Contribution from GTE Laboratories Inc.,
Waltham, Massachusetts 02154

Excitation Polarization of Luminescent Iridium(I) and Rhodium(I) Phosphine Complexes

LEONARD J. ANDREWS

Received April 17, 1978

Excitation polarization of the luminescent complexes [M(P=P)$_2$]Cl and [M(P—P)$_2$]Cl [M = Ir(I), Rh(I); P=P = *cis*-1,2-bis(diphenylphosphino)ethylene; P—P = 1,2-bis(diphenylphosphino)ethane] have been measured in 1-propanol at −165 °C. Detailed spectral assignments are made in terms of the spin-orbit coupling model which has evolved to describe the absorption of d^8 metal ions complexed with π-acceptor ligands. Comparisons are made with an earlier magnetic circular dichroism study of these complexes.

Introduction

There has been considerable effort over the years devoted to understanding the electronic absorption spectra of d^8 transition-metal ions complexed with π-acceptor ligands.[1-10] By far most attention has focused on the Ni(CN)$_4^{2-}$ and Pt(CN)$_4^{2-}$ anions. The intense lowest energy absorption bands in square-planar tetracyano complexes were originally interpreted by Gray and Ballhausen[1] as metal to ligand charge-transfer (MLCT) transitions from the highest occupied metal d orbitals to the lowest unoccupied ligand π orbital ($a_{2u} \leftarrow d$). Piepho et al.[3] refined this model on the basis of magnetic circular dichroism (MCD) studies to include the effects of spin-orbit coupling. Further MCD studies on a variety of Pt(II) complexes by Ici and Mason[5] and single-crystal polarized absorption measurements on Ni(CN)$_4^{2-}$ by Cowman, Ballhausen, and Gray[4] and on Pt(CN)$_4^{2-}$ by Cowman and Gray[9] were interpreted using the spin-orbit coupling model of Piepho et al.[3] On the other hand, Xα scattered-wave calculations on Pt(CN)$_4^{2-}$ have led Interrante and Messmer[6] to question several assignments principally due to their calculated reordering of metal d-orbital energies.

Recently, this work on tetracyano complexes has been used as a basis for interpreting the absorption of square-planar Rh(I) and Ir(I) complexes.[8,10,11] In particular, MCD spectra of [M(P=P)$_2$]Cl and [M(P—P)$_2$]Cl [M = Rh(I), Ir(I); P=P = *cis*-1,2-bis(diphenylphosphino)ethylene; P—P = 1,2-bis(diphenylphosphino)ethane] have been used by Geoffroy et al.[10] to make detailed spectral assignments. As pointed out by Gray,[4,9] it is desirable to complement MCD data with absorption polarization to provide a firm basis for assignments. We have done this for the above complexes by taking advantage of their photoluminescence at low temperatures in rigid organic glasses.

By use of the method of photoselection,[12] polarized excitation spectra were recorded of dilute solid solutions in 1-propanol. For luminescent molecules, photoselection is a convenient and powerful method for obtaining polarizations which does not require single crystals. The disadvantage of the technique is that excitation polarizations are measured relative to the orientation of the emission oscillator and are not directly related to the molecular framework. We will show, however, for the particular cases studied here, that transition moment orientations relative to molecular coordinates (in-plane or out-of-plane) can be inferred from the sign and magnitude of the excitation polarizations.

Experimental Section

Polarization Measurements. A 150-W xenon arc dispersed with a 0.25-m Jarrel Ash monochromator (82-410) was used for excitation and a 0.5-m Perkin-Elmer monochromator (E-1), equipped with an RCA C3103A photomultiplier, was used for detection. The slits of the excitation monochromator were set at 0.5 mm which corresponds to ~1.5 nm spectral resolution. The excitation beam was passed through a Glan Thompson polarizer and emission was detected through a Polaroid polarizer. Excitation and emission beams were at right angles. Samples were contained in a 0.5-cm quartz tube held in a quartz Dewar and cooled with N$_2$ gas. A thermocouple was immersed directly in the sample. Sample concentration was $\sim 1 \times 10^{-4}$ M.

Polarization (P) is defined

$$P \equiv (I_{\parallel} - I_{\perp})/(I_{\parallel} + I_{\perp})$$

where $I_{\parallel}$ and $I_{\perp}$ are emission intensities with parallel and perpendicular orientations of the detection polarizer with respect to the excitation polarizer which is held vertically. Correction was made for the polarization sensitivity of the detection monochromator using Azumi and McGlynn's procedure.[13]

All polarization spectra were measured near −165 °C in N$_2$-saturated 1-propanol. At this temperature, 1-propanol forms a stable and strain-free glass, although severe cracking does occur below −170 °C. Since it is important that rotational relaxation time of the emitting molecule be long compared with its emission lifetime, P was checked as a function of temperature and was found to be constant up to −135 °C. Usually emission was monitored at the luminescence maximum. In the case of [Ir(P=P)$_2$]Cl, however, extensive overlap between the 538-nm absorption band and the 545-nm emission band required that the polarization of the 538-nm band be measured by monitoring the red edge of emission. This introduced no error because the emission polarization was found invariant throughout its bandwidth. The accuracy of P is estimated to vary between ±10% at band maxima and ±50% in regions of low polarization and weak absorption.

