112. *The Metal–Metal Interaction in Magnus's Green Salt and Related Compounds.*

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The reflectance spectra of some platinum(II) and palladium(II) analogues of Magnus's green salt are discussed. The spectra show that metal–metal interactions occur in all the compounds, and are exceptionally strong in Magnus's green salt and in the corresponding bromide. In these two compounds there is a strong absorption at 6000 cm.$^{-1}$.

A theory for the metal–metal interaction involving ground states and excited states is suggested.

In a previous publication[1] it was shown that several copper, palladium, and platinum complexes of similar formulation were isostructural with Magnus's green salt, $[Pt(NH_3)_4][PtCl_4]$. Metal–metal interactions, made possible by the close approach of metal atoms which this lattice allows, were detected in a qualitative fashion by noting whether the salt had a colour essentially different from that of a simple mixture of anion and cation. Interactions detected in this way were found to be restricted to certain of those materials containing platinum in both anion and cation.

Reflectance spectra of some of the solids have now been measured, thus giving a more definite basis to the colours. This Paper is concerned with some chloroplatinates(II), bromoplatinates(II), and chloropalladates(II). The maximum absorption positions are shown in Tables 1, 2, and 3, together with those of the potassium salts. The numbering of the transitions is the same as that used by Fenske *et al.*[2] for potassium chloroplatinate(II). The compounds have been arranged in order of decreasing frequency of band 3.

Examination of the spectra in Tables 1 and 2 reveals that band 3 moves about 4000 cm.$^{-1}$ to lower frequencies on going down each of the two series. The positions of the band maxima are clearly related to the colours of the salts, such that the compounds have more or less " expected " colours when the maxima lie above about 18,000 cm.$^{-1}$, and are green when the maxima are below this value. Bands 1 and 2 also shift to the red, and it appears that band 1 shifts faster than band 2 so that it is usually difficult to distinguish them. It is hoped that they can be separated in all the compounds by using polarised light on single crystals.

In the chloropalladate(II) spectra, bands 1 and 2 combine in unpolarised light to give a single sharp band. Together with band 3, which is not always clearly resolved, the combined band shifts to the red in the double salts, causing the slight change of colour from yellow-brown to pink. The movement, however, is not nearly so great as in the platinate(II) anions. The fact that these salts remain pink and do not appear green is due to the weakness of band 3, together with the absence of a marked minimum in the absorption between bands 2 and 3.

The shifts in the spectra must be due to interactions with the cations, and so the earlier conclusion that the appearance of a green colour indicated the existence of a relatively strong metal–metal interaction was essentially correct. However, two significant modifications must be made. The absence of an abnormal colour certainly does not preclude the existence of interaction, although it is likely to be weak in such cases. In the bromoplatinates(II), only a very small shift of band 3 is required to make the compound green, and so a green colour should not necessarily be taken to indicate the occurrence of a very strong interaction in these salts.

The detection of some interaction in all the salts does not negate the author's opinion[1] that the interaction is not responsible for the adoption of the structure. The structure is

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[1] Miller, *J.*, 1961, 4452.

[2] Fenske, Martin, and Ruedenberg, *Inorg. Chem.*, 1963, **1**, 441.

TABLE 1.

Spectra of chloroplatinates(II).

Substance	Colour	Band 4	Band 3	Band 2	Band 1
K_2PtCl_4	Pink				
Crystal spectrum [a]			20·3 (16) unpolarised	27·7 (56) *xy*-polarised	29·9 (56) *z*-polarised
Reflectance			20·3 (0·54)	26·0 (0·58)	28·8 (0·60)
Solution [b]			21·0 (15)	25·5 (59)	30·2 (64)
$[Pd\,en_2][PtCl_4]$	Pink		19·3 (0·30)		27·1 (0·58)
$[Pt\,en_2][PtCl_4]$	Purple		18·9 (0·49)	25·1 (0·66)	
$[Pd(NH_3)_4][PtCl_4]$	Pink		18·7 (0·34)	25·5 (0·52)	26·7 * (0·5)
$[Pt(EtNH_2)_4][PtCl_4]$	Pink		18·7 (0·28)		26·7 (0·44)
$[Pt(MeNH_2)_4][PtCl_4]$	Green	6·7 [d] (0·35)	17·4 (0·65)	25·0 (0·90)	26·4 (0·89)
$[Pt(NH_3)_4][PtCl_4]$	Green				
Reflectance (room temp.)		6·4 (1·05)	16·7 (0·70)	25·6 (0·95)	29·4 (1·10)
Reflectance (liquid N_2)		6·4 (1·05)	16·4 (0·60)	25·0 (0·85)	22·5 * (0·73) 29·0 (1·00)
Crystal spectrum [c]		Not measured		24·7 (57) *xy*-polarised	22·7 (74) *z*-polarised

