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COOPERATIVE OPTICAL EFFECTS IN SOLID STATE COORDINATION CHEMISTRY

PETER DAY

Institut Laue-Langevin, 156X, 38042 Grenoble Cédex (France)

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CONTENTS

A. INTRODUCTION

From the beginning, coordination chemistry developed quite naturally with an emphasis on the behaviour of individual molecular entities called complexes, which might be charged or neutral, but whose structural and electronic properties were expected to remain the same whether they were isolated from one another in solution or packed together in a crystal lattice. For example, to a very good approximation, the ligand field transitions of octahedral $Ni(H_2O)_6^{2+}$ do not shift when a dilute aqueous solution of Ni^{2+} is concentrated up to the point where crystals of, say, $NiSO_4 \cdot 7H_2O$ are formed. Furthermore, from neutron diffraction measurements on aqueous solutions of Ni^{2+}, isotopically substituted in turn on nickel, oxygen and hydrogen, we know that the octahedral geometry of $Ni(H_2O)_6^{2+}$, and in particular the Ni–O bond length, is all but identical in the solution and crystalline phases. The physical properties of such crystals, for example magnetic and optical properties, are very close to the sum of the properties of the constituents, and the same is true even when the crystal contains two kinds of complex ion, e.g. $[Cr(NH_3)_6][FeCl_6]$.

In the early 1960s, instances began to be noticed where this generalization was far from borne out. Indeed, some spectacular cases such as Prussian Blue, formed from colourless or pale yellow $Fe(H_2O)_6^{3+}$ and yellow $Fe(CN)_6^{4-}$, had been known for two and a half centuries, and had even been commented on 80 years ago. The physical origins of what has been called the "non-additivity of ionic colours" are multifarious, ranging from small shifts and intensity changes in ligand field transitions to shifts of many

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thousands of reciprocal centimetres in intense allowed transitions, and the appearance of new absorption bands in the solid which have no direct analogue in the spectra of the constituent ions isolated from one another in dilute solution. When extended to other physical properties, such as magnetism and electron transport, the generic name "cooperative effects" was given to the consequences of the interactions between the complex ions in a crystal. A review published in 1969 [1] was arguably the first to collect evidence on optical cooperative effects in coordination chemistry, although most of the work available up to that time was qualitative and based on low resolution spectra over a limited temperature range. Since then, of course, the technical possibilities have widened greatly; for example, absorption and emission spectra can be recorded down to 300 mK and energy transfer can be followed into the picosecond regime. A spectral bandpass of less than 1 cm^{-1} is commonplace and magneto-optical spectroscopy (especially magnetic circular dichroism) has blossomed. The range of examples has also broadened, with an emphasis on low-dimensional interactions and categories of physical property not dreamed of earlier. For example, the first superconductors containing coordination complexes have been synthesized in the last few years ($(BEDT\text{-}TTF)_2AuI_2$ and $(TTF)Ni(DIMIT)_2$ where BEDT–TTF = bis-ethylenedithio-tetrathiofulvalene and $DIMIT^{2-}$ = 2-thioxo-1,3-dithiole-4,5-dithiolate), and there is growing interest in non-linear optical properties.

The present brief review takes its starting point from the 1969 review and, using examples from our own work in the intervening period, seeks to show how work on cooperative effects in solid state coordination chemistry has developed in 20 years, almost the time-span of *Coordination Chemistry Reviews*. Like the earlier review, it concentrates on optical properties.

B. MAGNETIC EXCHANGE EFFECTS ON LIGAND FIELD SPECTRA

In transition metal complexes in which covalency is not very marked, i.e. with metal ions in the +2 or +3 oxidation states and O- or N-donor ligands, magnetic exchange is usually weak and the exchange energy is a small fraction of the energy separation between the ground and lowest excited ligand field levels. Magnetic exchange therefore has only a small effect on the energies of the ligand field transitions, so high resolution and low temperatures are needed to observe them. However, the effect on the intensity, especially of spin-forbidden transitions, is much more spectacular. The earliest work in this field was by physicists investigating the fundamentals of the phenomena, who naturally worked on very simple prototype systems with three-dimensionally infinite lattices such as the cubic perovskite $KMnF_3$ and rutile MnF_2 structures. More immediately relevant to coordination chemistry were experiments on crystals of $KZnF_3$ and ZnF_2 containing sufficient substitutional Mn^{2+} (a few mole per cent) to yield a significant proportion of near-neighbour Mn–Mn pairs [2]. In this case the exchange Hamiltonian JS_aS_b between the two ions a and b leads to a discrete set of levels having energy

$$E_{S_{tot}} = \frac{J}{2}\left[S_{tot}(S_{tot}+1) - S_a(S_a+1) - S_b(S_b+1)\right] \tag{1}$$

where S_{tot} is the total spin of the pair, and thus for two Mn^{2+} ions in their ${}^6A_{1g}$ ground states, runs from zero to five. Typical values of J for these compounds lead to energy separations between the $E_{S_{tot}}$ levels of a few reciprocal centimetres, so unless the halfwidth of an absorption or emission band is of this order, the splitting is masked.

