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The Luminescence of Dipotassium Tetrachloroplatinate

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We have observed the luminescence of the title compound at 77°K in the solid (powder, single crystal, KBr pellet) and in frozen aqueous solution, both spectrographically and spectrophotometrically. Corrections of both types of spectra for detector sensitivity give equivalent distributions. No emission was observed at room temperature.

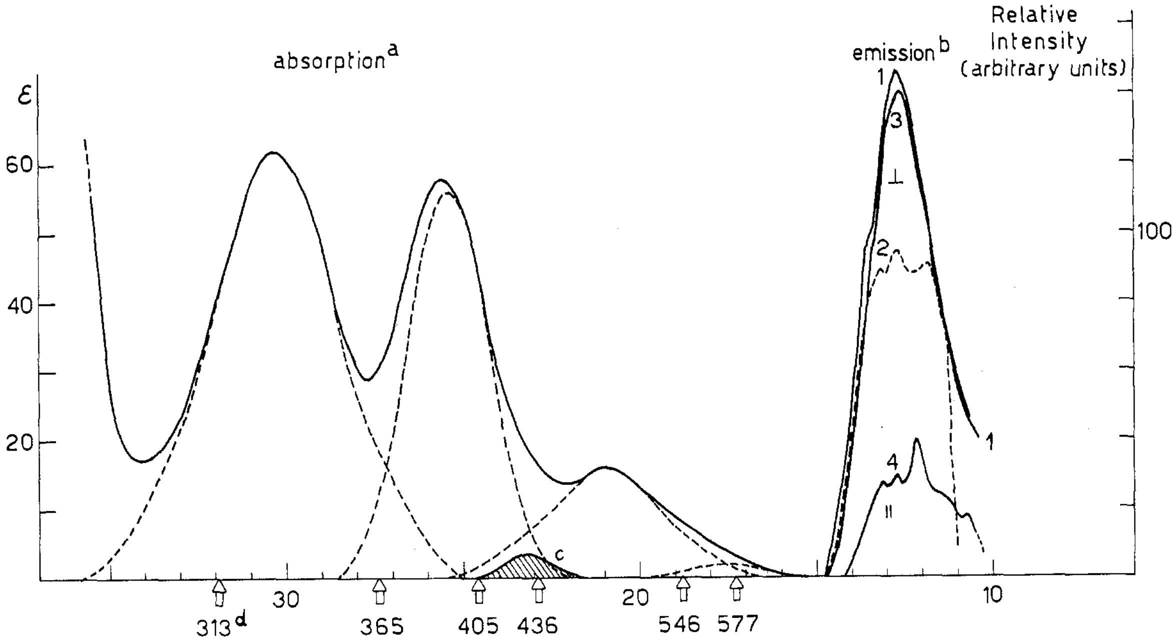

Figure 1.—Absorption and emission spectra of $PTCl_4^{2-}$. (a) Absorption of fresh aqueous solution at room temperature. (b) Emission at 77°K: (1) powder, spectrophotometrically (identical with the spectrum of a 10^{-2} *M* solution in H_2O, λ_{exc} 365 nm); (2) powder, spectrophotographically (photographic effects make the fine structure appear artificially as maxima); (3) single crystal, ⊥ polarized, exciting light; (4) single crystal, ‖ polarized exciting light. (c) The shaded area is obtained from Gaussian analysis and occurs just where a band is found in the single-crystal polarized absorption spectrum. (d) Wavelengths of irradiation (nm).

Photographs of the luminescence were made using a Hilger-Watts E-42 (medium) quartz prism spectrograph and Kodak I-N plates. The exciting light (from an HBO 200-W Osram Hg lamp) was filtered to give essentially the Hg lines from 300 to 410 nm. The spectrophotometric results were obtained with the same lamp and with a Beckman GM 1139 grating monochrometer in the incident light beam. The exciting light was directed onto the sample immersed in liquid N_2 and the emitted light was analyzed with a CGA Model DC/3000 grating monochrometer equipped with a Type S-1 photomultiplier. Both types of spectra were corrected for the sensitivity of the detector. Although this does not remove all distortions, the resultant spectra correspond very well for this and for other compounds.