Materials. The complexes were prepared from IrCl(CO)(PPh$_3$)$_2$ and RhCl(CO)(PPh$_3$)$_2$ and the free ligands (Strem Chemicals) according to Vaska and Catone's[14] procedure. Care was taken that handling and synthesis of the Ir(I) complexes were done in N$_2$-saturated solvents. 1-Propanol (Fisher) was used as received.

Results

Excitation spectra uncorrected for polarization induced by the emission monochromator and the calculated excitation polarization spectra are shown for [Ir(P=P)$_2$]Cl and [Rh(P=P)$_2$]Cl in Figures 1 and 2. Absorption between the two lowest energy bands in each spectrum was too weak to permit reliable measurements, so the polarizations are omitted in these regions. It is worth noting that the excitation spectra are also uncorrected for wavelength variations in lamp intensity and excitation monochromator transmission so that the excitation intensities bear little resemblance to absorption intensities, particularly below 400 nm. This is of no consequence in measuring P since all that is required is that the excitation remain constant for consecutive $I_{\parallel}$ and $I_{\perp}$ measurements. Low-temperature absorption and emission spectra for these complexes have been published.[11]

The first band for each complex is positively polarized with P ranging from 0.10 to 0.14. The differences among P for this band are close to the precision of the measurements and are not regarded as significant. An intense band with strong negative polarization (−0.24 to −0.30) comes next in each spectrum. Following this, a weak band, also negatively polarized, is resolved in [Rh(P=P)$_2$]Cl and [Ir(P=P)$_2$]Cl at ~370 and ~405 nm, respectively. This feature is not seen in [Rh(P—P)$_2$]Cl or [Ir(P—P)$_2$]Cl, presumably because the

0020-1669/78/1317-3180$01.00/0

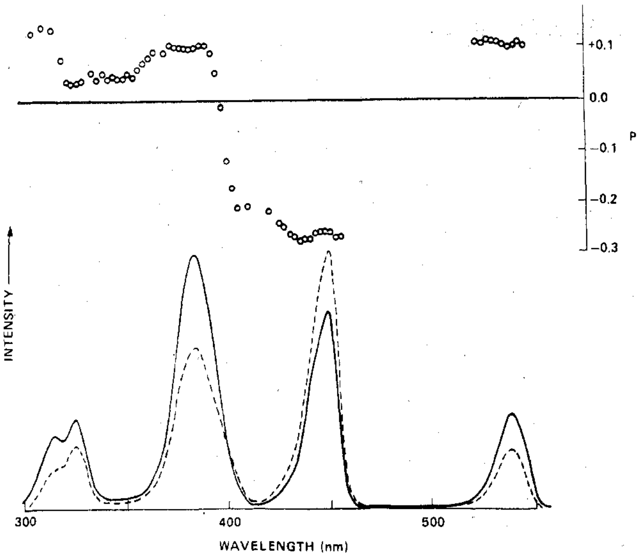

Figure 1. Polarized excitation spectra of $[Ir(P{=}P)_2]Cl$ in 1-propanol at −165 °C taken with $I_{\parallel}$ (—) and $I_{\perp}$ (- - -); calculated *P* values are shown by circles.

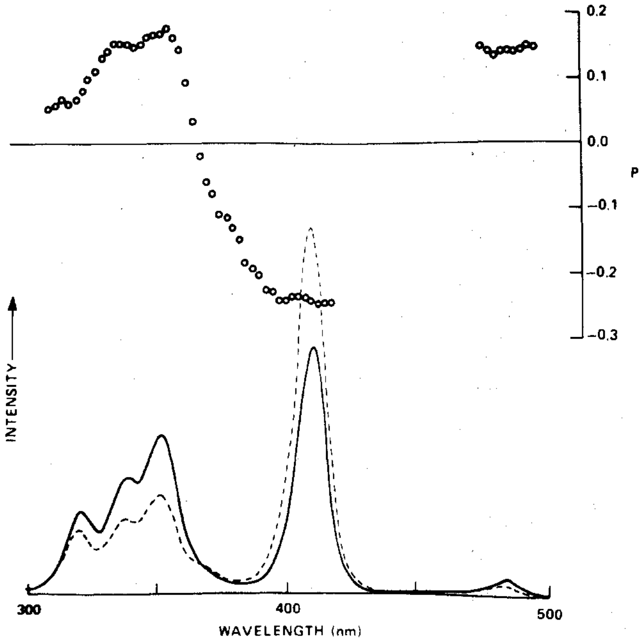

Figure 2. Polarized excitation spectra of $[Rh(P{=}P)_2]Cl$ in 1-propanol at −165 °C taken with $I_{\parallel}$ (—) and $I_{\perp}$ (- - -); calculated *P* values are shown by circles.