Band Maxima are in cm.$^{-1}$ × 10^{-3}. Intensities are shown in brackets as follows: for solutions, molar extinction coefficients; crystals, 2α (α is the extinction per mm.): reflectance of powders, optical " D " scale, the figures are relative only to others in the same sample.

* A poorly defined shoulder.

[a] See ref. 7. [b] See ref. 5. [c] See ref. 8. [d] This absorption is relatively weak, but much more prominent than in the bromide in Table 2.

TABLE 2.

Spectra of Bromoplatinates(II).

Substance	Colour	Band 4	Band 3	Band 2	Band 1
K_2PtBr_4	Red				
Crystal spectrum [a]			18·0 (36)	25·4 (80) *xy*-pol.	29·0 (80) *z*-pol.
Reflectance			18·9 (0·59)	23·0 *	26·5 (0·83)
Solution			19·8 (24)	24·5 (182)	27·5 (370)
$[Pd\,en_2][PtBr_4]$	Pink		18·1 (0·31)	23·5 *	25·9 (0·55)
$[Pd(NH_3)_4][PtBr_4]$	Olive green		17·3 (0·33)	23·4 (0·60)	24·8 *
$[Pt\,en_2][PtBr_4]$	Green		17·1 (0·45)	24·0 (0·68)	
$[Pt(MeNH_2)_4][PtBr_4]$	Green	6·7 [b] (0·15)	16·1 (0·45)	23·9 (0·57)	
$[Pt(NH_3)_4][PtBr_4]$	Green				
Reflectance		6·0 (1·12)	15·8 (0·58)	23·5 (0·98)	
Crystal [c]		Not measured		21·7 (66) *xy*-pol.	20·3 (93) *z*-pol.

[a] See ref. 7. [b] This is very weak and may be a vibrational overtone. [c] See ref. 8.

favoured by lattice-energy considerations and its natural adoption permits these interactions.

On comparing the positions of band 3 in Tables 1 and 2, it is seen that the order of cations with respect to decreasing frequency is very nearly the same. A plot of one set of frequencies against the other is not quite linear, but does show a most marked correlation. The spectra show some dependence on interionic distance,[1] and appear to become sensitive

TABLE 3.

Spectra of chloropalladates(II).

Substance	Colour	Band 3	Band 2	Band 1
K_2PdCl_4	Yellow-brown			
Solution in 2N·HCl		16·6 shoulder (7·9)	21·1 (157)	
Reflectance		17·2 (0·36)	21·3 (0·78)	
Crystal [a]		17·0 (7) shoulder, prob. *xy*-pol.	21·4 (87) *xy*-pol.	23·0 (56) *z*-pol.
[Pd en_2][$PdCl_4$]	Pink	16·2 (0·22)	20·6 (0·63)	
[$Pt(NH_3)_4$][$PdCl_4$]	Pink	15·7 (0·40)	20·3 (0·67)	
[$Pd(NH_3)_4$][$PdCl_4$]	Pink	15·4 (0·2)	20·2 (0·56)	
[Pt en_2][$PdCl_4$]	Purple	15·4 Shoulder	19·5 (0·68)	

[a] See ref. 7.

Bands 1 and 2 are resolvable only in polarised light.

to very small changes in the distance in the region of 3·25 Å for the chloroplatinites and 3·31 Å for the bromoplatinites. Some of the relevant spacings are shown.