The luminescence of the solid as a powder, single crystal, or KBr pellet (single-crystal spectrum and solution absorption spectrum shown in Figure 1) consists of a fairly wide band ($\bar{\nu}_{1/2}$ 2400 cm^{-1}) which peaks at 12.7 kK with weak shoulders at 11.8 and 13.2 kK. The spectral distribution is insensitive to change of λ_{exc} from 365 to 577 nm. Excitation by the latter Hg line (and by that at 546 nm) is of interest since these two wavelengths lie in the region of $T \leftarrow S_0$ absorption. A qualitative estimate of the relative intensities of the spectra so obtained shows a general increase of intensity with increasing irradiation wavelength which suggests that there are competing modes of energy dissipation in the higher excited states. The spectrum of a freshly prepared 10^{-3} *M* aqueous solution did show a slight wavelength dependence both in form and in position of $\bar{\nu}_{max}$ ($\Delta\bar{\nu}$ ~300 cm^{-1}).

While references to the luminescence of $PtCN_4^{2-}$ and its salts abound in the literature,[1] it is apparently not widely appreciated that a large number of simple Pt(II) ($5d^8$) complexes emit. A rapid search of the literature has turned up only three reports,[2-4] only one of which includes spectral distributions. The compound

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[1] (a) I. A. Khvostikov, *Tr. Gos. Opt. Inst.*, **12**, 104 (1937); (b) N. A. Tolstoi, A. K. Trofimov, A. M. Tkachuk, and N. N. Tkachuk, *Izv. Akad. Nauk SSSR, Ser. Fiz.*, **20**, 583 (1956); (c) A. M. Tkachuk, *ibid.*, **27**, 670 (1963); (d) A. M. Tkachuk and N. A. Tolstoi, *Opt. Spectrosc. (USSR)*, **20**, 570 (1966); **21**, 31, 310 (1966); (e) R. Berg, *U. S. At. Energy Comm.*, UCRL 9954 (1962); *Chem. Abstr.*, **57**, 6753*g* (1962).

[2] J. T. Randall, *Nature (London)*, **142**, 113 (1938).

[3] A. I. Ruskin, A. M. Tkachuk, and N. A. Tolstoi, *Opt. Spectrosc.*, **18**, 238 (1965), and references therein.

[4] L. G. Polytsyna and K. P. Stolyarov, *Vestn. Leningrad. Univ.*, **19** (22), *Fiz., Khim.*, No. 4, 136 (1964); *Chem. Abstr.*, **62**, 11148*a* (1965).

