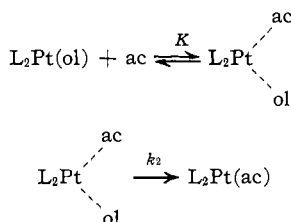


### Conclusion

The main purpose of this study was to obtain further information on the behavior of olefinic complexes of the type  $(P(C_6H_5)_3)_2M(C_2H_4)$  in solution. It is apparent from the above material that under the conditions used by Halpern, *et al.*,<sup>1</sup> for their kinetic studies (*i.e.*, excess ethylene present) the complex  $(P(C_6H_5)_3)_2Pt(C_2H_4)$  is associated in solution, presumably to  $(P(C_6H_5)_3)_2Pt(C_2H_4)_2$ . A reasonable *associative* scheme for the reaction of an acetylene (ac) with the olefin (ol) complex can be written as<sup>15</sup>



where  $L = P(C_6H_5)_3$ . For this scheme the rate is given by

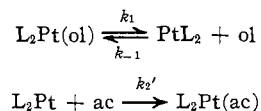
$$k_{obsd} = \frac{k_2 K [ac]}{1 + K [ac]} \quad (1)$$

This can be compared with the equation derived by Halpern for the same reaction

$$k_{obsd} = \frac{k_1 k_2' [ac]}{k_{-1} [ol] + k_2' [ac]} \quad (2)$$

(15) If free ethylene is present in the solution, there will be competition for the fourth coordination site between the acetylene and ethylene. However, the argument is unaffected provided that  $L_2Pt(ol)(ac)$  is the predominant intermediate. In view of the relative coordinating abilities of olefins and acetylenes to zerovalent platinum this seems to be a reasonable supposition.

for which the following stages were proposed



these stages being preceded by an immeasurably fast reaction. Equations 1 and 2 are identical with equations derived for  $SN_2IP$  and  $SN_1CB$  reaction pathways for  $Co(III)$  complexes,<sup>16,17</sup> the associative (IP) and dissociative (CB) processes both being consistent with the kinetic results. For  $(P(C_6H_5)_3)_2Pt(C_2H_4)$ , however, the additional pmr evidence is so strongly supportive of the associative process that we feel the kinetic data must be interpreted in terms of a bimolecular mechanism.

Allen and Cook<sup>18</sup> first proposed  $(P(C_6H_5)_3)_2Pt$  as the intermediate in substitution reactions of  $(P(C_6H_5)_3)_2Pt(ac)$  complexes, but recent synthetic work by Tripathy and Roundhill<sup>19</sup> and spectral observations of Greaves, Lock, and Maitlis<sup>20</sup> have cast some doubt on the validity of the proposal. In addition, Halpern<sup>21</sup> has shown that oxidation of  $(P(C_6H_5)_3)_2Pt$  to  $(P(C_6H_5)_3)_2Pt(O_2)$  does not involve the bis(phosphine)-platinum intermediate. In view of the increasingly precarious position occupied by  $(P(C_6H_5)_3)_2Pt$  in mechanistic schemes we have reexamined substitution reactions of  $(P(C_6H_5)_3)_2Pt(ac)$  complexes and these studies will form the basis of the second paper on this general topic.

(16) C. K. Poon and M. L. Tobe, *J. Chem. Soc. A*, 2069 (1967).

(17) S. C. Chan, *ibid.*, A, 1124 (1966).

(18) A. D. Allen and C. D. Cook, *Can. J. Chem.*, **42**, 1063 (1964).

(19) P. B. Tripathy and D. M. Roundhill, *J. Amer. Chem. Soc.*, **92**, 3825 (1970).

(20) E. O. Greaves, C. J. L. Lock, and P. M. Maitlis, *Can. J. Chem.*, **46**, 3879 (1968).

(21) J. Halpern and A. L. Pickard, *Inorg. Chem.*, **9**, 2798 (1970).

CONTRIBUTION FROM THE ISTITUTO DI CHIMICA GENERALE ED INORGANICA,  
UNIVERSITÀ DI ROMA, 00185 ROME, ITALY

## The Luminescence of Platinum(II) Complexes

By D. L. WEBB\* AND LAURA ANCARANI ROSSIELLO

Received July 9, 1970

Emission spectra of eight  $\sigma$  complexes of Pt(II) in the solid state are reported. The complexes are of two types, those whose lowest energy absorptions include  $d \leftarrow d$  transitions and those which show only CT bands at usual spectral concentrations. For the latter, new weak bands to the red of the first apparent band are reported and the possible origin of these is discussed. The emissions of three of the compounds in alcoholic solution are also presented.