The effect of the exchange on the intensity is especially marked for spin-forbidden transitions. This is because the exchange provides a mechanism of circumventing the spin selection rule. For example, an isolated Mn^{2+} ion, having the maximum spin multiplicity $S = 5/2$ in its ground state, undergoes all its ligand field transitions with a decrease of spin $\Delta S = -1$, a forbidden process. Where the spins of two Mn^{2+} ions are coupled together by an exchange interaction, one should properly consider the spin multiplicity S_{tot} of the pair. Thus, when one of the Mn^{2+} ions (say a) undergoes a ligand field transition to an excited state with $S_a = 3/2$, there is still an exchange interaction with the other ion b in its ground state, generating a manifold of sublevels $E_{S_{tot}}$ as in eqn. (1), with S_{tot} now running from unity to four. Transitions can then take place between the sublevels of the ground and excited electronic states with the same S_{tot} without violating the spin selection rule, provided of course that the ground state sublevel is thermally populated.

A particularly striking example of the change in selection rules from single ions to pairs is the case of Co^{2+} as a substitutional impurity in the hexagonal layer crystal $CdBr_2$ [3]. A sharp, well-resolved band system near 560 nm arises from the spin-forbidden ligand field transition ${}^4T_{1g}(F) \rightarrow {}^2T_{1g}(H)$. The ground term is split in first order by spin–orbit coupling, leaving an E_g' component lying at the lowest level. The upper state is likewise split into E_g' and U_g' components and the small trigonal distortion from the octahedral field further splits the latter into $U_g'(\pm 3/2)$ and $U_g'(\pm 1/2)$. Transitions from $E_g'({}^4T_{1g})$ to the two U_g' components are observed as sharp, purely electronic (zero phonon) absorption lines at 5632.0 and 5633.3 Å, as shown in Fig. 1. It is well known that in a uniaxial crystal one can distinguish between absorption due to the electric or magnetic dipole mechanisms by measuring three spectra, with the electric ($\boldsymbol{E}$) and magnetic ($\boldsymbol{M}$) vectors of the incident light parallel or perpendicular to the

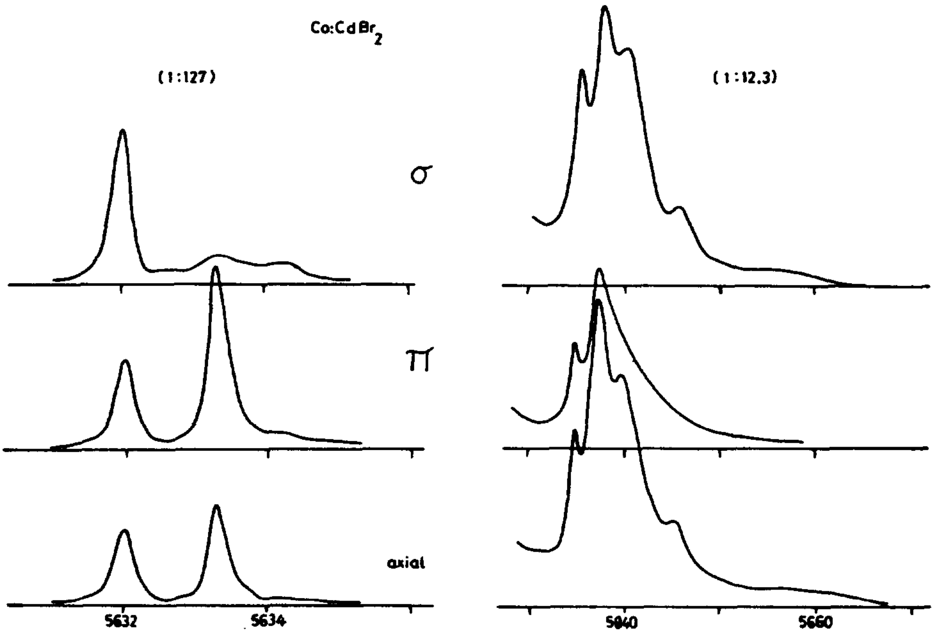


Fig. 1. Polarized absorption spectra of Co^{2+} in CdBr$_2$ between 5630 and 5660 Å (from ref. 3).