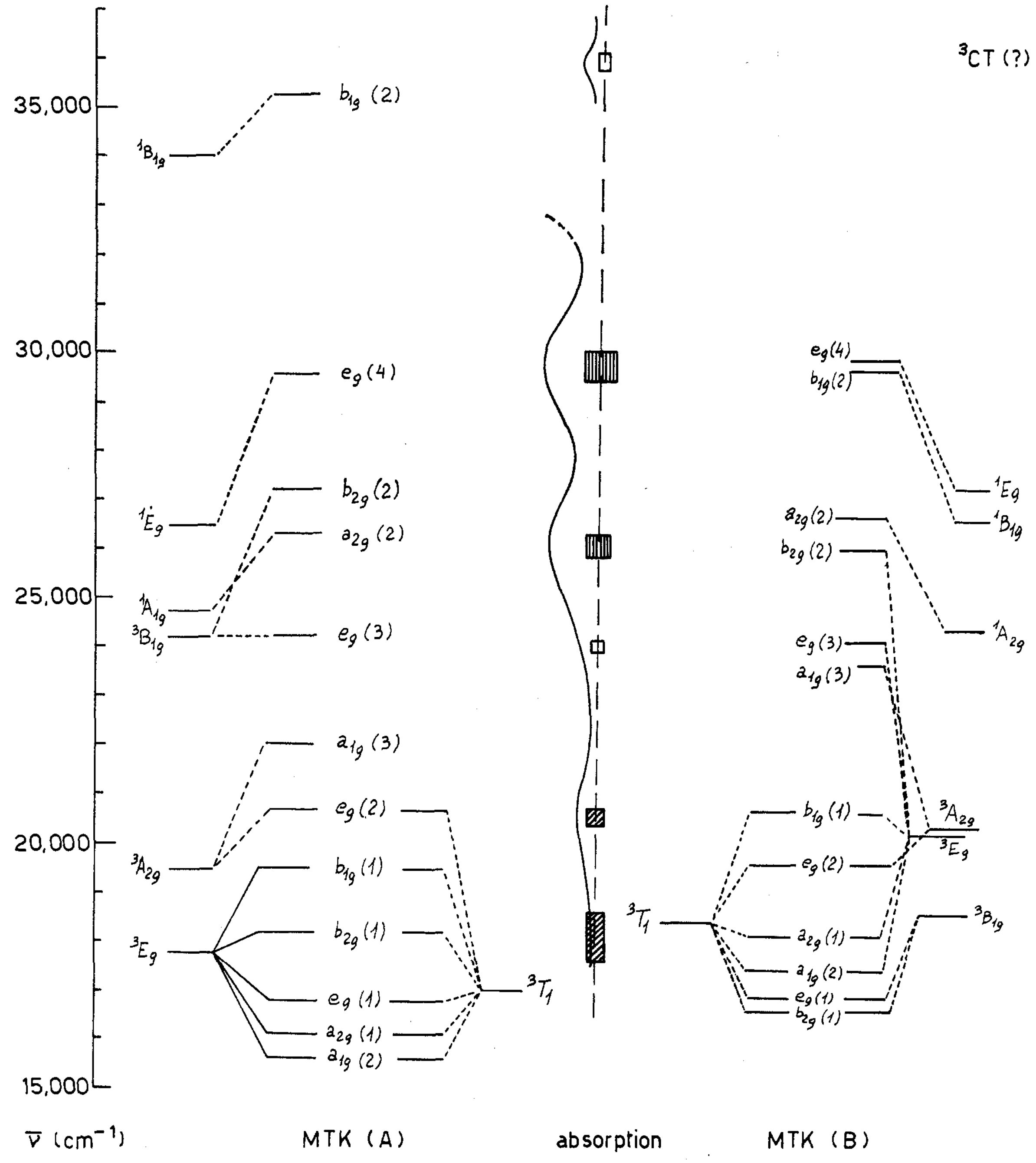


Figure 2.—Energy levels for $PtCl_4^{2-}$; ligand field calculations of Martin, Tucker, and Kassman.[6e]

K_2PtCl_4 bears a structural resemblance to the cyanide complex in that the chromophore in both cases is a square-planar ion, but it is in no way similar in its spectral behavior. The visible–uv absorption spectrum consists of a series of low-intensity d ← d transitions with CT bands toward higher energy (see Figure 1), and the assignment of these has been the source of considerable controversy.[5–8] Martin and coworkers, in particular, have been at some pains to resolve this problem, and, using results from circular magnetic dichroism[6d] and low-temperature single-crystal absorption spectra with polarized light,[6c] they were able to make unambiguous assignment of the bands at ~26 and ~30 kK. The experimental results were combined with semiempirical ligand field calculations to construct two alternative energy schemes[6e] (Figure 2A, B). The authors suggest that (B) is more consistent with all data while Basch and Gray[7b] preferred (A) on the basis of their MO calculations and spectral measurements.[7c]

With only two of the six possible transitions located on the basis of experimental evidence, problems still remain, one of which is the assignment of the lowest energy singlet–triplet band. Until now there has been

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

(6) (a) R. F. Fenske, D. S. Martin, Jr., and K. Rudenberg, *Inorg. Chem.*, **1**, 441 (1962); (b) D. S. Martin, Jr., and C. A. Lendhardt, *ibid.*, **3**, 1368 (1964); (c) D. S. Martin, Jr., M. A. Tucker, and A. J. Kassman, *ibid.*, **4**, 1682 (1965); (d) D. S. Martin, Jr., M. A. Tucker, and A. J. Kassman, *ibid.*, **5**, 491 (1966); (e) *ibid.*, **5**, 1298 (1966).

