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Polarized Absorption Spectra for Single Crystals of Dichloro(ethylenediamine)platinum(II). Effect of Metal-Metal Interactions[1]

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Received October 16, 1969

A recent X-ray diffraction study[2] has shown that crystals of the coordination complex Pt(en)Cl_2 belong to the orthorhombic system, space group $C222_1$. The nearly planar molecules stack in nearly a linear array as shown in Figure 1A with a uniform spacing of 3.39 Å, only 0.14 Å greater than between the ions in Magnus' green salt[3] (MGS), $[Pt(NH_3)_4][PtCl_4]$.

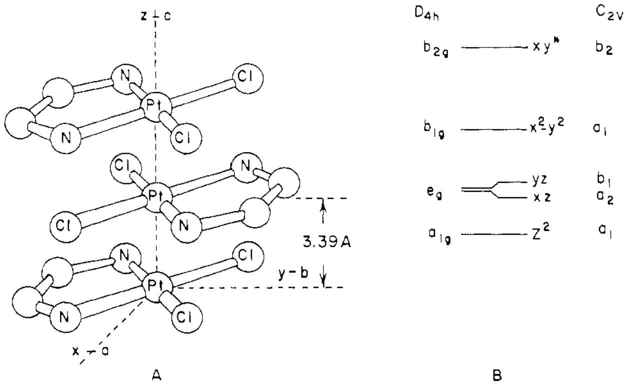

Figure 1.—(A) Stacking of Pt(en)Cl_2 molecules in the orthorhombic crystals. (B) Anticipated order of one-electron orbital energies with their symmetry designations for the d orbitals under the D_{4h} and the C_{2v} groups.

Crystals, grown as very thin plates, <10 μ thick, were suitable for spectral studies similar to those used for K_2PtCl_4.[4] The faces contained the *b* and *c* axes, so absorption of light, directed along the *a* axis and polarized in either of these directions, could be measured (see Figure 1A). Pale yellow in color, the crystals exhibited a weak dichroism in visible light with the higher absorption in the *c*, or chain, direction.

A solution spectrum of Pt(en)Cl_2 and polarized spectra of a crystal at room and liquid He (nominally 15°K) temperatures are shown in Figure 2. Although the very fragile crystals usually shattered upon cooling to He temperatures, a number survived to 77°K to confirm the important features shown in Figure 2. At 300°K the *b* polarization shows a weak band at 25,000 cm^{-1}, scarcely more intense than in the solution. A peak at 33,700 cm^{-1}, however, has an ϵ of 350 cm^{-1} M^{-1}. In the *c* absorption the 25,000-cm^{-1} band is enhanced at least tenfold, and ϵ for 33,700 cm^{-1} is 650 cm^{-1} M^{-1}. Although there has not been a strong shift of bands to longer wavelengths, the intensity features otherwise strongly resemble those of MGS.[5] Enhancement of the absorption in the chain direction for MGS was proposed as an expected consequence of delocalization of electrons along the chain by the overlap of orbitals on neighboring atoms by Rundle, *et al.*[3] However, Day, *et al.*,[5] have concluded that the spectrum of MGS corresponds to that of the $PtCl_4^{2-}$ ion whose energy states have been perturbed by the close presence of the cations along the symmetry axis of the stack, *i.e.*, by an axial crystal field in the D_{4h} symmetry. (The single weak band not accounted for by this model was later attributed to overtones of N–H stretching vibrations.[6]) They proposed that the higher intensities in MGS resulted from the shift of a high-intensity band at 42,500 cm^{-1} in K_2PtCl_4 to 34,500 cm^{-1} in MGS from which the intensity was "borrowed" under the vibronic excitation. This conclusion was supported by Anex, *et al.*,[7] who showed from the reflectance spectrum that the band at 34,500 cm^{-1} is also strongly polarized in the direction of the chain (*z* or *c*).