unique c axis as follows: $E \perp c$, $M \perp c$ (axial); $E \perp c$, $M \parallel c$ (σ); $E \parallel c$, $M \perp c$ (π). If the axial and σ spectra are the same, the electric dipole operator provides the dominant transition mechanism, whereas if the axial spectrum is the same as the π spectrum, it is the magnetic dipole mechanism that dominates. Following this recipe, Fig. 1 shows immediately that, in a crystal of CdBr$_2$ containing less than 1% Co^{2+}, the mechanism of the $E_g'(^4T_{1g}) \rightarrow U_g'(\pm 1/2 \pm 3/2)$ transitions is purely magnetic dipole. In striking contrast, however, if one measures the spectra of a CdBr$_2$ crystal in which about 8% of the Cd^{2+} is substituted by Co^{2+}, one finds that it is the σ spectrum that resembles the axial one, so that the mechanism has changed to electric dipole. Not only that but the spectrum is much more complicated, with at least five bands instead of two. That the multiplicity of bands arises from splitting of the ground state manifold as well as the excited state can be verified by measuring the temperature dependence of the spectrum. Figure 2(a) shows that the band labelled 4 increases rapidly in intensity with increasing temperature, so it originates from a thermally populated upper level within the electronic ground state. Its energy separation from the lowest level can be found by following the intensity qualitatively, as illustrated in Fig. 2(b). Since the lowest level of the single-ion spectrum is a Kramers doublet, the further splitting must be due to exchange.

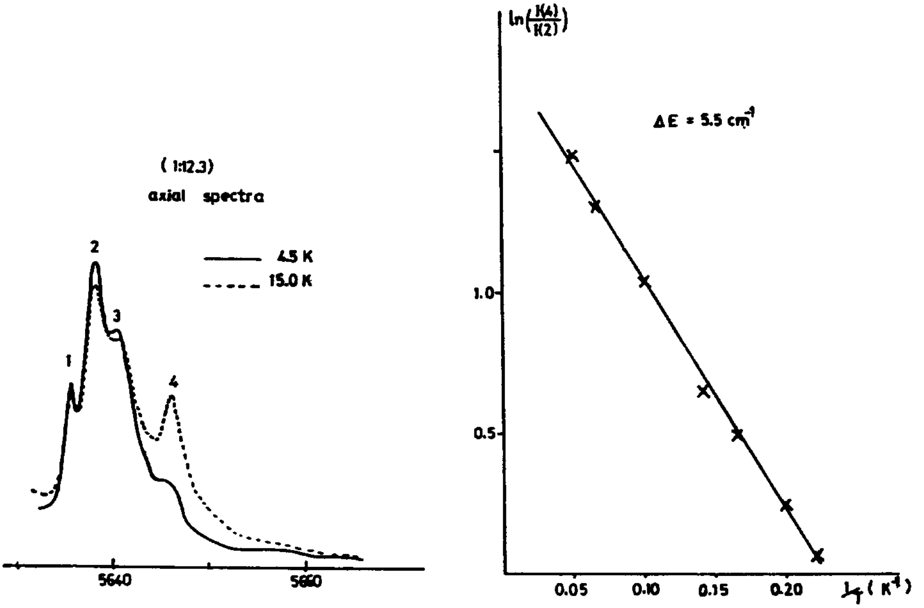
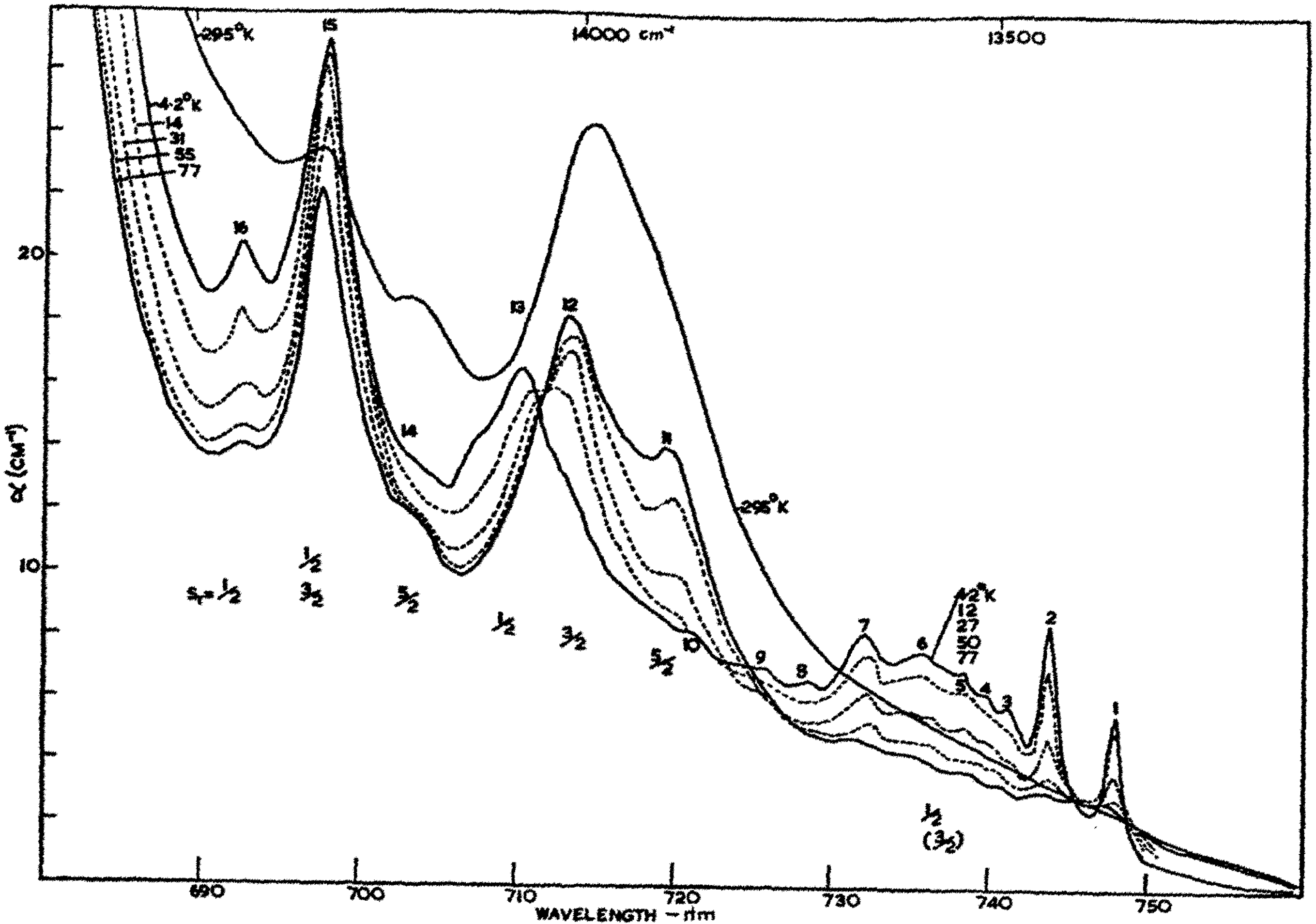