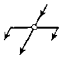
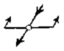
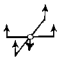
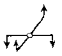
(7) (a) H. B. Gray and C. J. Ballhausen, *J. Amer. Chem. Soc.*, **85**, 260 (1963); (b) H. Basch and H. B. Gray, *Inorg. Chem.*, **6**, 365 (1967); (c) W. R. Mason and H. B. Gray, *J. Amer. Chem. Soc.*, **90**, 5721 (1968).

(8) P. Day, A. F. Orchard, A. J. Thomson, and R. J. P. Williams, *J. Chem. Phys.*, **42**, 1973 (1964).

TABLE I

POLARIZATION OF VIBRONIC DIPOLE TRANSITIONS IN $PtCl_4^{2-}$

Part a

Vibrational coordinates	Vibrational symmetry	$^3A_{2g} \leftarrow {^1A_{1g}}$ components		$^3B_{1g} \leftarrow {^1A_{1g}}$ components		$^3E_g \leftarrow {^1A_{1g}}$ components				
		a_{1g}	e_g	b_{2g}	e_g	a_{1g}	a_{2g}	b_{1g}	b_{2g}	e_g
(2)  (2)  S_6 S_7	e_u	xy	z	xy	z	xy	xy	xy	xy	z
 Q_2	a_{2u}	z	xy	. . .	xy	z	. . .	. . .	. . .	xy
 Q_4	b_{2u}	. . .	xy	. . .	xy	. . .	. . .	z	. . .	xy

Part b

	Exciting vibration	MTK (A) % xy polarization	MTK (B) % xy polarization	Noncontributing components
i	$(2)S_6 + (2)S_7$	87 (85)[a]	46 (83)	(b_{2g})
ii	Q_2	21 (21)	90 (62)	a_{2g}, b_{1g} (b_{2g})
iii	Q_4	62 (100)	94 (100)	a_{1g}, a_{2g} (b_{2g})
iv	$(2)S_6 + (2)S_7 + Q_2 + Q_4$	52 (68)	79 (89)	. . .

[a] For $\bar{\nu} < 19{,}000$ cm^{-1}.

no experimental information which would support either of the two alternatives. However, when we mounted a single crystal so that the crystal *c* axis (coincident with D_{4h} symmetry axis) was perpendicular to an incident light beam at 577 nm, in which a polarizer was placed, we found an approximate 70% reduction of integrated intensity on going from $\perp(xy)$ to $\|(z)$ polarization after corrections (the observed reduction was >80%). A part of the intensity in $\|$ polarization is due to the mechanical necessity of rotating the polarizer 90° while the polarization angle is only 77°. Structure is seen in $\|$ polarization (peaks at 13.07, 12.72, 12.47, 12.20, 11.2, and 10.7 kK), but no regular vibrational progression was found.[9]

Since the d ← d transitions are LaPorte forbidden, a simplified presentation of the vibronic model by which intensity is obtained is given in Table I for this molecule (for a more complete discussion see, *e.g.*, ref 6b, c).

In Table I it can be seen that there are three asymmetric normal vibrations which can mix with asymmetric upper-state wave functions so as to produce a nonzero transition moment. In D_{4h} the triplet states of the same orbital designation as the singlets consist of the components shown in Table I. Neglecting crystal lattice interactions (the crystal and solution spectra of $PtCl_4^{2-}$ are quite similar), the polarization of each of the components mixed with each of the vibrations is obtained. With this information it becomes possible to calculate the per cent polarization of the lowest energy band for the alternatives in ref 6e in the following manner.