[Pd en_2][$PtCl_4$]	3·40 Å	[Pt en_2][$PtCl_4$]	3·40 Å	[Pd en_2][$PdBr_4$]	3·46 Å
[$Pd(NH_3)_4$][$PtCl_4$]	3·25 Å	[$Pt(MeNH_2)_4$][$PtCl_4$]	3·25 Å	[$Pt(MeNH_2)_4$][$PtBr_4$]	3·31 Å
		[$Pt(NH_3)_4$][$PtCl_4$]	3·23 Å	[$Pt(NH_3)_4$][$PtBr_4$]	3·31 Å

Attempts to index powder photographs of [$Pt(EtNH_2)_4$][$PtCl_4$] on the basis of a unit cell similar to that of the methylamine derivatives have been unsuccessful, and so there is at present no indication of its structure, other than that it is crystallographically different from the tetragonal compounds.

The unit cell of [Pt en_2][$PdCl_4$], obtained from measurements with a precession camera, is triclinic with $a = 11{\cdot}72$A, $b = 8{\cdot}46$A, $c = 6{\cdot}82$A, $\alpha = 96^\circ 48'$, $\beta = 91^\circ 11'$, $\gamma = 106^\circ 46'$. $hk0$ Reflections are absent for $h + k$ odd. hkl Reflections are very weak. Powder photographs show that [Pd en_2][$PdCl_4$], [Ni en_2][$PtCl_4$], [Cu en_2][$PtCl_4$], [Pd en_2][$PtCl_4$], and [Pt en_2][$PtCl_4$] are isomorphous with very similar cell dimensions. [Pd en_2][$PdBr_4$] shows a very similar powder pattern, but the lattice dimensions are greater. The density of [Pt en_2][$PtCl_4$] is given [3] as 3·363 g. cm.$^{-1}$. The cell dimensions above give a calculated density of 3·360 g. cm.$^{-1}$, for two molecules per unit cell.

The preliminary X-ray results show that, in these ethylenediamine complexes, the ions lie almost in the 002 planes, and so the structure is quite comparable to that of Magnus's salt. The details of the orientation of the ions to each other and to the crystal planes are yet to be determined. The distances given above are the d_{002} spacings calculated from the positions of the very strong 002 reflections. From the measurements it is already clear that the cell dimensions of these salts are determined largely by the ligands; from the spacing given for [Pd en_2][$PdBr_4$] it is reasonable to conclude that the other bromides have interionic distances within the range 3·45—3·47 Å.

Much more striking than the dependence of the spectra on interionic distance alone however is the difference between platinum and palladium. Platinum cations cause considerably lower frequencies than palladium ones, when the same ligands are involved, although the metal–metal distances are practically identical.

Although the visible and near ultraviolet spectra are sufficient to explain the colours of these compounds, perhaps the most important feature in the spectra is the appearance of strong, broad absorption centred at about 6000 cm.$^{-1}$ in Magnus's green salt and in the

[3] Baranova, *Zhur. neorg. Khim.*, 1961, **6**, 746.

corresponding bromide. This absorption appears to be unsymmetrical, extending approximately from 4000 cm.$^{-1}$ to 13,500 cm.$^{-1}$. By comparison band 3, in all cases where it is not partly hidden, is symmetrical with a half-width of about 3000 cm.$^{-1}$. In order to reach any understanding of how this absorption arises, it is necessary to develop in more detail the " band " theory which has already been tentatively suggested.[1,4]

Band Theory.—Consider a chain of alternate anions and cations, the total length being N ions. Each platinum atom has a $5dz^2$ and a $6pz$ orbital which are able to overlap with corresponding orbitals on the two neighbouring platinum atoms. Other orbitals in the ions are assumed to retain their localised character. The $5dz^2$ orbitals may not be " pure," but are probably better described as $(s + d_z2)$ hybrids, which take little or no part in the bonding with the ligands. The $6pz$ orbital may well be involved in π-bonding with the ligands in $PtCl_4^{2-}$ and in $PtBr_4^{2-}$.