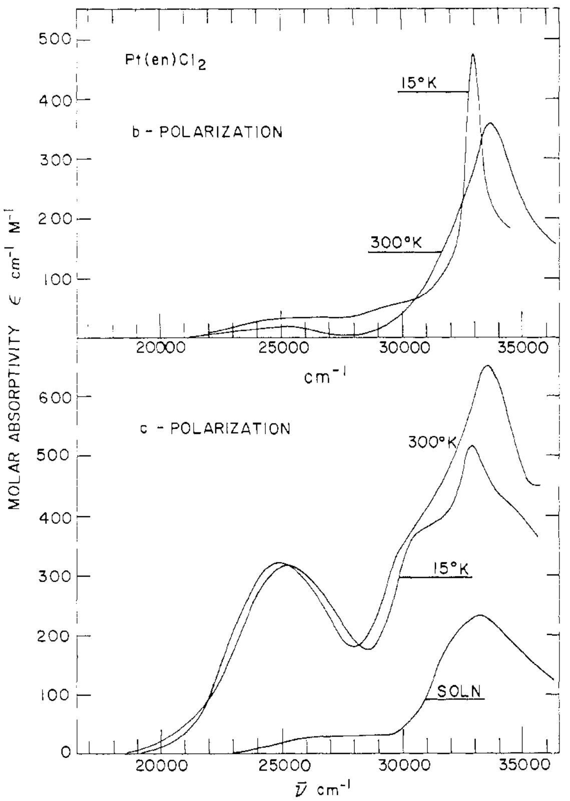

Figure 2.—Absorption spectra of Pt(en)Cl_2 in an aqueous 0.3 *M* Cl^- solution and in single crystals with polarized light at 300°K and at liquid helium temperature (nominally 15°K).

Lower temperatures are expected to narrow bands with an improvement of resolution and a reduction of intensities for vibronically excited transitions. The

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[1] Work performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

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absorption for *c* polarization in the spin-allowed region clearly shows such behavior although perhaps that of the central component at 33,700 cm^{-1} is not certain. In *b* polarization at He temperature, however, a narrowing of the band has clearly resulted in a higher peak than at 300°K. This is just the behavior expected for a symmetry-allowed transition since the integrated intensity is independent of vibrational excitation. Mason and Gray[8] have observed this behavior at 77°K for the allowed charge-transfer bands of several platinum(II) complexes in organic glasses. No such dipole-allowed transition in the d–d bands was observed for K_2PtCl_4 crystals,[4] where Pt–Pt distances are 4.21 Å. Any contribution to this allowed transition from an asymmetric crystal field can be excluded if C_{2v} symmetry is assumed for the molecules, for the product of the initial and final orbital functions must contain the representations of the components of the dipole vector **r**. Examination of the C_{2v} assignment of orbital energies (Figure 1B) reveals that for light entering along the *a* axis, there is only one dipole-allowed transition ($d_{xz} \rightarrow d_{xy}$), and this is polarized in the *z* direction (along the chains). C_{2v} symmetry should be a satisfactory approximation even though the molecular symmetry is only C_2 as a consequence of the puckered rings.

We have therefore examined the consequences of energy band formation from interactions of electrons in the platinum d orbitals only. This is an ideal case to apply a simple theory for a long one-dimensional array of equivalent atoms. It is simpler than the one required for Magnus' green salt where alternatingly charged ions have much different energy levels.[9] The simplifying approximation of D_{4h} symmetry, which at least will not introduce extra transitions, was applied with the expected relative one-electron orbital energies as shown in Figure 1B. An LCAO wave function, $\psi_n(z^2)$, involving the d_{z^2} orbitals, which are expected to have the greatest interaction, is written

$$\psi_n(z^2) = \sum_{j=1}^{N} c_{n,j}(d_{z^2})_j \tag{1}$$

where $\Sigma_{j=1}{}^N c_{n,j}{}^2 = 1$ and $(d_{z^2})_j$ is the d_{z^2} orbital of the *j*th atom in a chain of *N* platinum atoms. From the analogy to the simple theory of a particle in a one-dimensional box, the coefficients $c_{n,j}$ are taken as

$$c_{n,j} = \sqrt{\frac{2}{N+1}} \sin \frac{nj\pi}{N+1} \tag{2}$$

where *n* can be an integer, $0 < n < N + 1$. With very large *N*

$$E_n = \int \psi_n H \psi_n \, d\tau = H_{j,j} + 2H_{j,j+1} \cos \frac{n\pi}{N+1} \tag{3}$$

