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The Source of Spectral Band Intensity in Tris Ethylenediamine Complexes

Tris Ethylenediamine Nickel (II) Nitrate

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The crystal spectrum of Ni $en_3(NO_3)_2$ is assigned. At low temperatures, the development of discrete vibrational structure has allowed the identification of the transition $^3A_2 \to {}^1A_1$. This leads to the proposal that a major portion of the spectral band intensities arises from vibronic contributions in the molecular symmetry group. This agrees with our earlier observations on the $[Co\ en_3]^{3+}$ ion and the result is likely to be applicable to all tris ethylenediamine metal complexes.

Le spectre du cristal de Ni $en_3(NO_3)_2$ est analysé. A basse température, l'apparition d'une structure vibrationnelle discrète a permis l'identification de la transition $^3A_2 \to {}^1A_1$. Ceci conduit à la proposition selon laquelle la majeure partie de l'intensité de la bande spectrale est dûe à des contributions vibroniques dans le groupe de symétrie moléculaire. Ceci s'accorde avec nos observations antérieures sur l'ion $[Co\ en_3]^{3+}$ et ce résultat est susceptible d'être appliqué à tous les complexes métal tri-éthylène diamine.

Das Spektrum des Kristalls Ni $en_3(NO_3)_2$ wird untersucht. Bei niederer Temperatur ermöglicht das Auftreten einer diskreten Schwingungsstruktur die Identifizierung des Übergangs $^3A_2 \to {}^1A_1$. Dies führt zu dem Vorschlag, daß ein großer Teil der Intensität der Bande vom Beitrag der Schwingungen in der molekularen Symmetriegruppe herrührt. Das stimmt auch mit unseren früheren Beobachtungen beim $[Co\ en_3]^{3+}$-Ion überein. Das Resultat ist auf alle Tris-äthylendiamin-Metallkomplexe anwendbar.

Introduction

Recently [3] we have given some attention to the resolution of some fundamental aspects of the spectroscopy of trigonally distorted tris bidentate metal complexes. In some instances there remains some ambiguity in the conclusions because the crystal site symmetry of the central metal ion is lower than the symmetry assumed by the single complex units. In the crystal, tris ethylenediamine nickel (II) nitrate this problem is resolved because the site symmetry of the nickel ion and the molecular geometry of the complex ion are equivalent [9].

Since the energy level scheme for octahedral nickel (II) is well documented [6] this seems an ideal system on which to extend the former investigation.

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Crystal Structure

Tris ethylenediamine nickel (II) nitrate is hexagonal [9], space group $D_6^6 - P_{6_3}22$

$$\begin{array}{rl} a = b = 8.87\ \text{Å} & \text{Molecular symmetry } D_3 \\ c = 11.41\ \text{Å} & \text{nickel site symmetry } D_3 \\ z = 2\,. & \end{array}$$

The crystals were grown from aqueous solutions and are usually elongated along the c axis. The threefold axis of the nickel site and the three fold axis of the complex unit are both parallel to the c axis of the crystal. The chelate molecule appears to be substantially distorted away from an octahedron, the internal chelate angles are reported to be 82.3 ± 1.0°.

Experimental

Crystal spectra were obtained on a well developed face in the zones $\{11\bar{2}0\}$ or $\{10\bar{1}0\}$ with the electric vector of the incident radiation either parallel ($\pi = z$) or perpendicular ($\sigma = xy$) to the crystal c axis. Some crystals were sectioned normal to the c axis and spectra were obtained with radiation propagated down this axis. These represent axial spectra.

Deuteration of the compound was carried out by three sucsessive recrystallizations from D_2O. Infrarent spectra in the region of the N-H stretching and bonding modes indicate that at least $90^0/_0$ deuteration was achieved. Axial, π and σ spectra were obtained for the deuterated crystals.

Crystals were identified and oriented by X-ray methods. Measurements have been made with crystals held at 300°, 77°, 25° and 5°K using commercial dewars and a Cary 14 spectrophotometer.