While complexes of Pt(II) are among the earliest known luminophores,<sup>1</sup> they are also among the least studied. This is perhaps unfortunate since information yielded by comparison of absorption and emission spectra might prove useful in clarifying the unsettled problem of the assignment of electronic energy state levels in such compounds. One of the problems associated with making such assignments is that the uv absorption spectra do not always contain a sufficient number of clearly resolved bands in order to furnish the ligand field parameters necessary for calculations. In

(1) P. Pringsheim, "Fluorescence and Phosphorescence," Interscience, New York, N. Y., 1949.

compounds where molecular symmetry is reduced from the convenient  $O_h$  or  $T_d$  to some lesser group, more than just  $10Dq$  is required to describe splitting of the d orbitals. Thus further information is needed to provide the basis for reasonable energy schemes. In connection with this problem we have observed that a number of Pt(II) complexes are luminescent at low temperature. (We have already reported the emission of  $K_2PtCl_4$  and have inferred from this something of the nature of the lowest excited state.<sup>2</sup>) This paper is the preliminary report on the new emissions.

(2) D. L. Webb and L. A. Rossiello, *Inorg. Chem.*, **9**, 2622 (1970).

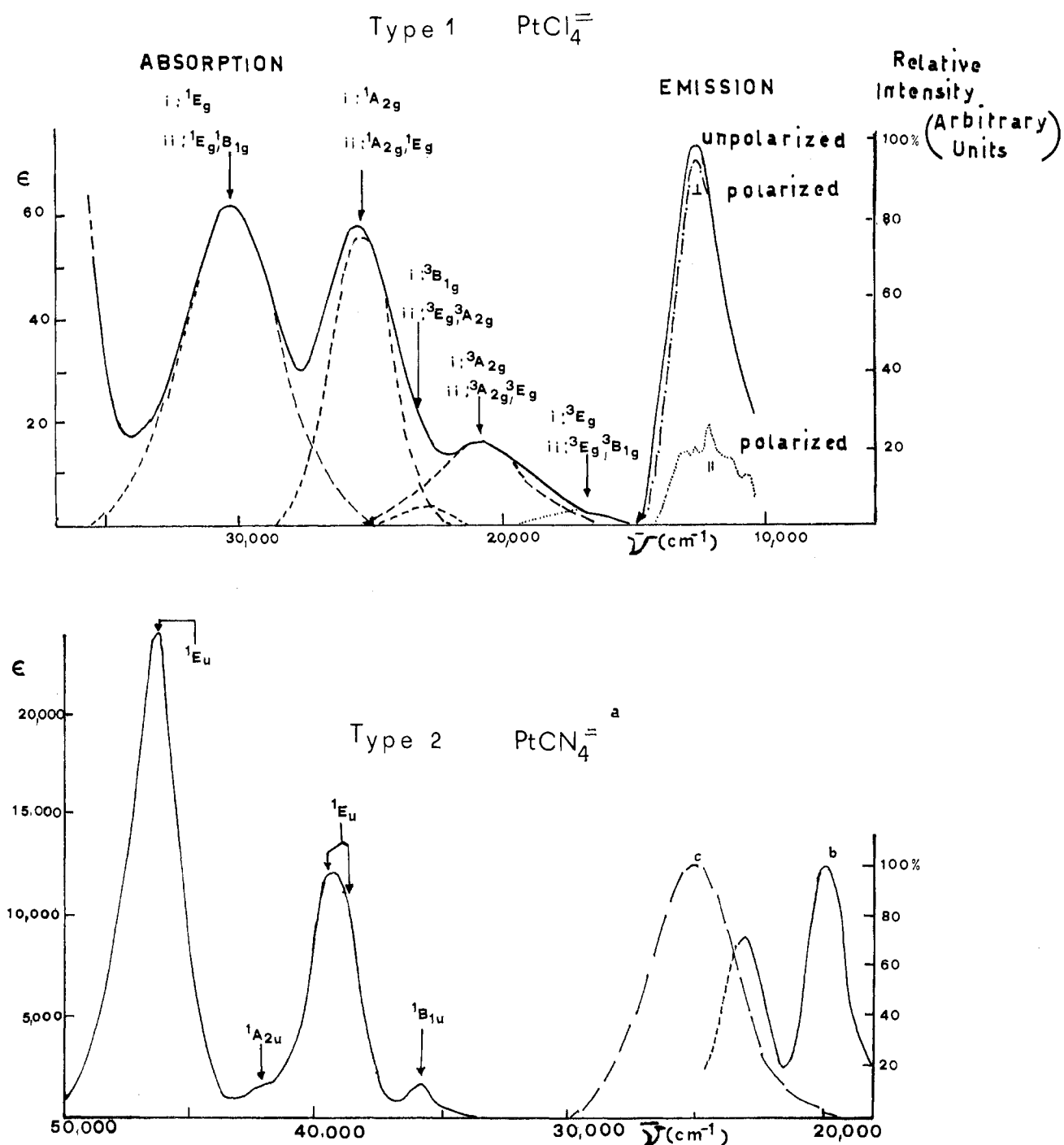


Figure 1.—Representative spectra of Pt(II)  $\sigma$  complexes. Type 1: i, MTK (A), ref 3; ii, MTK (B), ref 3. Type 2: (a) assignments according to ref 5; (b) 77°K, any salt,  $\sim 2 \times 10^{-6} M$  (aqueous), according to A. M. Tkachuk and N. A. Tolstoi, *Opt. Spectrosc. (USSR)*, 20, 570 (1966); (c) 296°K,  $\text{K}^+$  salt,  $\sim 10^{-1} M$  (aqueous) (first of four peaks).

There are two types of Pt(II)  $\sigma$  complex, represented by compounds formed from ligands at the extremes of the spectrochemical series, and the transition from one type to the other is gradual. The two chromophores  $\text{PtCl}_4^{2-}$  (low field, type 1) and  $\text{Pt}(\text{CN})_4^{2-}$  (high field, type 2) represent these two extremes and their absorption and emission spectra are shown in Figure 1. A type 1 spectrum consists of a series of low-intensity bands ( $\epsilon < 100$ ), starting in the visible region, and much higher intensity bands ( $\epsilon > 1000$ ) toward shorter wavelengths. The whole of a type 2 spectrum is displaced to the blue with respect to a type 1 spec-

trum and consists, apparently, only of high-intensity CT bands.

The general features of spectrum 1 are understood though detailed assignment is still being discussed. The low-energy bands are  $d \leftarrow d$  transitions to the antibonding  $d_{x^2-y^2}$  orbital and the high-intensity bands are considered to be CTTM (charge transfer to metal). The best assignment available is that of Martin, Tucker, and Kassman,<sup>3</sup> which is shown in Figure 1. Our prior work tends to support their proposal of a non-