latter complexes show somewhat broadened absorptions, and this weak band is obscured by the adjacent intense band which has positive polarization. The polarization pattern of the three highest energy bands differ between the Rh and Ir complexes. In Ir, the sequence is positive, negative, positive with the middle band only attaining $P \sim 0$ because of the extensive overlap with the highest energy positive band. In $[Rh(P{-}P)_2]Cl$ the three bands are positively polarized, whereas in $[Rh(P{=}P)_2]Cl$ the highest energy band shows somewhat diminished polarization relative to the preceding two. Band positions and excitation polarizations measured at these maxima are collected in Table I.

Discussion

By proper averaging over all molecular orientations, it can be shown that photoselection of a random array of absorbing molecules leads to polarization limits of $-{}^1/_3 \leq P \leq +{}^1/_2$.[12] These limits occur when the absorbing and emitting oscillators are orthogonal and collinear, respectively. In the special case of in-plane absorption and emission, the maximum for *P* is reduced to $+{}^1/_7$. In practice these limits are rarely, if ever, realized. Overlapping bands of different polarizations, forbidden vibronic intensity within band envelopes, and excited state distortion as well as instrumental imperfections all serve to lower *P* from its theoretical maxima. In spite of these potential difficulties, experimental photoselection results frequently approximate theoretical limits well enough to be a reliable guide in assigning symmetries of excited states.

We assume that the d^8 bidentate phosphine complexes studied here have D_{4h} symmetry in the electronic ground state. As such, all symmetry-allowed electronic transitions can be classified as in-plane (x,y) or out-of-plane (z) polarized. *P* for the lowest energy band in each complex (Table I) closely approximates $+{}^1/_7$ and is, therefore, assumed to be in-plane polarized. If this band were out-of-plane, a much higher value for *P* could reasonably be expected because this band is well isolated from higher energy transitions (Figures 1 and 2). Further, the high degree of polarization of the second band (close to $-{}^1/_3$) rules out systematic errors or massive excited-state distortions which could lower *P*. The in-plane assignment is in accord with recent MCD results of Geoffroy et al.[10] which show this band to be degenerate. We conclude, therefore, that positive polarization corresponds to in-plane and negative polarization to out-of-plane transition moments.

A partial representation of molecular orbitals appropriate for these Ir(I) and Rh(I) complexes is shown in Figure 3. The metal d orbitals follow the ordering of Piepho et al.[3] for $Pt(CN)_4^{2-}$ and the a_{2u} and e_u ligand π^* orbitals conform to Gray and Ballhausen's[1] conclusions. This model predicts that the visible absorption of Ir(I) and Rh(I) bidentate phosphines

Table I. Summary of Assignments, Band Positions, and Polarizations in 1-Propanol at −165 °C

λ, nm	*P*	λ, nm	*P*	assignment $\leftarrow {}^1A_{1g}$	
$[Ir(P{=}P)_2]Cl$		$[Ir(P{-}P)_2]Cl$			
538	+0.10	527	+0.11	$E_u\ ({}^3A_{2u})$	$a_{2u} \leftarrow a_{1g}$
449	−0.26	443	−0.30	$A_{2u}\ ({}^1A_{2u})$	
∼405[a]	−0.20				
383	+0.10	382	+0.07	$E_u\ ({}^3E_u)$	$a_{2u} \leftarrow e_g$
325	+0.03	∼323[a]	0.00	$A_{2u}\ ({}^3E_u)$	
315	+0.14	319	+0.17	$E_u\ ({}^1E_u)$	
$[Rh(P{=}P)_2]Cl$		$[Rh(P{-}P)_2]Cl$			
483	+0.14	473	+0.12	$E_u\ ({}^3A_{2u})$	$a_{2u} \leftarrow a_{1g}$
410	−0.25	412	−0.29	$A_{2u}\ ({}^1A_{2u})$	
∼370[a]	−0.10				
352	+0.17	351	+0.10	$E_u\ ({}^1E_u)$	$a_{2u} \leftarrow a_{1g}$
338	+0.15	338	+0.10		
321	+0.06	328	+0.10	(?)$E_u\ ({}^1E_u)$	$e_u \leftarrow a_{1g}$

[a] These bands are shoulders which are clearly resolved only in polarized spectra.