Now considering the $5dz^2$ orbitals alone, these will interact with each other to form N delocalised molecular orbitals, or " crystal orbitals," as they will in general extend right through a crystal along the c-axis.

Let a given crystal orbital have the wave-function ψ_n and energy E_n.

In the LCAO approximation,

$$(1)\quad \psi_n = \sum_{i=1}^{N} c_{ni}\phi_i$$

where ϕ_i is the dz^2 wave function of the i'th atom in the chain, and $\Sigma c_{ni}^2 = 1$

Thus
$$E_n = \int \psi_n^* H(\psi_n)\, d\tau$$

$$(2)\quad E_n = \sum_{i=1}^{N} c_{ni}\alpha_i + \sum_{i}\sum_{j} c_{ni}c_{nj}\beta_{ij}$$

where
$$\alpha_i = \int \phi_i^* H(\phi_i)\, d\tau \quad \text{and} \quad \beta_{ij} = \int \phi_i^* H(\phi_j)\, d\tau$$

Now α_i is essentially the perturbed starting energy of the i'th dz^2 orbital, and may have two values, α_A for the anions, α_C for the cations. It will be assumed that $\alpha_C < \alpha_A$.

The resonance integral β_{ij} is taken to be zero except for $j = i + 1$, *i.e.*, for neighbouring atoms.

By applying the simple theory of a particle in a one-dimensional box, it can be shown that the c_{ni} values will follow a sine-wave pattern such that

$$c_{ni} = F\frac{2}{\sqrt{(N+1)}}\sin\frac{in\pi}{N+1}$$

Here F is a weighting factor such that low-energy crystal orbitals contain a larger proportion of the cation d_{z^2} orbitals and those of higher energy a correspondingly high proportion of anion orbitals. For any given crystal orbital stabilised by an energy δ_n with respect to one of the starting cation orbitals, it can be shown that

$$F^2 \text{ cations} = \frac{\Delta + \delta n}{\Delta + 2\delta n}$$

$$F^2 \text{ anions} = \frac{\delta n}{\Delta + 2\delta n}$$

Thus, for the cations,

$$c_{ni} = \frac{2}{\sqrt{(N+1)}}\sqrt{\frac{\Delta + \delta n}{\Delta + 2\delta n}}\sin\frac{in\pi}{N+1}$$

[4] Rundle, *J. Phys. Chem.*, 1957, **61**, 45.

[5] Chatt, Gamlen, and Orgel, *J.*, 1958, 486.

[6] Gray and Ballhausen, *J. Amer. Chem. Soc.*, 1963, **85**, 260.

[7] Yamada, *J. Amer. Chem. Soc.*, 1951, **73**, 1182 and 1579.

and for the anions,

$$c_{ni} = \frac{2}{\sqrt{(N+1)}}\sqrt{\frac{\delta n}{\Delta + 2\delta n}}\sin\frac{in\pi}{N+1}$$

Substituting these expressions into (2), we have

$$E_n = \frac{4\alpha c}{N+1}\cdot\frac{\Delta+\delta n}{\Delta+2\delta n}\sum_{i\,\mathrm{odd}}\sin^2\frac{in\pi}{N+1} + \frac{4\alpha_{\mathrm{A}}}{N+1}\cdot\frac{\delta n}{\Delta+2\delta n}\sum_{i\,\mathrm{even}}\sin^2\frac{in\pi}{N+1}$$
$$+\frac{8\beta}{N+1}\cdot\frac{\sqrt{\delta n(\Delta+\delta n)}}{\Delta+2\delta n}\sum_{i=1}^{N-1}\sin\frac{in\pi}{N+1}\sin\frac{(i+1)n\pi}{N+1}$$

If N is large, this expression reduces to

$$E_n = \tfrac{1}{2}(\alpha_{\mathrm{A}} + \alpha_{\mathrm{C}}) \pm \tfrac{1}{2}\sqrt{[\Delta^2 + 16\beta^2\cos^2(n\pi/N+1)]}$$

The density of orbitals at a given energy is expressed by $\mathrm{d}n/\mathrm{d}E$.

$$\frac{\mathrm{d}n}{\mathrm{d}E} = \frac{(N+1)[2E - (\alpha_{\mathrm{A}} + \alpha_{\mathrm{C}})]}{2\pi\sqrt{(E-\alpha_{\mathrm{A}})(E-\alpha_{\mathrm{C}})[4\beta^2 - (E-\alpha_{\mathrm{A}})(E-\alpha_{\mathrm{C}})]}}$$

Pictorially, these results can be expressed as shown in Fig. 1.