Results

The 300° K spectrum is similar to the solution spectrum [1] and thus supports the assumption that the spectrum is intramolecular in origin. Tab. 1 and Fig. 1 summarize the results. At lower temperatures several new features appear.

Table 1. *Spectral details for* Ni en_3^{2+} *in crystals at 300° and 25°K. The assignments (see Fig. 1) identify, on the basis of polarization behaviour, the trigonal field components of each octahedral level*

Excited State	Temperature (°K)	ν_{max} (cm^{-1})	ε_{max}	$\Delta\nu^{1}/_{2}$ (cm^{-1})	f
$^3E[^3T_2(F)]$	300	11,330	5.8	3100	8.3×10^{-5}
	25	11,650	5.8	3000	8.0×10^{-5}
$^3A_1[^3T_2(F)]$	300	11,330	7.0	2800	9.0×10^{-5}
	25	11,650	7.0	2800	9.0×10^{-5}
$^1E(D)$	300, 25	(12,700)	—	—	—
$^3E[^3T, (F)]$	300	18,520	5.1	3200	7.5×10^{-5}
	25	18,600	4.4	2800	5.7×10^{-5}
$^3A_2[^3T_1(F)]$	300	18,600	3.3	3100	4.7×10^{-5}
	25	18,950	2.4	2600	2.9×10^{-5}
$^1A_1(G)$	25	21,363	0.7	23	7.4×10^{-8}
$^1T_1(D)$	25	24,700	0.1	ca. 2000	ca. 9×10^{-7}
$^3E[^3T_1(P)]$	25	29,750	6.0	ca. 2700	ca. 7.5×10^{-5}

In all cases the axial spectrum agrees substantially with the $\perp$ (or σ) spectrum.
$f = 4.6 \times 10^{-9}\ \varepsilon_{max} \cdot \Delta\nu_{1/2}$.