Fig. 2. Temperature dependence of intensity of the "hot" band in 1 : 12 Co^{2+} : $CdBr_2$ (from ref. 3).

The statistical distribution of dopant ions in an infinite lattice is not an ideal situation in which to observe spectra of near-neighbour pairs because there are bound to be single ions, triples, non-near-neighbour pairs etc., whose absorption can complicate the observations. A famous early example was that of Mn^{2+} in ZnS where, even at concentrations at which the proportion of pairs was much lower than that of single ions, the latter dominated in the measured spectrum [4]. A potentially "cleaner" method of generating pairs to examine exchange effects is simply to study discrete dimeric coordination complexes, since the exchange interaction between the molecular units is negligible. Plenty of classical Werner complexes, such as the "acid erythro" salts containing $[(NH_3)_5Cr(OH)Cr(NH_3)_5]^{5+}$, are of this type, and their serious spectroscopic study started around 1970. An early example from our own work concerns not a dimeric but a trimeric unit, namely the basic chromium(III) acetate cation $[Cr_3O(OAc)_6(H_2O)_3]^+$. The central Cr_3O unit is a planar triangle and the OAc^- and H_2O complete an octahedral configuration around each chromium(III) with a C_{4v} distortion. The region of the ${}^4A_{2g} \rightarrow {}^2E, {}^2T_{1g}(O_h)$ transitions shows a very complicated temperature dependence (Fig. 3) because the antiferromagnetic coupling of three $S = 3/2$ ions produces a manifold of levels from $S = 1/2$ to $9/2$ spanning about 250 cm^{-1} [5]. Unfortunately, the situation is even more complicated because the most easily prepared salt containing the



ig. 3. $^4A_{2g} \rightarrow {}^2E_1^2T_{1g}$ transitions in $[Cr_3O(OAc)_6(H_2O)_3]Cl \cdot 5H_2O$ (from ref. 5).

$[Cr_3O(OAc)_6(H_2O)_3]^+$ cation, namely the chloride, actually has two molecules per unit cell, with slightly different geometries. Ferguson and Güdel [6] used emission spectroscopy to sort out their ground state manifolds.

A very powerful type of spectroscopy that has begun to be applied to such systems in the last few years is incoherent inelastic neutron scattering (IINS). The neutron loses or gains energy as it excites a molecule or de-excites it from a thermally populated upper state. The state concerned could be vibrational or electronic, but since the neutron has a magnetic moment, transitions which result in a change in the spin of the system have strong scattering probabilities. Since the neutron also has finite mass, it can also exchange momentum with a sample so that, in contrast with photon scattering, the energies of states lying away from the Brillouin zone centre ($q \neq 0$) can be observed. The dependence of energy on wavevector q (the "dispersion" of the excitation) can be measured by coherent inelastic neutron scattering, for which, however, large single crystals are needed. For states whose dispersion is small, IINS using powder samples is a useful substitute because, over the complete q range, the energy varies little, and quite sharp energy gain or loss peaks can be observed. As we have already seen, the magnetic exchange sublevels of the electronic ground state in a dimeric or trimeric coordination complex form a discrete set spanning a few hundred reciprocal centimetres in typical cases, and since intercluster exchange is very weak, the overall q dependence of the energy is small. Furrer