Interaction of the p_z orbitals with each other would produce a similar pair of bands. There will then be four bands of crystal orbitals, the two lowest being occupied in the ground state, the higher pair being unoccupied.

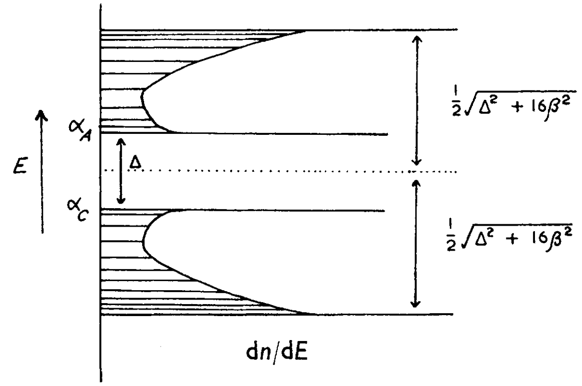

FIG. 1. The double-band structure obtained by interaction of a chain of atomic orbitals of different starting energies.

If the entire chain of atoms belongs to the point group D_{4h}, then alternate wave functions ψ_n will transform as a_{1g} and a_{2u} as a consequence of the sine form of the orbitals. Even values of n give a_{2u} orbitals, odd values a_{1g}. This means that half of the possible transitions from the filled "*d*" band to the empty "*p*" band are electronically allowed. Fig. 2 shows an energy-level diagram made out on the basis of these zones, together with the other original levels which remain unaffected. The arrow shows the allowed transition from the upper *d* band to the lower *p* band.

Spectra.—The unperturbed energies in Fig. 2 are drawn such that the $6pz$ orbital of the cation has a lower energy than that of the anion. In cases like this the band–band transition consists largely of an electron transfer from the anion to the cation. The transition is very broad, due to the spread of the two central bands. It consists of a series of $a_{1g} \longleftrightarrow a_{2u}$ transitions which would be z-polarised.

It is then possible to account qualitatively for the heavy absorption in the infrared spectrum by two of the compounds; this very explanation, however, immediately provokes the problem of finding reasons for the absence of the infrared absorption in all the other compounds investigated. The essential reasons must lie in the values of the unperturbed energy levels of the ions in relation to each other. For example if the unperturbed cation

a_{2u}-orbital lies higher than that of the anion a_{2u}, then the lower p band would be concentrated more on the anions than on the cations. The lowest transitions (given relatively large values of β) would then not have charge-transfer character and would have much lower intensities, but they would not be forbidden.

Before discussing the spectra in the visible region a few remarks must be made about the spectra of the potassium salts, as their assignment is a necessary foundation. The transitions in potassium chloroplatinate(II) have been disscused by Chatt, Gamlen, and Orgel,[5] by Fenske, Martin, and Ruedenberg,[2] and by Gray and Ballhausen.[6] They all agree that bands 1 and 2 are singlet transitions from non-bonding metal d-orbitals to the anti-bonding $d_{x^2-y^2}$ orbital (which transforms as b_{1g} in D_{4h} symmetry). The first two groups assigned band 3 as a singlet–triplet transition, but Gray and Ballhausen decided this was the ${}^1A_{1g} \longrightarrow {}^1A_{2g}$ transition. Chatt *et al.* resolved the two triplets by Gaussian analysis. Fenske *et al.* made extensive theoretical calculations using a point-dipole model and were able to obtain very good agreement with the observed spectra for a series of platinum(II) complexes.