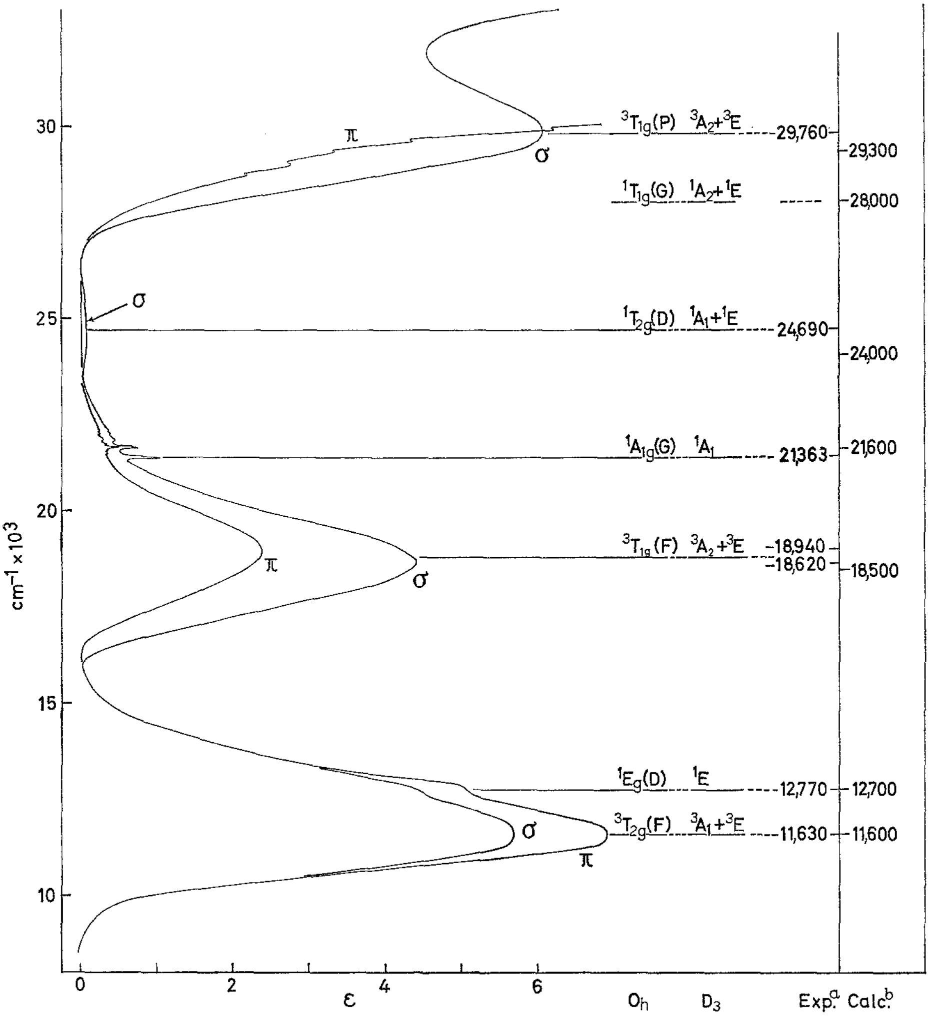

Fig. 1. The polarized absorption spectrum of Ni en_3 $(NO_3)_2$. To higher energies a smooth intense absorption sets in and precludes further measurement. The assignments are those arrived at by assuming the molecule to be octahedral

Firstly, there is an overall reduction in absorption band intensities*. Secondly, extensive, well resolved finestructure develops in the region between 21,300 and 23,000 cm^{-1} (Tab. 1, Fig. 2) and finally, less well resolved structure, with its lowest member at 28,700 cm^{-1} (Tab. 1), appears in the $\pi(z)$ polarization.

In all cases the coincidence of the $\sigma(xy)$ spectrum with the axial spectrum confirms the operation of an electric dipole intensity gaining mechanism.

Apart from very minor energy shifts, up to 50 cm^{-1} in zero point energy changes and effectively zero in vibrational structure, the deuterated crystals show spectra equivalent to the protonated species.

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* This does not appear to be so for the 21,363 cm^{-1} system although, at higher temperatures, the band is so ill defined that very little of a quantitative nature may be said about the intensity variation with temperature.

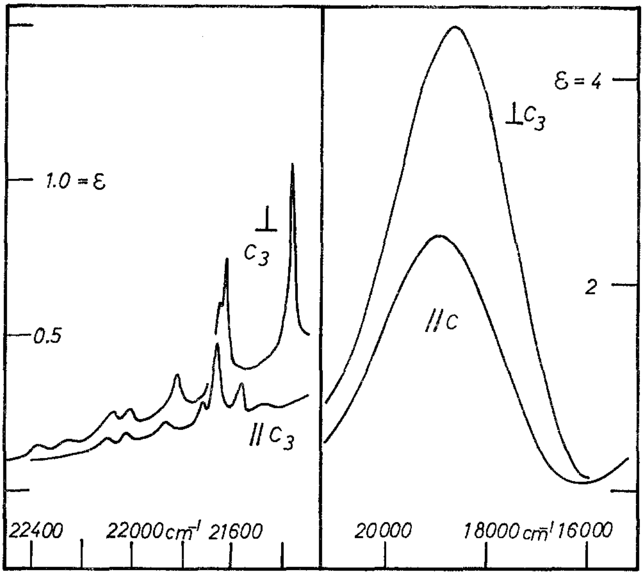

Fig. 2. An enlarged section of the visible absorption systems. The scale for the two halves of the figure differs and it is drawn thus in order to demonstrate the correspondence between the "allowed" σ (xy) components and the "forbidden" π (z) components (see text)

Assignments

The correspondence between solution and crystal results confirms the near octahedral nature of the potential field and, as far as energies are concerned, assignments may be made in an octahedral model*. This is demonstrated in Fig. 1. From a consideration of the energy level scheme [*6*], it is expected that all absorption bands should be broad and with $\nu_{\max}$ well removed from the (0, 0) position excepting those corresponding to the intraconfigurational transitions $^3A_{2g} \rightarrow {}^1A_{1g}$ and $^3A_{2g} \rightarrow {}^1E_g$ for which just the opposite behaviour may be anticipated. In the case of the latter transition, the inclusion of spin-orbit coupling (with $Dq \sim 1100$ cm^{-1}) somewhat modifies these arguments. The assignments, arrived at from energy considerations alone, are in complete accord with this proposal and this lends strong support to the assigments, especially in the visible region.