The sum of the singlet eigenvector coefficients, c_i, calculated by MTK[6e] for each of the components of $\bar{\nu} < 20{,}000$ cm^{-1} was used to indicate the total band intensity: $I_t = \Sigma c_i$. The contribution to the band polarization for each active component was summed over all components to give $\%(\text{pol})_{xy} = \Sigma[\%(xy)_i c_i / I_t]$.

Since the magnitudes of the vibrational mixing integrals are not available, one can only speculate on which vibration or combination of vibrations are responsible for the observed intensity. From the crude approximation made as above and shown in Table Ib it was found that alternative (B) tended to give a higher degree of in-plane polarization than alternative (A). Only in the case of unique e_u mixing did (A) seem preferable. The difficulty with alternative (B) is that the low-energy absorption band consists of components from two different orbital states, ^3E_g and $^3B_{1g}$. Although absorption is possible to two separate close-lying states, emission is almost always found from one state only. The width of the emission, however, is of the same general magnitude as the corresponding absorption band, which suggests that the same components are involved in both. Therefore the assignment of either ^3E_g, $^3B_{1g} \rightarrow {^1A_{1g}}$ or $^3B_{1g} \rightarrow {^1A_{1g}}$ is not pleasing. (If the minima of the two potential surfaces are approximately isoenergetic, one might conceive of a rapid thermal equilibrium, but in this unlikely event one might equally expect two emission maxima.)

Further indirect evidence mitigating against the $^3B_{1g} \rightarrow {^1A_{1g}}$ assignment is obtained from variation of the cation. In the series of counterions Li^+, K^+, Rb^+, and

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(9) This may result from the wide slit which was required in order to obtain measurable intensity. In the unpolarized emission spectrum some indication of fine structure was observed, but we can make no certain claim that this is a vibrational progression for the same reason. We merely note that there are slight irregularities in the unpolarized spectral curve, which do not seem to derive from eccentric recorder response, with an apparent frequency of 300 ± 40 cm^{-1}, a value obtained from seven spectra having an average of nine inflections per spectrum at slit widths of 160–180 μ.

Cs^+ the shift of $\bar{\nu}_{max}$ is only -500 cm^{-1}.[10] In the same series in $PtCN_4^{2-}$, where the emission is thought to involve the orbitals ($6p_z$, $5d_{z^2}$), the variation is $\sim$2000 cm^{-1} in the other direction. Since a major component of the proposed transition is the $5d_{z^2}$ orbital, one might expect considerably more variation than is seen.

It is disappointing that no clear choice is indicated for the assignment. However, one can examine the possibilities of a further assumption of the authors cited.[6e] In the cases where there is little or no structure evident in the absorption band they suggest that the transition can be correlated, through intermediate D_{2d} symmetry, to a low-lying ^3T_d state; this is the case for the weak red absorption. This would explain the observed similarity of the absorption and emission bands. Another point to be noted in this respect is that the absorption and emission do not overlap; that is, there is no obvious $\bar{\nu}_{0'-0}$ transition. While there are a number of possible conditions under which the intensity of this transition may be made very low, it is also consistent with a transition between two states of greatly differing geometry such as square planar to (distorted) tetrahedral.

The experimental evidence is then that the emission (a) has a band width similar to the nearest absorption, (b) does not clearly overlap the absorption, (c) is primarily polarized in the *xy* plane, and (d) is quite insensitive to *z*-axis perturbation. This behavior is consistent either with MTK alternative (A) with unique e_u vibration mixing or with emission from a low-lying T_d-like state.

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[10] A. Zanobi, Laurea Thesis, Istituto Chimico, Università di Roma, Oct 1969.