if $H_{j,k} = 0$ unless $k = j$ or $j \pm 1$. The density of states is

$$\frac{dn}{dE} = \frac{-(N+1)}{2\pi H_{j,j+1}} \csc \frac{n\pi}{N+1} \tag{4}$$

Similar bands will be developed from the d_{xz} and d_{yz} orbitals, although $H_{j,j+1}$ and the corresponding band widths should be smaller. Accordingly, bands derived from $d_{x^2-y^2}$ and d^*_{xy} should be narrower still. With the low-spin atomic d^8 configuration the four lower bands are completely filled and the d^*_{xy} band is empty.

The dipole transition moment between the *n*th state of the d_{z^2} band and the *m*th state of the unfilled d^*_{xy} band can be written

$$\rho_{n\rightarrow m} = \int \psi_n(z^2)\mathbf{r}\psi_m(xy) \, d\tau = \sum_{j=1}^{N} c_{n,j}c_{m,j}(\mathbf{r})_{j,j} + \sum_{j=1}^{N-1} c_{n,j}c_{m,j+1}(\mathbf{r})_{j,j+1} + \sum_{j=2}^{N} c_{n,j}c_{m,j-1}(\mathbf{r})_{j,j-1} \tag{5}$$

Here $(\mathbf{r})_{j,j+1} = \int (d_{z^2})_j \mathbf{r} (d_{xy})_{j+1} \, d\tau$, etc., where the origin for **r** is taken as the position of the *j*th nucleus. In expression 5, $(\mathbf{r})_{j,j} = 0$ since both wave functions are even. An examination of the $\mathbf{r}_x$, $\mathbf{r}_y$, and $\mathbf{r}_z$ components of $(\mathbf{r})_{j,j+1}$ and $(\mathbf{r})_{j,j-1}$ for the d_{z^2} and d^*_{xy} orbitals reveals they are all exactly zero from symmetry. All transitions between these bands are therefore dipole forbidden and presumably occur because of vibronic or perhaps ligand field perturbations. The same condition applies to transitions between the $d_{x^2-y^2}$ and the d^*_{xy} bands, *viz.*, $\rho_{n\rightarrow m} = 0$. However, for the transitions $d_{xz} \rightarrow d^*_{xy}$, $(\mathbf{r}_y)_{j,j+1} = -(\mathbf{r}_y)_{j,j-1} \neq 0$, and for $d_{yz} \rightarrow d^*_{xy}$, $(\mathbf{r}_x)_{j,j+1} = -(\mathbf{r}_x)_{j,j-1} \neq 0$, although $(\mathbf{r}_z)_{j,j+1} = (\mathbf{r}_z)_{j,j-1} = 0$ for both transitions. Interactions between the d orbtials on adjacent atoms, therefore, lead to allowed transitions from only the degenerate bands which are polarized *normal* to the chains.

From eq 5 the expression for the transition moment from the *n*th state of the d_{xz} band to the *m*th state of the d^*_{xy} band in a very long chain is

$$\rho_{n\rightarrow m} = \frac{2}{N+1} \sum_{j=1}^{N} \sin \frac{n\pi j}{N+1} \left[\sin \frac{m\pi(j+1)}{N+1} - \sin \frac{m\pi(j-1)}{N+1} \right] (\mathbf{r}_y)_{j,j+1} \tag{6}$$

This expression reduces to

$$\rho_{n\rightarrow m} = \frac{4(\mathbf{r}_y)_{j,j+1}}{\pi} \sin \frac{m\pi}{N+1} \left[\frac{1}{n-m} + \frac{1}{n+m} \right] \tag{7}$$

if $n + m$ is odd or to 0 if $n + m$ is even.