In addition, in the lower symmetry of the chelated complex and the nickel ion site (D_3), polarization data, combined with symmetry determined selection rules, should allow further identifications and a confirmation of the proposed assignment. In D_3 the octahedral representations transform as shown in Fig. 1 and the electric dipole selection rules are,

$A_2 \longleftrightarrow A_2$	forbidden
$A_2 \longleftrightarrow A_1$	allowed, z polarized
$A_2 \longleftrightarrow E$	allowed, xy polarized .

For the broad band spectra (Figs. 1 and 2) it is seen that there is a violation of these selection rules in the region of the transition (O_h), $^3A_{2g} \rightarrow {}^3T_{1g}(F)$. In the

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* Karipides [*5*] has reported crystal spectra of Ni en$_3$ (NO$_3$)$_2$ diluted in Zn en$_3$ (NO$_3$)$_2$ at room temperature and at liquid nitrogen temperature. His assignment of the spectra at these temperatures agress with that presented here.

absence of other effects this violation must be interpreted as the result of vibronic interaction under D_3 symmetry. Either of the transitions

$$^3A_2 \rightarrow {}^3A_2 \times \alpha_2$$
$$^3A_2 \rightarrow {}^3E \times \varepsilon$$

may give rise to the observed $\pi(z)$ intensity. The appearance of vibronic intensity is not surprising [*3*] and it is quite in accordance with the temperature dependence of the absorption band intensity. Since vibrational structure does not develop, it is not profitable to persue this aspect further.

The sharp, weak lines at 21,363 cm^{-1} and above are assigned, on band shape and energy considerations, to the spin-forbidden transition $^3A_2 \rightarrow {}^1A_1$. In particular, the strongest line, which falls at lowest energy and appears only in the $\sigma(xy)$ spectrum (21,363 cm^{-1}), is assigned as the (0,0) member of the transition (see next section).

The other *d-d* absorption bands in the spectrum follow the scheme in Fig. 1.

At the high energy end of the spectrum there is a near degeneracy between the $^3A_2 \rightarrow {}^3A_2$; $^3E[^3T_1(P)]$ transition of the nickel complex and the lowest electronic transition of the nitrate ion [*8*]. This precludes any discussion of the intensity distribution in the former transition.

Since no decisive information can be gained from these portions of the spectrum they will not be considered further.

Discussion

The Spectrum of the [Ni $\mathrm{en}_3]^{2+}$ *-ion:*

The immediate aim of the present investigation has been to characterize the source of spectral intensity in the *d-d* absorption bands. This aim has been thwarted in the case of the triplet/triplet transitions because detailed vibrational structure has not been observed. On the other hand, the violation of the D_3 electronic selection rules in the $^3A_2 \rightarrow {}^3A_2$ transition, as well as the temperature dependence of the total intensity, must be a reflection of a vibronic interaction, because in the crystal, the nickel ion occupies a D_3 site, and this is also the symmetry of the complex ion. Thus the complications, encountered in the spectrum of [Co $\mathrm{en}_3]^{3+}$ in crystals [*3*] are avoided.

D_3	D'_3
$^3A_2$	$\Gamma_1 + \Gamma_3$
^3E	$\Gamma_1 + \Gamma_2 + 2\Gamma_3$
$^3A_1$	$\Gamma_1 + \Gamma_3$
$^1A_1$	Γ_1

It is much more illustrative to describe the manner in which the absorption band at 21,363 cm^{-1} [$^3A_2 \rightarrow {}^1A_1$], derives its intensity. Firstly, this transition gains intensity by mixing, under the influence of the spin-orbit coupling term in the Hamiltonian, with nearby spin-allowed transitions. This is, of course true no matter whether the transition is magnetic or electric dipole allowed (with such a low intensity either mechanism is possible although the results have shown the transition to be electric dipole allowed). In these circumstances it is necessary to classify the electronic states under their appropriate double group representations.