(3) D. S. Martin, Jr., M. A. Tucker, and A. J. Kassman, *Inorg. Chem.*, 5, 1298 (1966), and references therein.

tetragonal lowest excited state.<sup>2</sup> (Such a geometry has been proposed also for an intermediate in the intramolecular *cis* → *trans* photoisomerization of Pt(gly)<sub>2</sub> (gly = glycinate).<sup>4</sup>)

The assignments for spectrum 2 are much less satisfactory in that none made so far explains all the experimental data. The two most recent attempts<sup>5,6</sup> are not completely convincing. For example, in ref 5, the two transitions of equal intensity at 35,800 and 41,400 cm<sup>-1</sup> are, respectively, assigned as <sup>1</sup>B<sub>1u</sub> (forbidden) and <sup>1</sup>A<sub>2u</sub> (allowed) transitions. In ref 6, where evidence for three E<sub>u</sub> ← A<sub>1g</sub> transitions is presented (inconsistent with the scheme in ref 5), the assignments are made to spin-orbit coupled states of high triplet character. (Recognizing that spin-orbit coupling in Pt is so large that formal spin states do not exist, it is nevertheless convenient to distinguish between certain transitions of different intensities in the language of Russel-Saunders coupled states. In this paper the terms "singlet" and "triplet" are used in this sense.) In order to obtain the necessary intensity, the authors used a spin-orbit coupling constant of 0.85 the free-atom value, or ~3500 cm<sup>-1</sup>. However, the value of this parameter in PtCl<sub>4</sub><sup>2-</sup> appears to be only ~3400 cm<sup>-1</sup>.<sup>3</sup> Since the calculations are formulated in such a way that π interactions of the metal and the ligands are reflected in the size of this parameter, it is strange that both Cl<sup>-</sup> and CN<sup>-</sup> complexes, whose π interactions are certainly different, should require the same value. This is how the situation stands at the moment. However, the general argument that antibonding, essentially ligand, π levels have decreased to the point where they lie below the metal d<sub>x<sup>2</sup>-y<sup>2</sup></sub> (b<sub>1g</sub>) orbital seems valid and we assume that the transitions seen are from metal d orbitals, even if one cannot be precise as to the order of these.

### Results and Discussion

The absorption and emission spectra of the following complexes are reported in Figure 2: (I) PtBr<sup>2-</sup>, (II) PtCl<sub>4</sub><sup>2-</sup>, (III) *trans*-Pt(gly)<sub>2</sub> (gly = glycinate), (IV) Pt(dipy)Cl<sub>2</sub> (dipy = dipyrindine, a = yellow form, b = red form), (V) Pt(*o*-phen)Cl<sub>2</sub> (*o*-phen = 1,10-phenanthroline), (VI) Pt(dipy)(en)Cl<sub>2</sub> (en = ethylenediamine), (VII) Pt(dipy)<sub>2</sub>X<sub>2</sub> (a, X<sup>-</sup> = Cl<sup>-</sup>; b, X<sup>-</sup> = ClO<sub>4</sub><sup>-</sup>), and (VIII) Pt(*o*-phen)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>. Compounds I-III represent type 1 species; the rest are all type 2.