The sum $\Sigma_{m-1}{}^N \rho_{n\rightarrow m}{}^2$ over the entire d_{xy} band indicates the relative probability for the transition from a single state in the d_{xz} band. An examination of this sum indicates that

$$\sum_{m = n-\sqrt{N}}^{m = n+\sqrt{N}} \rho_{n\rightarrow m}{}^2 \gtrsim (1 - (1\sqrt{N})) \sum_{m=1}^{N} \rho_{m\rightarrow n}{}^2$$

Therefore the transition from the *n*th state of the d_{xz} band will be primarily to within a negligibly small energy region around the *n*th state in the upper band and

$$\sum_m \rho_{n\rightarrow m}{}^2 = \frac{32}{\pi^2} (\mathbf{r}_y)^2{}_{j,j+1} \sin^2 \frac{n\pi}{N+1} \times \left(1 + \frac{1}{3^2} + \frac{1}{5^2} + \cdots\right) \tag{8}$$

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(8) W. R. Mason, III, and H. B. Gray, *J. Am. Chem. Soc.*, **90**, 5722 (1968).

(9) J. R. Miller, *J. Chem. Soc.*, 713 (1965).

The selection rules can be confirmed qualitatively by a group-theory consideration of the wave functions, ψ_n and ψ_m, over the entire chain. For the d_{xz}, d_{yz} bands, ψ_n is e_g if n is odd and e_u if n is even. For the d^*_{xy} band, ψ_m is b_{2g} if m is odd and b_{1u} if m is even. The product e_ub_{2g} or e_gb_{1u} gives e_u which is the representation for the dipole vector normal to the chain. Hence such transitions are allowed between odd and even states. For the other bands, although transitions u ↔ g are possible, none of the appropriate products yields the required a_{2u} or e_u representations for the dipole vector.

The quantity $H_{j,j+1}$ for d_{xy} orbitals should be negative, corresponding to bonding; hence the state $n = 1$ is the totally bonding or lowest energy MO in the band. However, $H_{j,j+1}$ for d_{xz} and d_{yz} orbitals are positive and the state $n = 1$ is totally antibonding or the highest in energy. The transitions between the bands will therefore be broadened by the sum of the widths of the two bands. The fact that the observed dipole-allowed absorption peak is quite narrow is additional evidence for only weak overlap of d orbitals and corresponding interactions between adjacent atoms. Thus the $(\mathbf{r})_{j,j+1}$, which measures the extent of $\pi \rightarrow \Delta$ charge transfer between two adjacent platinum atoms, is much smaller than the charge-transfer moments between the ligands and the platinum.

The experimental observation of a single dipole-allowed but weak transition polarized normal to the chains is therefore very nicely explained by the band theory involving the interactions between the d orbitals on adjacent metal atoms. Enhancement of the absorption in the direction of the chains (c) is apparently a consequence of the same factors which influence the corresponding intensities in MGS. To this end it would be interesting to determine if there has been a shift to lower frequencies of a high-intensity band in the crystal and whether this band is highly polarized in the c direction as in the case of MGS. Continuing studies are in progress with the objective of improving the quality of the spectra.

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Reformulation of Previously Reported *trans*-Dichlorobis(1,10-phenanthroline)cobalt(III) Complexes

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Received October 24, 1969

The preparation of the *trans*-$Co(NN)_2Cl_2^+$ cation, where NN = 1,10-phenanthroline or 2,2′-bipyridine, has been reported by several workers.[1-4] Recently, it was shown[5] that one such complex,[3] *trans*-$[Co(bipy)_2Cl_2]Cl$, is actually a mixture of *cis*-$Co(bipy)_2Cl_2^+$ and $Co(bipy)_3^{3+}$ cations and $CoCl_4^{2-}$ and Cl^- anions. While investigating various techniques to assign *cis–trans* configurations to complexes of this type, we have been led to reinvestigate the corresponding phen complexes.

Experimental Section

Apparatus and Analyses.—Visible spectra were measured with Cary 14 and Beckman DK2-A spectrophotometers. X-Ray powder patterns were obtained using Ni-filtered X-radiation from a copper source and a Philips Debye–Scherrer type powder camera. Conductivities were measured at 25° using a Yellow Springs Instrument bridge, Model 31. Elemental analyses were performed by Baron Consulting Co., Orange, Conn., and Alfred Bernhardt, Mülheim (Ruhr), Germany.