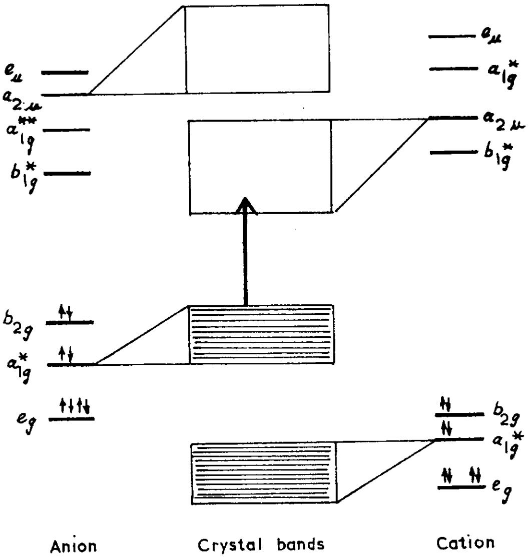

FIG. 2. Relative energy-levels in the Magnus's salt lattice.

Their assignments for chloroplatinate(II) were:

$$\begin{array}{lll} \text{Band 1.} & {}^1A_{1g} \longrightarrow {}^1B_{1g}: & 5d_{z^2} \longrightarrow 5d_{x^2-y^2} \\ \text{Band 2.} & {}^1A_{1g} \longrightarrow {}^1A_{2g}: & 5d_{xy} \longrightarrow 5d_{x^2-y^2} \\ \text{Band 3.} & {}^1A_{1g} \longrightarrow {}^3B_{1g}: & 5d_{z^2} \longrightarrow 5d_{x^2-y^2} \\ & {}^1A_{1g} \longrightarrow {}^3A_{2g}: & 5d_{xy} \longrightarrow 5d_{x^2-y^2} \end{array}$$

Chatt *et al.* and Gray and Ballhausen assigned band 1 as ${}^1A_{1g} \longrightarrow {}^1E_g(d_{yz},d_{zx} \longrightarrow d_{x^2-y^2})$ but Fenske *et al.* consider that the ${}^1E_g$ transition is of higher energy and is most likely to be hidden underneath more intense absorptions, probably of a $5d \longrightarrow 6p$ character. The assignment of band 2 to ${}^1A_{1g} \longrightarrow {}^1A_{2g}$ is supported by its xy polarisation, as reported by Yamada.[7] Table 4 shows the ways in which coupling with the fundamental modes of vibration of the ion can cause these normally forbidden d–d transitions to become allowed. It is seen that transitions to B_{1g} and to E_g states *may* have either xy, or z polarisations, but that a transition to an A_{2g} state can be excited only by coupling with an E_u vibration and *must* be xy polarised.

The fact that, in the double salts discussed in this Paper, bands 1 and 3 are much

TABLE 4.

Vibronic coupling in a molecule of D_{4h} symmetry.

Electronic transition		Coupled vibration	Polarisation of transition
$d_{xy} \longrightarrow d_{x^2-y^2}$	$A_{1g} \longrightarrow A_{2g}$	E_u	xy
$d_{z^2} \longrightarrow d_{x^2-y^2}$	$A_{1g} \longrightarrow B_{1g}$	E_u	xy
		B_{2u}	z
$d_{zx}, d_{yz} \longrightarrow d_{x^2-y^2}$	$A_{1g} \longrightarrow E_g$	E_u	z
		A_{2u}	xy
		B_{2u}	xy

affected by the cations, offers very strong support to Fenske's assignment of B_{1g} excited states. The $A_{1g} \longrightarrow B_{1g}$ transitions would be markedly affected by perturbations of the d_{z^2} orbital. This consideration, together with the extremely good overall agreement of Fenske's calculations with observed spectra, leads to the belief that these assignments are the correct ones.