Correspondence

Phosphine Exchange in Carbonylchlorobis(dimethylphenylphosphine)-rhodium(I)

Sir:

Early in 1969 we described[1] the conditions that lead to nuclear magnetic resonance AX decoupling in A′AX systems. We showed specifically that the methyl proton magnetic resonance (pmr) in some planar methylphosphine complexes might appear as a singlet, a doublet (with varied splitting), or a complex multiplet, the "virtually coupled" triplet of trans planar complexes being a well-known example.

To summarize these results for an equilibrium such as that indicated by reaction 1 under nonparamagnetic conditions, where L = L*, a methylphosphine, B, is a

$$ML_2B_2 + L^* \rightleftharpoons MLL^*B_2 + L \qquad (1)$$

nonmagnetic ligand, and M is a metal to which L and B are coordinated, the following pmr spectra of the methyl group may be expected.[2]

I. With[3] $[L] \ll [ML_2B_2]$ and very slow chemical exchange of L, the spectrum will appear as a doublet, $J_{PH} \approx 10–14$ Hz,[4] if $J_{PP'} \approx 0$ as in a cis planar complex. If $J_{PP'} \gg (J_{HP} - J_{HP'})$ as in a trans planar complex, then the pmr spectrum will appear as a triplet.[5]

II. With $[L] \ll [ML_2B_2]$, $J_{PP'}/J_{PH} > 5$, and $J_{PH}/J_{P'H}$ near unit magnitude,[6] the pmr spectrum will appear as a "triplet" under slow-exchange conditions, a "singlet" with intermediate exchange rates, and a "doublet" under conditions of fast chemical exchange of L.

III. With $[L] \approx [ML_2B_2]$, fast chemical exchange, and the coupling conditions for ML_2B_2 present in II, the pmr spectrum for the methyl group will be a doublet in which the coupling constant is related to the weighted average of the coupling constants for coordinated and uncoordinated phosphine. The chemical shift should also be an average value.[7] Since the sign of J_{PH} is positive for L and negative for ML_2B_2 in those cases studied,[4] a singlet will be produced at a ratio of free to coordinated phosphine near 3–5, depending on the specific value of J_{P-H} in coordinated and uncoordinated phosphine.

IV. With $[L] \gg [ML_2B_2]$ and fast chemical exchange, a narrow doublet typical of uncoordinated L will appear.

At the time of our[1] study we were unaware of any *single system* which clearly *displays* the *conditions set out in all four of the above*. The *trans*-$RhCl(CO)(P(CH_3)_2C_6H_5)_2$ complex studied by Deeming and Shaw[8] appears to fit these conditions so well that this correspondence is prompted. As reported (loosely quoted) by Deeming and Shaw, the complex (*ca.* 0.3 *M* in benzene) shows a 1:2:1 triplet pattern (conditions as in I) which is almost unaltered by the addition of 0.01 mol of $P(CH_3)_2C_6H_5$ (slow-exchange conditions of II). With 0.02–0.03 mol of added phosphine a singlet is obtained (intermediate exchange rate conditions of II) which on further addition broadens and starts to form a doublet until, with 0.08 mol of added phosphine, a well-defined 1:1 doublet

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[1] J. P. Fackler, Jr., J. A. Fetchin, J. Mayhew, W. C. Seidel, T. J. Swift, and M. Weeks, *J. Amer. Chem. Soc.*, **91**, 1941 (1969).

[2] The captions in Figures 2 and 3 of ref 1 were inadvertently interchanged.

[3] The brackets refer to the concentrations of the species.

[4] W. McFarlane, *Chem. Commun.*, 58 (1967).

[5] R. K. Harris, *Can. J. Chem.*, **42**, 2275 (1964); *Inorg. Chem.*, **5**, 701 (1966).

[6] A reasonable value for a *trans*-ML_2B_2 complex appears to be $\sim$3.

[7] A. R. Cullingworth, A. Pidcock, and J. D. Smith, *Chem. Commun.*, 89 (1966).

[8] A. J. Deeming and B. L. Shaw, *J. Chem. Soc. A*, 597 (1969).