The emission spectra of powder samples of most of these compounds consist of single diffuse bands. Only in the case of the C<sub>2v</sub> type 2 complex (VI) is there any apparent structure. As the ligand field strength increases there is progressively less overlap between the apparent absorption and the emission. This observation was bothersome and the absorption spectra were remeasured either at higher concentrations or, where this was not possible for lack of solubility, by using longer cells or diffuse reflectance spectra. In every case a weak (ε < 100) tail to the red of the first apparent absorption band was found (see Table I). Such a tail appears either as an inflection in the descending

TABLE I  
LOW-ENERGY ABSORPTIONS OF TYPE 2 Pt(II) COMPLEXES

Compound	Solvent	λ <sub>max</sub> , <sup>a</sup> nm	ν <sub>max</sub> , <sup>a</sup> cm <sup>-1</sup>	ε	
Pt(dipy)Cl <sub>2</sub> (yellow) (IVa)	CH <sub>3</sub> OH	440	22,800	80	
		462	21,600	65	
		500	20,000	20	
	CHCl <sub>3</sub>	454	22,000	115	
		481	20,800	55	
		Reflectance	440	22,800	...
Pt(dipy)Cl <sub>2</sub> (red) (IVb)	CH <sub>3</sub> OH	453	22,100	...	
		473	21,100	...	
		452	22,100	20	
	Reflectance	541	18,500	15	
		634 (?)	15,800	6	
		530	18,900	...	
Pt( <i>o</i> -phen)Cl <sub>2</sub> (V)	CH <sub>3</sub> OH	463	21,600	~42	
		CHCl <sub>3</sub>	446	22,400	88
		477	21,000	25	
	Reflectance	461	21,700	...	
		Pt(dipy)(en)Cl <sub>2</sub> (VI)	393	25,400	16
		CH <sub>3</sub> OH	419	23,800	12
Pt(dipy)(en)Cl <sub>2</sub> (VI)	CH <sub>3</sub> OH	460	21,800	~4	
		Reflectance	420	23,800	...
		452	22,100	...	
	Pt(dipy) <sub>2</sub> Cl <sub>2</sub> (VIIa)	CH <sub>3</sub> OH-H <sub>2</sub> O	~500 (?)	~20,000	...
			458	21,800	20
			482	20,700	9
H <sub>2</sub> O		~520	19,100	~3	
		462	21,600	10	
		508	19,700	7	
Pt(dipy) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> (VIIb)	CH <sub>3</sub> OH	560	17,900	~3	
		440	22,800	26	
		492	20,300	3	
	Reflectance	536	18,600	3	
		440	22,800	...	
		452	22,100	...	
Pt( <i>o</i> -phen) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> (VIII)	Reflectance	473	21,100	...	
		435	23,000	...	

<sup>a</sup> All solution values were obtained by Gaussian analysis and are subject to appreciable experimental error.

slope of the spectral curve or as a discrete maximum (see Figure 3 for examples). Gaussian curve fitting was performed to locate the approximate positions of the components, using, wherever possible, at least two concentrations and/or two different cell lengths. A Gaussian component from curve fitting does not constitute proof of a transition and the situation is compounded by the severe overlap of the apparent bands and the greatly differing intensities of the strong and weak components. Admitting these difficulties, the solutions obtained as above were fairly reproducible and we feel moderately confident in placing transitions near the wavelengths given. In passing, we note that the aqueous spectrum of Pt(CN)<sub>4</sub><sup>2-</sup>, much discussed in recent literature, also shows such a tail although less pronounced. The detailed investigation of this species will be the subject of a forthcoming paper. Again, we caution readers against using the values given except in the approximate sense in which they are presented.

There are at least two possible alternatives for the origin of these bands: they may be d ← d transitions which have not moved under the strong CT bands near which they lie, or they may be the "triplet" components of the latter. We have no direct evidence which permits us to distinguish between these two possibilities. We note, however, that Orgel, *et al.*,<sup>7</sup> found that in the series Pt(NH<sub>3</sub>)<sub>4-x</sub>Cl<sub>x</sub><sup>(2-x)+</sup> the d ← d bands move smoothly to the blue as a function of increasing ligand field strength and that in the compound *cis*-Pt(NH<sub>3</sub>)<sub>2</sub>-Cl<sub>2</sub> the lowest energy band occurs at 417 nm (ε 3). The much higher positions in the spectrochemical series of the ligands in our complexes should shift the

(4) V. Balzani, V. Carassiti, L. Moggi, and F. Scandola, *Inorg. Chem.*, **4**, 1243 (1965).

