow T_d$ correspondence). The choice of axes is not of particular importance in the present context, but it should be noted that the notations b_{1g} and b_{2g} become interchanged in going from one coordinate system to the other.

$$\vec{H} \cdot \langle \varphi_f | \hat{L}_z | \varphi_i \rangle$$

where φ_f and φ_i are the wavefunctions for the final and initial states, respectively, and \vec{H} is the magnetic vector of the incident light. Since \hat{L}_z transforms as A_{2g} in the D_{4h} point group, the ${}^1A_{1g} \rightarrow {}^1A_{2g}$ transition should only be seen when the magnetic vector, \vec{H} , has a component along the z -axis (Fig. 4b). In particular, it should not be seen when the propagation vector of the light is along the z -axis. The specific barium band has exactly these polarization properties: it is absent in the axial spectrum and in π -polarization, present in σ -polarization.

The assignment ${}^1A_{1g} \rightarrow {}^1A_{2g}$ for the barium band is also in agreement with the theoretical investigations of Ballhausen *et al.*¹ regarding the geometries of the $\text{Ni}(\text{CN})_4^{2-}$ unit in the various excited states. These investigations showed (see Fig. 6 of Ref. 1), that $\text{Ni}(\text{CN})_4^{2-}$ should remain square planar in the ${}^1A_{2g}$ state, whereas it should distort during the other $d-d$ transitions of the singlet-singlet type. If the barium band had been associated with a transition to a distorted excited state, a broadening of the band due to the exciting vibration would have been expected, as well as vibrational structure at low temperatures. But the band remains sharp and without structure even at helium temperatures, which is understandable only for the assignment ${}^1A_{1g} \rightarrow {}^1A_{2g}$.

Having identified the special band we turn to the specific crystal effects which prohibit the observation of the band in compounds not containing barium.

B. Crystal effects in the ligand field transitions. The precisely determined Ni—Ni distance of 3.36 Å in $\text{BaNi}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$ ³ corresponds to the van der Waals' distance between two carbon atoms; the distance between two sheets in graphite being 3.35 Å. This distance is probably too large for an effective metal-metal bond to be formed. It is comparable with the Ni—Ni distance in nickel dimethylglyoxime, for which several authors have proposed a strong metal-metal bond. However, as shown by Ingraham,⁹ the required $3d-4p$ promotion energy is too large for a metal-metal bond to be formed in the ground state of the crystal. On the basis of these considerations, we conclude that the single $\text{Ni}(\text{CN})_4^{2-}$ units preserve their identity in the ground state.

The orbital diagram of Fig. 4 can therefore be applied also when the $\text{Ni}(\text{CN})_4^{2-}$ unit is embedded in a crystal. The one-electron orbitals are, however, perturbed by the crystalline environment. We are here interested in that part of the perturbation, $V(\gamma)$, which depends upon the angle γ . This perturbation is the same for all $\text{Ni}(\text{CN})_4^{2-}$ units. Fixing our attention on a B-site unit (Fig. 3), we get an approximate expression for $V(\gamma)$ by placing eight point charges $-q$ on the cyanide groups of the neighbouring A-units. Expanding the electrostatic field from these eight charges we get

$$V(\gamma) = - \frac{\sqrt{70\pi}}{3} q \frac{r^4}{R^5} (1 - \cos^2\omega)^2 \{ Y_4^4(\vartheta, \varphi) e^{4i\gamma} + Y_4^{-4}(\vartheta, \varphi) e^{-4i\gamma} \} + \dots (1)$$

where r, ϑ, φ are spherical coordinates on B, referred to the coordinate system x_B, y_B, z_B of Fig. 3. R is the distance from the nickel B-ion to the charges q , and ω gives the angle between the z -axis (Fig. 3) and the radius vector \vec{R} . In (1) we have retained only the first term which shows deviation from axial symmetry.

We now find the following matrix elements between d -orbitals on center B, expressed in the coordinate system x_B, y_B, z_B :

$$\langle d_{z^2} | V(\gamma) | d_{z^2} \rangle = \langle d_{xz} | V(\gamma) | d_{xz} \rangle = \langle d_{yz} | V(\gamma) | d_{yz} \rangle = 0 \quad (2)$$

$$\langle d_{x^2-y^2} | V(\gamma) | d_{x^2-y^2} \rangle = -\langle d_{xy} | V(\gamma) | d_{xy} \rangle = \frac{5}{3} \frac{q\alpha}{R^5} (1 - \cos^2\omega)^2 \cos 4\gamma \quad (3)$$

where

$$\alpha = \int_0^\infty [R_{3d}(r)]^2 r^4 r^2 dr \quad (4)$$

R_{3d} being the normalized radial function for a $3d$ -orbital. α depends upon the effective nuclear charge Z for the d -orbital through a factor Z^{-4} .¹⁰

The molecular orbitals e_g, a_{1g}, b_{2g} , and b_{1g} of Fig. 4 are not d -orbitals, but are linear combinations of d -orbitals and ligand orbitals. As in ordinary crystal field theory we represent them by d -orbitals. Doing so requires

$$Z(b_{2g}) \ll Z(b_{1g}) \quad (5)$$

with Z the effective nuclear charge. This is so because the metal d_{xy} orbital can combine with bonding as well as antibonding π -orbitals of the CN^- ligands, whereas the $d_{x^2-y^2}$ orbital can only combine with the ligand σ -orbitals.⁸ Thus the $b_{2g}(d_{xy})$ orbital is expected to be delocalized to a much greater extent than the $b_{1g}(d_{x^2-y^2})$ orbital, hence (5).