In the spectra of the Magnus salts in the visible region, it has been shown that the most marked effect is a red shift of the transition ${}^1A_{1g} \longrightarrow {}^3B_{1g},{}^3A_{2g}$ (band 3). The singlet transition ${}^1A_{1g} \longrightarrow {}^1B_{1g}$ (band 1) also moves sharply, but cannot be followed closely as it becomes entangled with band 2, ${}^1A_{1g} \longrightarrow {}^1A_{2g}$. The B_{1g} transitions involve excitation from d_{z^2} to $d_{x^2-y^2}$ (b_{1g}*). Now it is assumed throughout this work that the b_{1g}* orbitals, which lie in the plane of the ion, are not perturbed by the cations. It follows then that the red shifts of the B_{1g} bands are directly due to the raising of the d_{z^2} orbital energies by interaction with the d_{z^2} orbitals of the cations. This is due partly to electrostatic repulsion between the electron pairs in neighbouring d_{z^2} orbitals, and partly due to overlap. The d_{z^2}–d_{z^2} interaction is present in all the double salts, being strongest in the salts of $[Pt(NH_3)_4]^{2+}$. This cation must have therefore an exceptionally active d_{z^2} orbital, certainly far more active than that in $[Pd(NH_3)_4]^{2+}$. The weaker interaction in the chloropalladates(II) indicates that this ion similarly has a d_{z^2} orbital much less easily perturbed than that of the platinate(II) ions.

The absence of the infrared band in most of the salts is then not due to the absence of d_{z^2}–d_{z^2} interaction. As the absorption depends on transitions between two energy zones, then it may be tentatively concluded that, when it is absent, the p_z–p_z interaction is weak. Small overlap between p_z-orbitals would tend to prohibit charge-transfer transitions from the anion d_{z^2} to cation p_z.

It is to be noted that in the tetrammine platinum(II) salts, the promotion of electrons from a filled zone to a higher-energy unoccupied zone by the absorption of infrared radiation should induce electrical conductivity along the c-axis of the crystal, as the excited electrons in the upper zone would have considerable freedom of movement. No experiments have yet been carried out to verify this suggestion.

EXPERIMENTAL

Compounds.—The ammine, methylamine, and ethylamine salts have been described previously.[1] Ethylenediamine salts were prepared in a similar fashion. Analyses of these materials are listed:

Bisethylenediaminepalladium chloropalladate(II) (Found: C, 9·8; H, 3·5; N, 11·5; Pd, 30·7. Calc. for $C_4H_8Cl_2N_2Pd$: C, 10·1; H, 3·4; N, 11·8; Pd, 29·9%).

Bisethylenediamineplatinum chloropalladate(II) (Found: C, 8·9; H, 3·15; N, 10·1; Cl, 24·6. Calc. for $C_8H_{16}Cl_4N_4PdPt$: C, 8·5; H, 2·9; N, 9·9; Cl, 25·2%).

Bisethylenediaminepalladium chloroplatinate(II) (Found: C, 8·7; H, 3·3; N, 10·2; Cl, 25·1%).

Bisethylenediamineplatinum chloroplatinate(II) (Found: C, 7·3; H, 3·0; N, 8·7; Cl, 21·2. Calc. for $C_4H_8Cl_2N_2Pt$: C, 7·4; H, 2·5; N, 8·6; Cl, 21·75%).

Bisethylenediaminepalladium bromoplatinate(II) (Found: C, 6·75; H, 2·15; Br, 44·0. Calc. for $C_8H_{16}Br_4N_4PdPt$: C, 6·5; H, 2·1; Br, 43·15%).

Bisethylenediamineplatinum bromoplatinate(II) (Found: C, 6·0; H, 2·0; Br, 38·2. Calc. for $C_4H_8Br_2N_2Pt$: C, 5·8; H, 1·9; Br, 38·4%).

Reflectance Spectra.—In the region 1000—340 mμ these were measured on a Unicam S.P. 500 spectrophotometer fitted with a reflectance attachment, and in the region 2500—700 mμ on a Beckman DK2A instrument with reflectance attachment. The spectrum of Magnus's green salt was measured at liquid-nitrogen temperature on the Beckman instrument. Unsuccessful attempts were made to measure spectra in the region 2500—700 mμ by placing mulls of finely powdered samples in nujol and hexachlorobutadiene between silica plates. The instrument used in these experiments was a Perkin-Elmer Spectracord 4000.

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