(5) W. R. Mason and H. B. Gray, *J. Amer. Chem. Soc.*, **90**, 5721 (1968); cf. H. Basch and H. B. Gray, *Inorg. Chem.*, **6**, 365 (1967).

(6) S. B. Piepho, P. N. Schatz, and A. J. McCaffery, *J. Amer. Chem. Soc.*, **91**, 5994 (1969).

(7) J. Chatt, G. A. Gamlen, and L. E. Orgel, *J. Chem. Soc.*, 486 (1958).

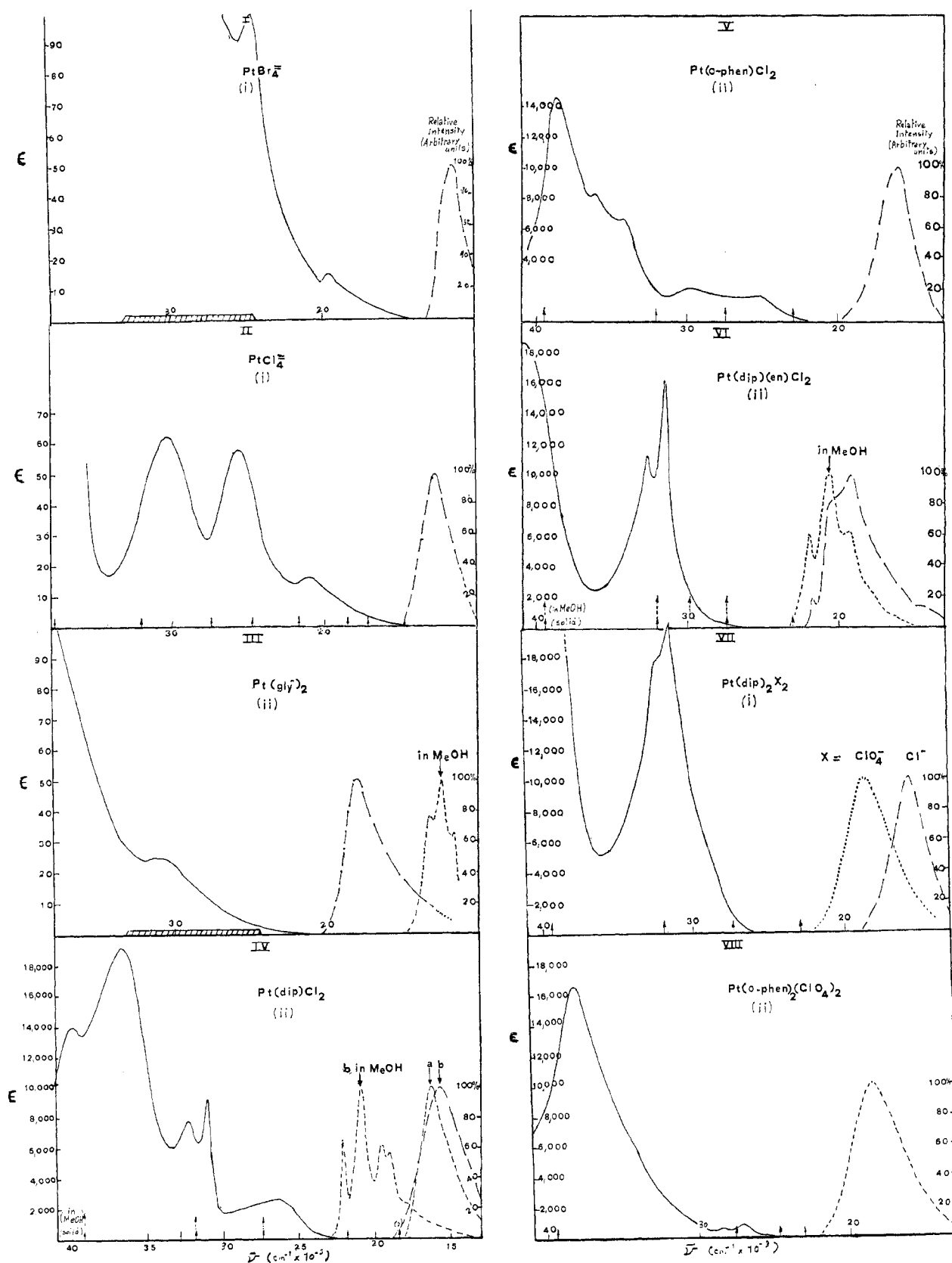


Figure 2.—Absorption and emission spectra of some Pt(II)  $\sigma$  complexes. All absorption spectra at ambient temperature in either aqueous (i) or methanolic (ii) solution (solid lines). All emission spectra at 77°K from crystalline powders unless otherwise indicated (dotted lines). Wavelengths of irradiation shown by arrows underneath the absorption curves. Irradiation of frozen  $\text{CH}_3\text{OH}$  solutions (where performed) shown by dotted arrows above these. Where a band-pass filter was used the wavelength range is indicated by a shaded block. (Note: Emission spectrum IVa = red form, ambient temperature; spectrum IVb = yellow form, 77°K. The red form has the same  $\tilde{\nu}_{\text{max}}$  but is narrower and has shoulders.)