Secondly, from the point of view of a perturbation calculation the spin-forbidden transition will certainly derive most of its intensity by mixing with the nearby $^3T_{1g}(F)$ state of O_h. (This level is some 2500 cm^{-1} away whereas the next nearest triplet state is 8500 cm^{-1} to higher energy.)

Finally, it is known [7] that the zero field splitting of the ground state in trigonally distorted complexes of nickel (II) is in the region of 0.5 cm^{-1}. Thus, at the temperatures at which the present experiments were conducted, the two ground state components Γ_1 and Γ_3 may be considered degenerate.

Within this framework the transition that appears at 21,363 cm^{-1} may be formulated

$$\Gamma_1, \Gamma_3 \rightarrow \Gamma_1 .$$

The excited state eigenfunction will be of the form,

$$\Psi(\Gamma_1) = \Phi(^1A_1) + a\Phi(^3A_2) + b\Phi(^3E^a) + c\Phi(^3E^b)$$

where $^3A_2$, $^3E^a$ and $^3E^b$ are the three components of the octahedral $^3T_{1g}$.

In the last section, the prominent peak at 21,363 cm^{-1} (xy) polarized is assigned as the (0,0) transition of this band system. Consider what this means in the present model. If the spectral distribution is entirely governed by spin-orbit forces then all transitions from Γ_1, Γ_3 to Γ_1 will be xy polarized. On the other hand, if the spin-orbit term is only a minor perturbation on the crystal field determined potential* then the $\Gamma_1(^1A_1)$ state must mix with some triplet state, or states, to which transitions are allowed. Since this is likely to be the case, mixing with $\Gamma_1(^3A_2)$ and $\Gamma_1(^3E)$ ought to determine the intensity and its distribution in the formally forbidden triplet-singlet transition. The matrix elements $\langle\Gamma_1(^1A_1) \mid \mathrm{l.s} \mid \Gamma_1(^3E)\rangle$ and $\langle\Gamma_1(^1A_1) \mid \mathrm{l.s} \mid \Gamma_1(^3A_2)\rangle$ are non-zero and to good approximation we expect $a = b = c$ in the above eigenfunction. Then, apart from differences in potential energy curves, the triplet/singlet band should reflect the triplet/triplet band, especially with respect to the intensity distribution in the (0,0) band. Casting back to the last section, it was shown that $^3A_2 \rightarrow {}^3A_2$ is forbidden under the D_3 selection rules and that the transition intensity is vibronic in nature. This means that the (0,0) band of that transition must be absent; that only mixing of the singlet with $^3A_2 \rightarrow {}^3E$ will give rise to a (0,0) band and that this (0,0) band will be polarized in the same manner as that band in $^3A_2 \rightarrow {}^3E$. Thus, by explaining the occurrence of this 21,363 cm^{-1} band, via the mixing of singlets and triplets, it is also possible to give sound evidence in support of the vibronic nature of the z polarized triplet intensity. The one-fold degeneracy of the excited singlet state removes many ambiguities that would have otherwise existed.

The apparent increase in intensity of this band on cooling is difficult to explain since it behaves in the opposite manner to that of the band from which the intensity is gained. Band shape variations are possibly responsible for the intensity behaviour in the singlet although, if the ground state zero field splitting is considerably larger than anticipated, and in the sense that Γ_3 is lower, then the increase is understandable. At present, this point remains unresolved.

