

## Luminescence of $d^8$ Complexes of Iridium and Rhodium, and Its Quenching by Molecular Oxygen and Other Gases

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**Summary** Certain cationic square-planar  $\text{Ir}^{\text{I}}$  and  $\text{Rh}^{\text{I}}$  complexes with chelating tertiary diphosphine ligands,  $[\text{M}(\text{L-L})_2]^+$ , exhibit photoluminescence in the solid state at  $25^\circ$ , while their adducts with  $\text{O}_2$ ,  $\text{CO}$ , and  $\text{H}_2$  do not; emission and absorption spectra for a number of emitting compounds are compared, and some practical uses of the phenomena are suggested.

ALTHOUGH luminescence of a number of  $d^8$  platinum complexes is well known and has been extensively studied<sup>1,2</sup> (and also, to some extent, that of analogous  $\text{Pd}^{\text{II}}$  and  $\text{Ni}^{\text{II}}$  species), no such observations on related square-planar compounds of univalent iridium and rhodium seem to have been reported.<sup>4</sup> We summarize here our discovery that a series of the title compounds exhibit this property (see Table, which includes a few established examples for comparison). We have also examined several other complexes and found that the addition compounds of  $[\text{M}(\text{L-L})_2]^+$

with dioxygen [ $\text{O}_2$ -(**1**),  $\text{O}_2$ -(**2**),  $\text{O}_2$ -(**4**),  $\text{O}_2$ -(**8**), and  $\text{O}_2$ -(**11**)], dihydrogen [ $\text{H}_2$ -(**2**)], and carbon monoxide [ $\text{CO}$ -(**1**),  $\text{CO}$ -(**2**),  $\text{CO}$ -(**4**), and  $\text{CO}$ -(**5**)] did not luminesce under the same conditions as their square-planar precursors (Table). The following complexes were also devoid of visible light emission (for conditions, see Table and footnote g):  $[\text{IrA}(\text{CO})(\text{Ph}_3\text{P})_2]$ ,  $\text{A} = \text{Cl}^g, \text{Br}, \text{or I}$ ;  $[\text{IrCl}(\text{CO})(\text{Ph}_3\text{As})_2]$ ;  $[\text{IrH}(\text{CO})(\text{Ph}_3\text{P})_3]$ ;  $[(\text{SO}_2)\text{IrCl}(\text{CO})(\text{Ph}_3\text{P})_2]^g$ ;  $[\text{RhCl}(\text{CO})(\text{Ph}_3\text{P})_2]^g$ ;  $[\text{RhCl}(\text{Ph}_3\text{P})_3]^g$ ;  $[\text{PtA}_2(\text{Ph}_3\text{P})_2]$ ,  $\text{A} = \text{Cl} \text{ or } \text{Br}$ ;  $[\text{PdCl}_2(\text{Ph}_3\text{P})_2]$ .

The data cited above and in the Table point to some significant applications: (i) theoretical understanding of the electronic structures of these square-planar complexes,<sup>4</sup> and prediction of their reactivity toward small molecules;<sup>5</sup> (ii) determination of the equilibria of oxygenation,  $[\text{M}(\text{L-L})_2]^+ + \text{O}_2 \rightleftharpoons [\text{O}_2\text{M}(\text{L-L})_2]^+$ , and related processes, (iii) convenience in judging the purity of certain compounds: *e.g.*, in a preparation of (**16**) from (**15**) we detected some unchanged

(15) in the product by simply exposing it to black light; note that the dioxygen adduct (16) is not luminescent at 25° while its precursor (15) is luminescent (Table); (iv) possible development of these or similar types of complexes into devices for detecting the presence or absence of some important gases, visually or photometrically.

and emission spectra were obtained in different media (solution, solid), the respective peaks for the iridium complexes are in relatively close proximity (see footnote a to the Table). (c) The intensity of emission is lower for arsine than phosphine complexes, and the band widths are larger for rhodium than for analogous iridium compounds. None