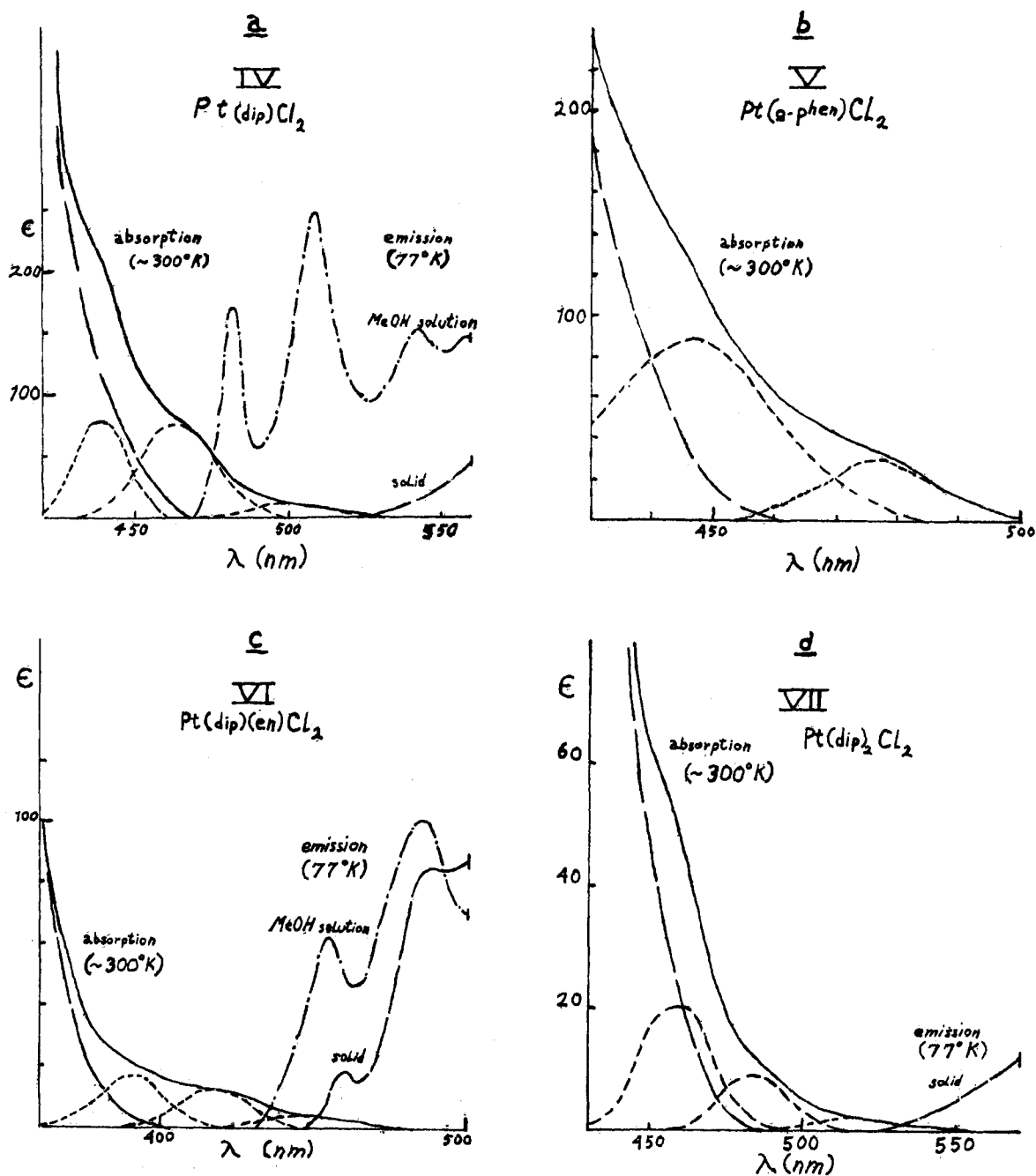


Figure 3.—Low-intensity absorption spectra for type 2 complexes: Solid lines, spectral curves; dotted lines, Gaussian components. Solvents: a, c, CH<sub>3</sub>OH; b, CHCl<sub>3</sub>; d, 5:1 CH<sub>3</sub>OH-H<sub>2</sub>O. Partial emission spectra are shown as dotted lines (note the temperature difference with respect to the absorptions).