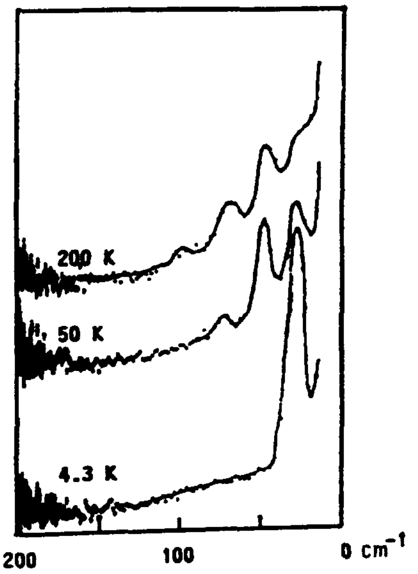


Fig. 4. Inelastic neutron scattering spectrum of $[Cr_3O(OAc)_6(H_2O)_3]Cl \cdot 5H_2O$ (from ref. 8).

and Güdel [7] were among the first to exploit this fact to study exchange effects in transition metal cluster complexes. Transitions between the exchange sublevels provide very precise estimates of the ground state exchange constant and even its temperature dependence. A recent example, the $[Cr_3O(OAc)_6(H_2O)_3]^+$ species referred to above, is shown in Fig. 4 [8].

C. DIPOLAR INTERACTIONS IN ONE-DIMENSIONAL COMPLEXES

A prototypical case in the optical spectroscopy of molecular crystals arises when there is more than one molecule in each unit cell. The excited state of the crystal after absorbing a photon is a Frenkel exciton, signified by a Bloch function or travelling plane wave that has as its basis the excited state of a unit cell rather than that of an individual molecule. If a single photon is absorbed into a unit cell containing two molecules A and B, for example, only one is excited (e.g. $0 \rightarrow 1$), but the excited state wavefunction of the unit cell must allow for the excitation to reside on either. Suitable functions would be $\Psi_{\pm} = |0,1\rangle \pm |1,0\rangle$. Furthermore, since A_0 and B_1 (or A_1 and B_0) interact, Ψ_+ and Ψ_- have different energies. In the special case where the individual transition dipole vectors are parallel, the excitation to Ψ_- has zero oscillator strength, since the dipoles cancel. Relative to the energy of the transition in a single isolated molecule, the transition to Ψ_+ would then appear shifted. The amount of the shift could be very large: an electrostatic calculation indicates 18000 cm^{-1} for 1 Å dipoles at a distance of 3.25 Å.

In organic molecular crystals it is very rare to find the units stacked in this way, but it does occur widely in coordination complexes with square planar d^8 configurations, where the central metal ions form linear chains. In particular, the unusual optical properties of the one-dimensional tetracyanoplatinate(II) salts were first noticed early in the last century [9] and were investigated by physicists such as Brewster [10] and Stokes [11]. More recently, it was found that their absorption spectra were dominated by an extremely intense broad band whose frequency varied with the plane-to-plane spacing within the stacks [12,13]. It was argued [1] that the simplest approach to the excited states of these ionic molecular crystals was to treat them as neutral Frenkel excitons propagating along the stacks. This hypothesis was supported by the fact that for at least a dozen salts of this kind the frequency of the intense absorption band decreased in proportion to the inverse cube of the Pt–Pt separation [14,15], as required if the energy gap arises from interaction between molecular transition electric dipoles.

Because of their high reflectivity, the absorption spectra of crystals of this kind cannot simply be found by measuring the optical density. Rather, one should measure the transmission (T) and reflection (R) coefficients and