TABLE

Electronic absorption and emission spectral data for some iridium, rhodium, and related complexes at room temperature (unless noted otherwise)

No.	Compound <sup>c</sup>	Absorption, solution <sup>a</sup>		Emission, solid state <sup>b</sup>		
		$\nu \times 10^{-3}/\text{cm}^{-1}$	$\epsilon/l \text{ mol}^{-1} \text{ cm}^{-1}$	$\nu \times 10^{-3}/\text{cm}^{-1}$	$\epsilon$ , relative <sup>e</sup>	Halfwidth/ $\text{cm}^{-1d}$
(1)	[Ir(mbdp) <sub>2</sub> ]BPh <sub>4</sub> .. ..	17.1	480	15.9	110	560
(2a)	[Ir(ebdp) <sub>2</sub> ]Cl .. ..	19.2	540	17.9	110	600
(2b)	[Ir(ebdp) <sub>2</sub> ]I .. ..			17.5	30	650
(2c)	[Ir(ebdp) <sub>2</sub> ]BF <sub>4</sub> .. ..			17.6	30	620
(2d)	[Ir(ebdp) <sub>2</sub> ]BPh <sub>4</sub> .. ..	19.2	870	Red-orange, 77 K <sup>f</sup>		
(3)	[Ir(ebda) <sub>2</sub> ]BPh <sub>4</sub> <sup>g</sup> .. ..	18.5				
(4a)	[Ir(bdpe) <sub>2</sub> ]Cl .. ..			18.2	10	920
(4b)	[Ir(bdpe) <sub>2</sub> ]BPh <sub>4</sub> <sup>h</sup> .. ..	19.1	760			
(5)	[Ir(pbdp) <sub>2</sub> ]Cl .. ..	(20) <sup>i</sup>	(550) <sup>i</sup>	18.2	30	1100
(6)	[(SO <sub>2</sub> )Ir(ebdp) <sub>2</sub> ]BF <sub>4</sub> .. ..			Orange <sup>j</sup>		
(7)	[Cl <sub>2</sub> Ir(ebdp) <sub>2</sub> ]BF <sub>4</sub> .. ..			Pinkish-orange <sup>j</sup>		
(8)	[Rh(mbdp) <sub>2</sub> ]BPh <sub>4</sub> .. ..	(19.2) <sup>i</sup>	(100) <sup>i</sup>	Red-orange		
(9)	[Rh(ebdp) <sub>2</sub> ]BF <sub>4</sub> .. ..	24.8	5780	Pink-orange, 77 K <sup>f</sup>		
(10)	[Rh(ebda) <sub>2</sub> ]BPh <sub>4</sub> .. ..	(23.3) <sup>i</sup>		Red-orange, 77 K <sup>f</sup>		
(11a)	[Rh(bdpe) <sub>2</sub> ]Cl .. ..			16.7	40	1450
(11b)	[Rh(bdpe) <sub>2</sub> ]BF <sub>4</sub> .. ..			17.0	140	1650
(11c)	[Rh(bdpe) <sub>2</sub> ]BPh <sub>4</sub> .. ..	24.7	6160	17.6	110	1860
(12a)	[Rh(pbdp) <sub>2</sub> ]Cl .. ..			Orange, 77 K <sup>f</sup>		
(12b)	[Rh(pbdp) <sub>2</sub> ]BPh <sub>4</sub> .. ..	24.7	3040	Red-orange, 77 K <sup>f</sup>		
(13)	[RhH(ebdp) <sub>2</sub> ] .. ..			Red orange		
(14)	[PtL <sub>2</sub> (Ph <sub>3</sub> P) <sub>2</sub> ] <sup>k,1</sup> .. ..			Red-orange <sup>j</sup>		
(15)	[Pt(Ph <sub>3</sub> P) <sub>4</sub> ] <sup>k,1</sup> .. ..			16.0	50	1800
(16)	[OsPt(Ph <sub>3</sub> P) <sub>2</sub> ] .. ..			Orange, 77 K <sup>f</sup>		
(17)	[Pd(Ph <sub>3</sub> P) <sub>4</sub> ] <sup>k,1</sup> .. ..			19.5	270	>3000
(18)	Ba[Pt(CN) <sub>4</sub> ] <sup>k,m</sup> .. ..			18.7	260	>3000
(19)	[Ru(bipy) <sub>3</sub> ]Cl <sub>2</sub> <sup>k,n</sup> .. ..			19.6	1240	1150
				16.6	100 <sup>e</sup>	590