$[Co(phen)_3][CoCl_4]_3 \cdot 2HCl$.—The green compound reported as *trans*-$[Co(phen)_2Cl_2]Cl \cdot 2HCl$ in ref 1 was synthesized exactly according to the reported instructions and repeated several times with similar results. *Anal.* Calcd for $C_{72}H_{50}Cl_{14}Co_5N_{12}$: C, 46.14; H, 2.69; N, 8.97; Cl, 26.48. Found: C, 46.44; H, 2.94; N, 9.15; Cl, 27.06. An aqueous solution (10^{-3} *M*) of the dried (−2HCl) material gave a molar conductance of 1675 ohm^{-1} (calcd,[6] 1650 ohm^{-1}).

$[Co(phen)_3](ClO_4)_3 \cdot 3H_2O$ was prepared as a derivative of the green compound by passing a solution (0.4 g in 20 ml of concentrated HCl) of the material through an anion-exchange resin (Cl^- form). The resulting yellow solution was diluted to 50 ml and excess sodium perchlorate was added until precipitation was complete. The yellow product was isolated and washed twice with ethanol. *Anal.* Calcd for $C_{36}H_{30}Cl_3CoN_6O_{15}$: C, 45.42; H, 3.18; N, 8.83; Cl, 11.17. Found: C, 45.79; H, 2.93; N, 8.90; Cl, 11.76.

$[(C_4H_9)_4N]_2CoCl_4$ was prepared as a second derivative by slow addition of tetrabutylammonium chloride to a solution of the green material (0.5 g in 20 ml of concentrated HCl). When precipitation seemed complete, the blue product was isolated, washed with ethanol and ether, and dried in air over $CaCl_2$. *Anal.* Calcd for $C_{32}H_{72}Cl_4CoN_2$: C, 56.05; H, 10.58; N, 4.09; Cl, 20.68. Found: C, 56.54; H, 10.30; N, 4.27; Cl, 20.61.

Aqueous solutions of the compound had a dirty yellow color, consistent with the simultaneous presence of yellow $Co(phen)_3^{3+}$ and pink $Co(H_2O)_6^{2+}$. Stable green HCl solutions gave visible spectra characteristic of the $CoCl_4^{2-}$ species (575–750 mμ).

***cis*-$[Co(phen)_2Cl_2][Co(phen)_3][CoCl_4]_2 \cdot 3H_2O$.**—The green compound reported as *trans*-$[Co(phen)_2Cl_2]^+(H_7O_3)^+Cl^-{}_2$ in ref 2 was synthesized several times with similar results. *Anal.* Calcd for $C_{60}H_{46}Cl_{10}Co_4N_{10}O_3$: C, 46.63; H, 3.00; N, 9.06; Cl, 22.94; Co, 15.25. Found: C, 46.73; H, 3.06; N, 9.03; Cl, 23.63, 23.16; Co, 15.17, 15.06. An aqueous solution (10^{-3} *M*) of the material gave a molar conductance of 1060 ohm^{-1} (calcd,[6] 1050 ohm^{-1}).

A voluminous mixed precipitate of *cis*-$[Co(phen)_2Cl_2]ClO_4 \cdot 3H_2O$ and $[Co(phen)_3](ClO_4)_3 \cdot 3H_2O$ resulted on addition of excess $NaClO_4$ to a concentrated aqueous solution of the compound. Surprisingly, these two compounds separated into two distinct layers on centrifugation. Repeated washings with water of the violet layer yielded a product having a powder pattern identical with that of the known *cis* compound.[7]

Visible spectra of the stable green HCl solutions of the material showed peaks characteristic of $CoCl_4^{2-}$. When these solutions were passed through cation-exchange resins (H^+ form),

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(6) Assuming (a) hydrolysis of $CoCl_4^{2-}$ in aqueous solution to give Co^{2+}(aq), (b) molar conductances of 450, 250, and 100 ohm^{-1} for $[Co(phen)_3]Cl_3$, $CoCl_2$, and *cis*-$[Co(phen)_2Cl_2]Cl$, respectively, and (c) additivity of these molar conductances.

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