The z polarized intensity ($\nu_{\max} = 18600$ cm^{-1}) in the region of $^3A_2 \rightarrow {}^3E$, $^3A_2$ is entirely vibronic in nature (see before, Assignments). In agreement with this it is

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* KARIPIDES [5] has calculated the mixing of the $^3A_1$ and $^3A_2$ states via spin-orbit coupling and he predicts $f_{^3A_2}/f_{^3A_1} = 0{,}0016$.

seen that there is a fairly complicated pattern of lines immediately above 21,363 cm^{-1} and this pattern is both xy and z polarized. It is possible to pick out progressions involving vibrations with upper state frequencies of 200 ± 10 cm^{-1} and 455 ± 10 cm^{-1}. In the xy polarization some of these progressions are based upon (0,0) whereas others are built upon vibronic origins. Only α_2 and ε vibrations, built on (0,0), may give z polarized intensity in these electronic transitions. Since processes involving the latter vibration will appear xy and z polarized, any vibronic band, that represents $(0,0) + \nu'$ and that appears z polarized only, must correspond to an α_2 vibration. xy and z polarized bands are due to ε vibrations or nearly degenerate α_2/ε pairs that arise from t_{1u} or t_{1g} modes of the octahedron. Some identifications for the group at $(0,0) + (200\text{—}400\ cm^{-1})$ are shown in Tab. 2. Because of the complexity of the spectrum and because of the high incidence of near accidental degeneracy it does not appear profitable to extend the analysis further.

Table 2. *Vibronic and electronic components of the transition* $^3A_2 - {}^1A_1$ *are shown and some tentative assignments of vibrational symmetries are given*

Band Maxima (cm^{-1})	Polarization	Assignment
21363	xy	(0,0)
21468	z	$+105$; α_2
21566	z	$+203$; α_2
21626	xy	$+263$; ε or ε and α_1 or α_2
21659	z, xy	$+296$; α_2
21725	z	$+362$; α_2
21824	xy	$+461$; α_1 or α_2 or $+263 + 200$ (α_1)
21867	z	$+296 + 208$ (α_1)
22012	xy	$+263 + 2 \times 198$ (α_1)
22022	z	$+461 + 198$ (α_1)
22080	xy	$+263 + 454$ (α_1)
22099	z	$+296 + 440$ (α_1)
22270	xy	$+2 \times 454$ (α_1)

A comparison of the electronic intensity [$(0,0) + n\nu'$ where ν' is totally symmetric] with the vibronic contributions demonstrates that the vibronic contributions play a major part in the determination of the spectrum. This is also true for the triplet/triplet band because the same vibronic arguments apply to that transition as well.

An analysis of the same type may be carried through for the weak, broad band at 24,700 cm^{-1} (mainly xy polarized), that is assigned to the $^1T_{2g}(D)$ state of the octahedron, and similar results obtained.

The Spectrum of the NO_3^-*-ion*

Although not related to the main theme of this communication we include here a brief description of the nitrate ion absorption. In the crystal the ion has symmetry

D_{3h} and it lies in the *ab* crystal plane with the nitrogen atom at a site of C_3 symmetry. The absorption with $\nu_{\max} = 33{,}000\ \text{cm}^{-1}$, due to this ion, is mainly $\pi(z)$ polarized and may be described in an electric dipole radiation field as

$$^1A_1' \rightarrow {}^1A_2'' \text{ or } {}^1A_1' \rightarrow {}^1E'' \times \varepsilon \text{ in } D_{3h} \text{ or } {}^1A_1 \rightarrow {}^1A_1$$

in C_3 symmetry.

The vibrational structure in this band appears to be a progression with an upper state frequency of 250—300 cm^{-1}. This agrees with a previous report [*8*] of the spectral details seen in simple nitrate containing crystals. This frequency does not correspond in any way with the known ground state vibration frequencies [*4*] of $\nu_1 = 1050$; $\nu_2 = 831$; $\nu_3 = 1390$ and $\nu_4 = 720\ \text{cm}^{-1}$. Thus the only conclusion that may be drawn is, that the excited state of this transition is greatly altered from the equilibrium configuration of the ground state. This is very different behaviour from that observed in the equivalent transition in the nitrite ion [*2*].

On the basis of these results a more complete investigation of these bands is underway and the results will be reported in due course.

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