<sup>a</sup> ca. 10<sup>-4</sup>M in degassed PhCl. Only the lowest energy band is given; for Rh complexes, however, the spectra may include still lower-energy absorptions not detectable in these dilute solutions; all of these Ir and Rh complexes usually show three maxima in the visible and near-u.v. region.<sup>5</sup> Band positions in these spectra are not significantly dependent on the type of the anion. <sup>b</sup> Measured with a modified Jarrell-Ash laser Raman spectrometer; excitation,  $\lambda = 3652 \text{ \AA}$ . <sup>c</sup> mbdp = Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>, ebdp = Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>, bdpe = *cis*-Ph<sub>2</sub>PCH=CHPPh<sub>2</sub>, pbdp = Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>, ebda = Ph<sub>2</sub>AsCH<sub>2</sub>CH<sub>2</sub>AsPh<sub>2</sub>, bipy = 2,2'-bipyridyl. <sup>d</sup> ± 50 cm<sup>-1</sup>. <sup>e</sup> Estimated relative intensities, based on  $\epsilon = 100$  for (19), are intended to provide approximate comparisons only. <sup>f</sup> Visual observation of solid suspension in hexane; complex not luminescent at 25°. <sup>g</sup> Not luminescent down to 77 K. <sup>h</sup> Not luminescent at 25°. <sup>i</sup> Shoulder. <sup>j</sup> Very weak luminescence, discernible to eye, but no maximum could be measured. <sup>k</sup> Observed in this laboratory. <sup>l</sup> Reported also by Z. Dori and R. F. Ziolo, U.S.P. 3,666,675, May 30, 1972. <sup>m</sup> Ref. 1c. <sup>n</sup> J. N. Demas and G. A. Crosby, *J. Amer. Chem. Soc.*, 1971, 93, 2841.

Although we report here only initial, limited results, certain trends are evident (see Table): (a) the energy as well as the intensity of the cationic luminescence seems somewhat dependent on the anion (most of the derivatives of the large BPh<sub>4</sub><sup>-</sup> appear, in general, as the weakest emitters) which may be related to the metal-metal distances in the crystals (*cf.* refs. 1c and 6). (b) Although the absorption

of the complexes given in the Table luminesce in solution at 25°.

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<sup>1</sup> (a) P. D. Fleischauer and P. Fleischauer, *Chem. Rev.*, 1970, 70, 199; (b) D. L. Webb and L. A. Rosiello, *Inorg. Chem.*, 1971, 10, 2213; (c) M. L. Moreau-Colin, *Structure and Bonding*, 1972, 10, 167.

<sup>2</sup> J. B. Callis, M. Gouterman, Y. M. Jones, and B. H. Henderson, *J. Mol. Spectroscopy*, 1971, 39, 410.

<sup>3</sup> D. M. Gruen, J. R. Clifton, and C. W. DeKock, *J. Chem. Phys.*, 1971, 48, 1394.

<sup>4</sup> Professor H. B. Gray and his co-workers have independently observed luminescence from [M(L-L)<sub>2</sub>]Cl (M = Ir and Rh; L-L = ebdp and bdpe). Their work, to be published elsewhere, will provide a theoretical interpretation of the phenomenon (H. B. Gray, personal communication). We are grateful to Professor H. B. Gray for informing us of these unpublished results.

<sup>5</sup> L. Vaska, L. S. Chen, and W. V. Miller, *J. Amer. Chem. Soc.*, 1971, 93, 6671.

<sup>6</sup> T. W. Thomas and A. E. Underhill, *Chem. Soc. Rev.*, 1972, 1, 99.