Since α (from Eqn. 4) is proportional to Z^{-4} we neglect the perturbation of the b_{1g} orbital, *i.e.* $\langle b_{1g} | V(\gamma) | b_{1g} \rangle$, relative to the perturbation of the b_{2g} orbital, *i.e.* $\langle b_{2g} | V(\gamma) | b_{2g} \rangle$. We therefore obtain:

$$\langle e_g | V(\gamma) | e_g \rangle = \langle a_{1g} | V(\gamma) | a_{1g} \rangle = \langle b_{1g} | V(\gamma) | b_{1g} \rangle = 0 \quad (6)$$

$$\langle b_{2g} | V(\gamma) | b_{2g} \rangle = D \cos 4\gamma \quad (7)$$

where D is a constant. Using these matrix elements, we obtain the level scheme of Fig. 5 for the ligand field orbitals as functions of γ . It should be

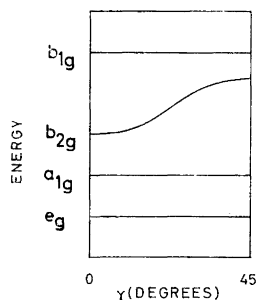


Fig. 5. Orbital energies of ligand field orbitals as function of γ .

emphasized that this energy scheme is a qualitative one and whether or not the b_{1g} orbital has a slight functional dependence on γ is unimportant to the analysis.

It follows from Fig. 5 that the only transition sensitive to the value of γ is the ${}^1A_{1g} \rightarrow {}^1A_{2g}$ ($b_{2g} \rightarrow b_{1g}$) transition which is displaced towards longer wavelengths as γ increases from 0 to 45° . For $\text{BaNi}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$ (and presumably $\text{K}_2\text{Ba}[\text{Ni}(\text{CN})_4]_2 \cdot 4\text{H}_2\text{O}$ ¹¹) $\gamma \sim 45^\circ$ so the appearance of the special band in these two crystals is now understandable, the transition energy having been pushed down to $22\,400\text{ cm}^{-1}$ by $V(\gamma)$.* The exact range of γ over which this transition may be observed is, of course, not possible to determine.** That the transition is not seen in the Ca crystal, in which $\gamma = 26^\circ 56'$ (Table 1), probably means that the band is occurring at higher energies and is covered by the more intense band at $27\,000\text{ cm}^{-1}$. This reasoning may also be applied to the Sr crystal, in which $\gamma = 0$ (Table 1); in this crystal the perturbation $V(\gamma)$ of Eqn. 1 is also diminished by the larger value of R (smaller value of ω), due to the larger Ni—Ni distance (Table 1).

Several authors^{8,12} have claimed that they have observed the special band in solution. We have been unable to verify this finding, and it is also made unlikely by the present analysis. Solvent perturbations are, in all probability, axial in nature and therefore have no influence on in-plane transitions.

C. *Dilute mixed crystals.* It has been shown above that the ${}^1A_{1g} \rightarrow {}^1A_{2g}$ transition is very dependent upon the crystalline environment through the angle γ . When $\text{BaNi}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$ is dissolved in the isomorphous $\text{BaPd}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$ the ${}^1A_{1g} \rightarrow {}^1A_{2g}$ transition shifts continuously to higher energies (Fig. 3). This frequency shift is not due to a dependence on γ under our assumption that the packing in the Ni and Pd salt is the same.

The large frequency shift can best be explained within our qualitative model by ascribing it to the charge (q) dependence of the perturbing potential V (see (1)) since q is likely to be smaller for a $\text{Pd}(\text{CN})_4^{2-}$ unit than for a $\text{Ni}(\text{CN})_4^{2-}$ unit.

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* $\text{BaPd}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$ and $\text{BaPt}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$ are isomorphous with $\text{BaNi}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$.² For the former two, dissolved in aqueous solution, the lowest energy at which absorption is observed is $39\,000\text{ cm}^{-1}$ (shoulder, $41\,700\text{ cm}^{-1}$ maximum) and $35\,850\text{ cm}^{-1}$, respectively. In single crystals, there is absorption at $27\,000\text{ cm}^{-1}$ and $22\,000\text{ cm}^{-1}$, respectively. The high intensity of these bands rules out a magnetic dipole mechanism although it is possible that they represent electric dipole transitions associated with the ${}^1A_{1g} \rightarrow {}^1A_{2g}$ transition, perturbed by the crystalline environment.

** The green form of Magnus' salt, $\text{PtCl}_4 \cdot \text{Pt}(\text{NH}_3)_4$ has a similar arrangement of PtX_4 units in the crystal to that seen in $\text{BaNi}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$ and specifically $\gamma \sim 45^\circ$. It is possible that the crystalline perturbation model used in the present paper will be applicable to this green Magnus' salt as well as to other complexes which exhibit similar structures in the solid state. This aspect is presently under investigation in these laboratories.

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