$d \leftarrow d$  bands even further to the blue. Moreover,  $d \leftarrow d$  bands in PtCl<sub>4</sub><sup>2-</sup> are relatively insensitive to  $z$ -axis perturbation, such as change of solvent, while the new bands, where it was possible to measure such effect, are appreciably sensitive (Table I).

The fact that there are always several components in the tails should not be taken as evidence that these are a series of  $d \leftarrow d$  bands. The splitting of the "triplet" components of the orbital states in  $D_{4h}$ ,  $D_{2h}$ , and  $C_{2v}$  symmetries produces several components for each state and multiplicity of bands is therefore not sufficient reason to exclude <sup>3</sup>CT assignment.

Additional evidence of the sensitivity of the weak bands to axial perturbation is seen in the shifts of the emission maxima in the solid state on change of coun-

terion. In type 1 complexes these are small or non-existent in the solid. In type 2 species they are large. For example, in solid PtCl<sub>4</sub><sup>2-</sup> salts the range of frequencies of the emission maxima on changing the cation from Li<sup>+</sup> to Cs<sup>+</sup> is  $-500 \text{ cm}^{-1}$ .<sup>2</sup> In Pt(CN)<sub>4</sub><sup>2-</sup>, the exemplar of type 2, the shift is  $+1800 \text{ cm}^{-1}$ . Even more striking is the shift in the cationic chromophore Pt(dip)<sub>2</sub><sup>2+</sup> on changing the counteranion from Cl<sup>-</sup> to ClO<sub>4</sub><sup>-</sup>: from 15,600 to 18,600  $\text{cm}^{-1}$ . The latter emission is very close to the fluorescence maximum of the free dipyrindine but the half-width of the complex is larger and, unlike free dipy, the spectral distribution varies with time of irradiation, indicating photodecomposition. Recrystallization of the complex does not change the position of the maximum and we feel that

the reported spectrum is probably very close to the true one since (a) the original spectrum can be regenerated by changing the position of the sample in the holder and (b) measurement of the spectrum with time and extrapolation of this to zero time gives a distribution identical with that of (a). (The photoreaction will be the subject of a subsequent paper on the excited-state behavior of Pt(II) complexes.)

We feel that this evidence, while not excluding the possibility that the bands are  $d \leftarrow d$ , is more consistent with assignment to triplet CT transitions.

Work is just beginning on the emission of these species from frozen solution and initial results are most interesting. The emissions of the three complexes III, IV, and VI have been measured in  $\text{CH}_3\text{OH}$  at  $77^\circ\text{K}$  and are indicated in Figure 2 by dotted lines. The three chromophores are, respectively, type 1 (neutral), type 2 (?) (neutral), and type 2 (cationic). The spectrum of III shows a strong red shift ( $-5600\text{ cm}^{-1}$ ) with the appearance of structure and is very similar to that of  $\text{PtCl}_4^{2-}$  both in position and in the three-peaked structure. This behavior is strange, since the lowest energy transition is said to be  $d \leftarrow d$  and this should not be so sensitive to solvation effects. The spectrum of IV shows a strong blue shift and the spectral distribution is remarkably similar to the phosphorescence spectrum of free dipy except that it is shifted some  $1300\text{ cm}^{-1}$  to the red of the latter. We have not succeeded in finding a suitable solvent for the recrystallization of this material, but exhaustive extraction of the powder with ether does not alter the spectrum and it is unlikely that the emission is from a dipyridine residue in some associated form. Spectra of similar shape have been seen from dipy complexes of Ir(III), Os(II), and Ru(II)<sup>8</sup> and have been assigned in these complexes to CT emission. If our suggestion concerning the origin of the weak red absorption is correct, such assignment can be made for this emission also. In compound VI, which is the only species whose emission in the solid is structured, the spectral distribution of the emission does not change on dissolution in  $\text{CH}_3\text{OH}$  but the relative intensities of the peaks differ significantly. It is possible that in this complex there is appreciable ion pairing in alcoholic solution and/or that freezing of the solution induces such association.

In summary, several compounds of Pt(II) have been found to emit at liquid nitrogen temperature and the luminescence always seems to be associated with a weak long-wavelength absorption for both low-field and high-field complexes. The emissions of examples of these two types of complex differ in their sensitivity to axial perturbation and give evidence of being of different origins.