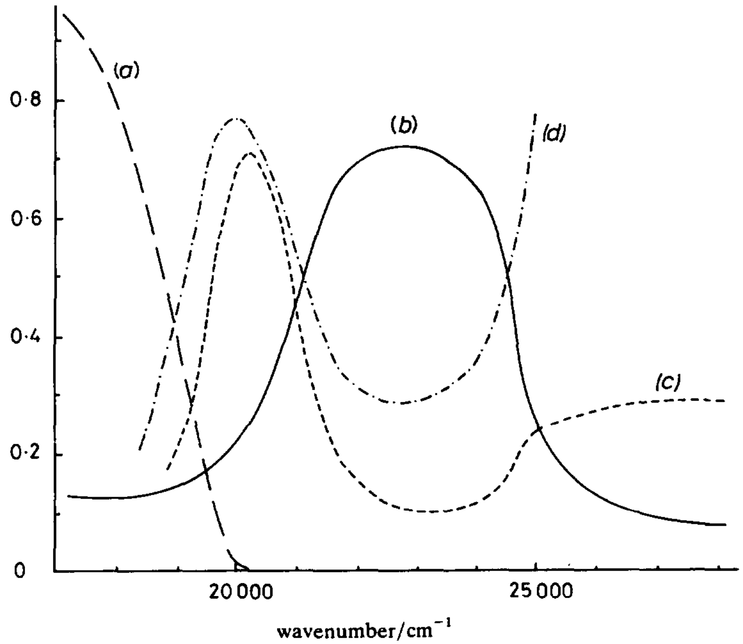


Fig. 5. $E \| c$ spectra of $BaPt(CN)_4 \cdot 4H_2O$ at 9 K: (a) transmission T; (b) reflectivity R; (c) fluorescence excitation; (d) $1 - T - R$ (from ref. 18).

obtain the absorption (A) from the conservation law

$$A + R + T = 1 \tag{2}$$

Since the crystals also fluoresce, another means of estimating the absorption coefficient is to determine the fluorescence excitation spectrum, a procedure used to study the zero-phonon absorption in very thin anthracene crystals near 25000 cm^{-1} [16,17]. To ensure that the results are directly comparable, the transmission, reflectivity and fluorescence excitation spectra must be measured on the same crystal within the same apparatus. We carried out such an experiment on $BaPt(CN)_4 \cdot 4H_2O$ at 9 K [18]. Figure 5 shows the frequency dependence of T (curve a) and R (curve b), together with the variation of (1 − T − R) (curve d), which should measure the true absorption, A, for $E \| c$. Curve c in Fig. 5 shows the fluorescence excitation. Up to approximately 25000 cm^{-1} the frequency dependence of the fluorescence excitation parallels the (1 − T − R) curve for $E \| c$ quite closely. Further into the UV, the fluorescence excitation levels off, while the ($1 - T - R$) curve continues to rise as a result of light being scattered from imperfections in the crystal.

With the electric vector of the incident light perpendicular to the c axis, the reflectivity is low and does not vary with frequency. Consequently, the

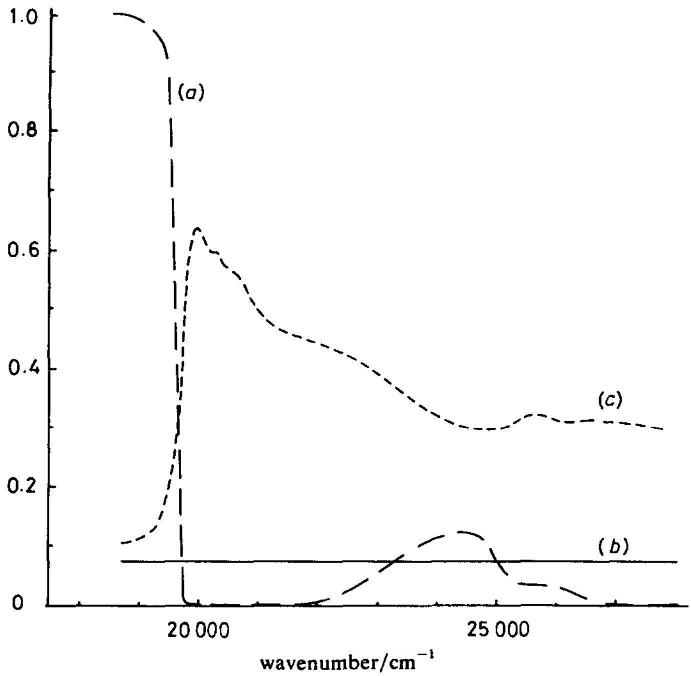


Fig. 6. $E \perp c$ spectra of $BaPt(CN)_4 \cdot 4H_2O$ at 9 K: (a) transmission T; (b) reflectivity R; (c) fluorescence excitation (from ref. 18).

absorption, and hence the fluorescence excitation, should vary as $(1 - T)$. That this is approximately so can be seen from Fig. 6, in which curves (a) and (c) have roughly a mirror-image relationship. The lowest frequency peak in the $E \perp c$ fluorescence excitation exhibits some fine structure at low temperature. It is possible that the interval of 320 cm^{-1} built on this peak is the a_{1g} Pt–C intramolecular stretching mode of $Pt(CN)_4^{2-}$, which has a frequency of 465 cm^{-1} in the ground state. Because the peak positions in the $E \| c$ and $E \perp c$ fluorescence excitation spectra are so similar, they relate to the same electronic state with intensity in both polarizations.