### Experimental Section

**Preparation of the Complexes.**—I,  $\text{K}_3\text{PtBr}_4$ , was the recrystallized commercial product. II,  $\text{K}_2\text{PtCl}_4$ , was the commercial product recrystallized according to ref 9. III,  $\text{Pt}(\text{gly})_2$ , was

(8) (a) G. A. Crosby and D. M. Klassen, *J. Chem. Phys.*, **48**, 1498 (1968), and references therein; (b) K. R. Wunschel, Jr., and W. E. Ohnesorge, *J. Amer. Chem. Soc.*, **89**, 2777 (1967).

(9) F. Scandola, O. Traverso, and V. Carasiti, *Mol. Photochem.*, **1**, 11 (1969).

prepared according to ref 10. IVa and b,  $\text{Pt}(\text{dipy})\text{Cl}_2$ , red and yellow forms, were prepared according to ref 11. V,  $\text{Pt}(o\text{-phen})\text{Cl}_2$ , was prepared according to ref 12 and references therein. VI,  $\text{Pt}(\text{dipy})(\text{en})\text{Cl}_2$ , was prepared according to ref 11. VIIa,  $\text{Pt}(\text{dipy})_2\text{Cl}_2$ , was prepared as follows. Solid IVa (2.4 mmol) ( $\text{H}_2\text{O}$  insoluble) was placed in a round-bottomed flask containing an aqueous solution of twice-recrystallized dipyridine (2.3 mmol) and the mixture was gently warmed ( $80^\circ$ ) until no more solid would dissolve. Excess IVa was filtered off, dried, and weighed (4% recovery or quantitative reaction). Removal of the water to dryness *in vacuo* resulted in decomposition to starting materials. Attempts to extract the material with several organic solvents were also unsuccessful. The concentration of dipyridine reacted was therefore taken as the product concentration. On one occasion only it was possible to isolate a crystalline product by reducing the volume of the reaction solution to ca. 3 ml and precipitating an unstable golden yellow material by addition of dioxane. On washing this material with  $\text{CH}_3\text{OH}$ , benzene, or other solvents, it rapidly decomposed to a mixture of IVa and b and free dipyridine. The unwashed material, redissolved in  $\text{H}_2\text{O}$  immediately after filtration, had a uv spectrum identical with that of the reaction mixture. VIIb was prepared according to ref 12 and was recrystallized from hot water until the absorption and emission spectra showed no further change. VIII,  $\text{Pt}(o\text{-phen})_2(\text{ClO}_4)_2$ , was prepared according to ref 12.

Initial preparations of these compounds were submitted for elemental analysis; all subsequent preparations were considered to be operationally pure if the uv and emission spectra corresponded to those of authentic samples.

**Uv Absorption Spectra.**—All spectra were measured on a Beckman Model DK-2 spectrophotometer equipped with a reflectance attachment when required. They were measured at room temperature in aqueous or methanolic solution.

**Emission Spectra.**—Powder samples of the various materials were mounted on black Bakelite strips, immersed in liquid  $\text{N}_2$ , and irradiated with light from a 200-W high-pressure mercury lamp. A filter combination (Corning 7-54 + 2 cm of 0.1 M aqueous  $\text{CuSO}_4$ ) was used to pass a band of exciting light (wavelengths between 300 and 410 nm), except for wavelength-dependence studies when a Beckman GM 1139 monochromator was used (see Figure 2 for wavelengths). No variation of spectral distribution as a function of  $\lambda_{\text{ex}}$  was found. The emission was analyzed with a Model CGA DC/3000 grating monochromator fitted with a nitrogen-cooled Type S-1 photomultiplier. Photographic recording was performed with a Hilger-Watts E.42 prism spectrograph, using Kodak I-N or II-N plates. Where there was no photoreaction, both types of registration gave equivalent spectra, following correction for detector response. The spectra shown are all photometric results because of the better resolution of the grating instrument in the range where emission is found.

**Curve Analysis.**—Gaussian analyses of the absorption spectra were performed on a Du Pont 310 curve analyzer and the solutions obtained are empirical "best fits" to the experimental curves. Determination of the position of the weak red bands was made by placing the nearest strong band, obtained from total spectrum analysis, and filling in the remaining area with one-component, two-component, etc., solutions until the best fit was found. This does not preclude solutions with a greater number of components and the results in Table I are to be taken only as approximations.

**Acknowledgment.**—We are grateful to A. Zanobi for preparing and obtaining the emission spectra of the salts of the tetrachloroplatinate ion. We are also grateful for the interest and assistance of Professor G. Sartori of this institute, and D. L. W. acknowledges with thanks financial support from the Science Committee of NATO.

(10) F. Scandola, O. Traverso, V. Balzani, G. L. Zucchini, and V. Carasiti, *Inorg. Chim. Acta*, **1**, 76 (1967).

(11) G. T. Morgan and F. H. Bursall, *J. Chem. Soc.*, 935 (1934).

(12) L. A. Rossiello, *Gazz. Chim. Ital.*, **97**, 1177 (1967).