In $BaPt(CN)_4 \cdot 4H_2O$, the normals to the planes of the $Pt(CN)_4^{2-}$ are tilted by approximately 3° from the c axis [19]. Thus electronic transitions polarized either parallel or perpendicular to the anion plane have a small component of intensity perpendicular or parallel to the crystalline c axis respectively. In contrast with the reflectivity and fluorescence excitation with $E \| c$, the absorption spectrum with $E \perp c$ varies remarkably with temperature, both in shape and frequency. The band is asymmetric, falling sharply on the lower frequency side, but having a pronounced tail towards higher frequency. The maximum shifts by 900 cm^{-1} to lower frequency from 240 to 9 K, but the low frequency side shifts first to the red and then back to the blue. This remarkable effect is the sum of two factors. First, the frequency of the $k = 0$ exciton decreases if the Pt–Pt distance decreases, since it varies as $R(\text{Pt–Pt})^{-3}$ [14,15]. In fact, one can even estimate the contraction along the c axis as 0.038 Å from this relationship. No data are available on the variation of the unit cell parameters of $BaPt(CN)_4 \cdot 4H_2O$ with temperature: the only measurements on any related compound are for the mixed-valence one-dimensional metallic conductor KCP, $K_2Pt(CN)_4Br_{0.30} \cdot 3H_2O$, where the Pt–Pt spacing contracts by 0.033 Å from 295 to 77 K [20]. The second factor is the very large change in the band area with temperature. Either the intensity has a large vibronically induced component or the angle between the $Pt(CN)_4^{2-}$ planes and the c axis varies with temperature, so that the projection of the molecular transition dipole on that axis changes.

At a frequency of several thousand reciprocal centimetres lower than the absorption, the emission of these tetracyanoplatinate salts (whose frequency also decreases as $R(\text{Pt–Pt})^{-3}$) [15] has components with polarization both parallel and perpendicular to the stacks [21], the latter being the more intense. Both components shift strongly to the red as the temperature is lowered [18], and since a similar shift occurs under pressure at fixed temperature [21,22], the temperature-induced shift must be due to lattice contraction. Decay curves and time-resolved emission spectra [23] revealed that the two emission peaks have very different lifetimes and temperature dependences. The higher frequency band has an extremely short lifetime (less than 3 ns) while the other, which cannot be described by a single exponential decay, contains at least one component that becomes very long lived at low temperature.

Concentration quenching by impurities is a powerful probe of the exciton dynamics in crystals, and it has been known for many years that small quantities of $Ni(CN)_4^{2-}$ quench the fluorescence of the tetracyanoplatinates [24]. The reduction in the emission intensity is a power law function of the dopant concentration and 10^{-3} mol.% Ni has a detectable effect on the intensity [25]. These conclusions have been confirmed by detailed measurements on single crystals [26] which indicate that impurity quenching is confined to the lower frequency $E \perp c$ emission, the intensity of the higher frequency $E \| c$ band remaining almost unaffected by impurity concentration. Lifetime measurements have also been reported for $BaPt(CN)_4 \cdot 4H_2O$ crystals containing high (1 : 65) and low (1 : 650) mole ratios of $Ni(CN)_4^{2-}$ [27].

We used a three-level phenomenological model to interpret the emission from pure and nickel-doped $BaPt(CN)_4 \cdot 4H_2O$, with the states and radiation (or radiationless) probabilities indicated in Fig. 7 [27]. The temperature dependence of the lifetimes and the ratios of the intensities of the two emission peaks lead to the following thermal activation energies and transi-

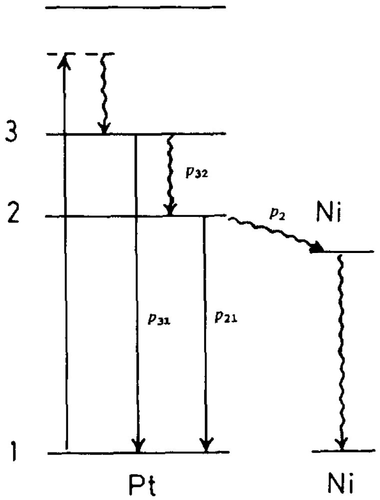


Fig. 7. Schematic level scheme for nickel-doped $BaPt(CN)_4 \cdot 4H_2O$. Wavy lines represent radiationless processes.

tion probabilities for the undoped crystal: $E_{21} = 27$ cm^{-1}, $E_{31} = 22$ cm^{-1} and $E_{32} = 61$ cm^{-1}; $p_{21}^0 = 2 \times 10^6$ s^{-1}, $p_{31}^0 = 6.9 \times 10^5$ s^{-1} and $p_{32}^0 = 2.3 \times 10^8$ s^{-1}. The activation energies are low and presumably arise from low frequency vibrations. If we assume that p_{31}^0 etc. remain unaffected by the nickel doping and retain the values found in the undoped crystal, $p_{2\mathrm{Ni}}^0/p_{21}^0 \approx 2$ in the 1:650 crystal, whereas in the 1:65 crystal this ratio is approximately 20.

The low radiative probabilities of states 2 and 3 suggest that they have a triplet parentage [28]. From the filled $a_{1g}(z^2)$, $e_g(xz, yz)$ and $b_{2g}(xy)$ orbitals of $Pt(CN)_4^{2-}$, mainly localized on the metal, the lowest energy excited configurations are formed by transferring electrons to empty orbitals of a_{2u} symmetry, either of CN π^* type or Pt $6p_z$. The terms which result are ${}^{1,3}A_{2u}$, ${}^{1,3}E_u$ and ${}^{1,3}B_{1u}$. Spin–orbit coupling ($\tau_{5d} \approx 3500$ cm^{-1}) mixes the singlets and triplets so that, for example, there are four E_u (D_{4h}^*) states which are allowed when the electric dipole vector is parallel to the molecular plane. The magnetic circular dichroism spectrum of $Pt(CN)_4^{2-}$ shows that the one lowest in energy is that having predominantly ${}^3A_{2u}$ parentage [22]. Next comes a B_{1u} state originating from ${}^3E_u$, which is forbidden in both xy and z polarization, and then an A_{2u} state formed from an admixture of ${}^3E_u$ and ${}^1A_{2u}$, which is z polarized. The frequency range spanned by these three states is approximately 3000 cm^{-1}, which is compatible with the separation between the two emission peaks in $BaPt(CN)_4 \cdot 4H_2O$. Thus we assigned the lowest emission band (state 2, $E \perp c$, 18400 cm^{-1} at 4 K) as $E_u({}^3A_{2u})$ and the higher one (state 3, $E \| c$, 20100 cm^{-1} at 4 K) as $A_{2u}({}^3E_u, {}^1A_{2u})$. Then the fast process 3 → 2 is due to spin–orbit coupling, which mixes ${}^3A_{2u}$ and ${}^1A_{2u}$.

We have emphasized several times that the frequencies of the absorption and emission peaks in the tetracyanoplatinate salts vary with Pt–Pt spacing as R^{-3}, precisely what would be expected if the dominant term in the interaction causing the shift is the dipole–dipole term. This is peculiar because the complexes forming the crystal are charged. Thus, one might anticipate that ion–ion (R^{-1}) and ion–dipole (R^{-2}) terms would also contribute. However, we have shown that for non-overlapping charged chromophores A and B, these terms do not contribute [29]. Writing the interaction V between A and B as a multipole expansion, the general matrix element of ν can be written

$$\langle \epsilon\eta | \nu | \epsilon'\eta' \rangle = R^{-1}\delta_{\epsilon\epsilon'}\delta_{\eta\eta'}q_{\mathrm{A}}q_{\mathrm{B}} - R^{-2}\left[\delta_{\epsilon\epsilon'}q_{\mathrm{A}}(n \cdot \mu_{\mathrm{B}}^{\eta\eta'}) - \delta_{\eta\eta'}q_{\mathrm{B}}(n \cdot \mu_{\mathrm{A}}^{\epsilon\epsilon'})\right]$$

$$+ R^{-3}\left[(\mu_{\mathrm{A}}^{\epsilon\epsilon'}, \mu_{\mathrm{B}}^{\eta\eta'}) - 3(n \cdot \mu_{\mathrm{A}}^{\epsilon\epsilon'})(n \cdot \mu_{\mathrm{B}}^{\eta\eta'})\right] + \cdots \tag{3}$$

where ϵ and η are either zero or unity.

We see at once that the charge–charge term has only diagonal matrix elements and, furthermore, they are all equal, so it can never contribute to shifts or splittings. The charge–dipole term has diagonal matrix elements such as $\langle 0, 0 | \nu | 0, 0 \rangle$ and $\langle 0, 1 | \nu | 0, 1 \rangle$, but its only off-diagonal matrix elements are ones such as $\langle 0, 0 | \nu | 0, 1 \rangle$, which have only a second-order effect on energies. In contrast, the dipole–dipole term makes the leading contribution to off-diagonal matrix elements $\langle 0, 1 | \nu | 1, 0 \rangle$ between the excited states. These are the matrix elements responsible for the resonance interactions which lead to Davydov shifts and splittings.

Ion–dipole terms do not contribute to resonance interactions between excited states, but nevertheless they could influence excitation energies in crystals containing charged molecules. However, they may be eliminated altogether as a result of symmetry. The ion–dipole term represents the interaction between a dipole at a given centre and the electric field at the same centre. Therefore we ought to include the electric fields from all other ions in the lattice. In doing so we may find that there is no net field in the direction of the dipole and so the ion–dipole term must be zero. This will happen whenever the chromophore occupies a site at a centre of symmetry, or indeed contains a plane or axis of symmetry perpendicular to the dipole direction.

The point symmetry of the $\mathrm{Pt(CN)}_4^{2-}$ ion is D_{4h}, and in the crystal-line tetracyanoplatinates the site group at the platinum approximates quite closely to D_{4h}. Thus no charge–dipole term is expected in these compounds.

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