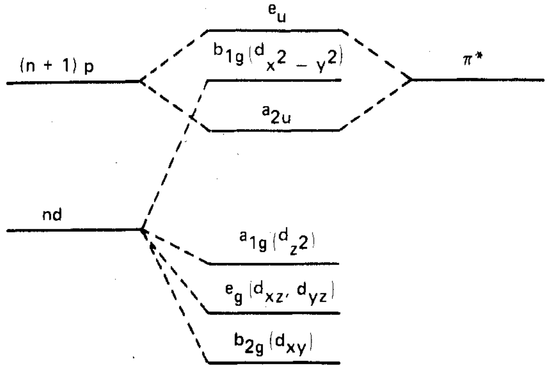

Figure 3. Partial molecular orbital diagram appropriate for iridium(I) and rhodium(I) phosphine complexes; D_{4h} symmetry is assumed.

should be dominated by allowed MLCT transitions of the type $a_{2u} \leftarrow d$. The evidence has been summarized by others[10,11] that the lowest energy bands do fit the criteria for MLCT transitions.

The one-electron transitions $a_{2u} \leftarrow d$ give rise to three singlet and three triplet states of which two are optically accessible from the $^1A_{1g}$ ground state from spin and symmetry considerations ($^1E_u \leftarrow {}^1A_{1g}$ and $^1A_{2u} \leftarrow {}^1A_{1g}$). Spin–orbit coupling splits the triplets to yield a total of 12 states of which six are optically accessible (the E_u and A_{2u} double group states). The intensity of transitions to spin–orbit states of triplet origin will depend on the extent of singlet character acquired by the spin–orbit perturbation. For convenience, the double group states are listed in Table II.

Table II. Double Group Theoretical States Generated from Lowest Energy $\pi^* \leftarrow d$ One-Electron Transitions

one-electron transition	double group (spin-orbit) excited states
$a_{2u} \leftarrow a_{1u}$	A_{2u} ($^1A_{2u}$), A_{1u} ($^3A_{2u}$), E_u ($^3A_{2u}$)
$a_{2u} \leftarrow e_g$	E_u (^1E_u), E_u (^3E_u), A_{1u} (^3E_u) A_{2u} (^3E_u), B_{1u} (^3E_u), B_{2u} (^3E_u)
$a_{2u} \leftarrow b_{2g}$	B_{1u} ($^1B_{1u}$), B_{2u} ($^3B_{1u}$), E_u ($^3B_{1u}$)
$e_u \leftarrow a_{1g}$	E_u (^1E_u), E_u (^3E_u), A_{1u} (^3E_u) A_{2u} (^3E_u), B_{1u} (^3E_u), B_{2u} (^3E_u)

The lowest energy band in each complex is positively polarized and is assigned to the in-plane transition E_u ($^3A_{2u}$) $\leftarrow$ $^1A_{1g}$. As pointed out by Geoffroy et al.,[10] this band is stronger in Ir(I) than Rh(I) complexes which is consistent with the increase in spin–orbit coupling. The intense, negatively polarized second band is assigned to the out-of-plane A_{2u} ($^1A_{2u}$) $\leftarrow$ $^1A_{1g}$. The intensities and polarizations of these two bands are consistent with the ordering of Piepho et al. for metal d orbitals which places a_{1g} as the highest occupied orbital. On the other hand, Interrante and Messmer's[6] calculation on $Pt(CN)_4^{2-}$, which predicts b_{2g} to be the highest occupied d orbital, leads to difficulties. If b_{2g} is highest, the second band could only arise from the A_{2u} component of ^3E_u ($a_{2u} \leftarrow e_g$). However, this interpretation requires that, at least in the case of Rh(I) complexes, the E_u component of ^3E_u ($a_{2u} \leftarrow e_g$) lie in the same spectral region. This is not observed in the spectra, and we conclude that the metal d-orbital ordering of Piepho et al.[3] is appropriate for these iridium(I) and rhodium(I) phosphines.

A previously unreported weak band with negative polarization is resolved as a shoulder near 405 nm in [Ir(P=P)$_2$]Cl and 370 nm in [Rh(P=P)$_2$]Cl. The origin of the feature is uncertain. It possibly is a vibronic transition associated with A_{2u} ($^1A_{2u}$) $\leftarrow$ $^1A_{1g}$ since the separation of these bands is ~2600 cm^{-1} in both complexes.

Following Geoffroy et al.[10] the 383-, 325-, and 315-nm bands in [Ir(P=P)$_2$]Cl are assigned to E_u (^3E_u) $\leftarrow$ $^1A_{1g}$, A_{2u} (^3E_u) $\leftarrow$ $^1A_{1g}$, and E_u (^1E_u) $\leftarrow$ $^1A_{1g}$, respectively. All of these originate from $a_{2u} \leftarrow e_g$. This is in agreement with the polarization spectrum which shows the 325-nm band to be A_{2u}, although it strongly overlaps the adjacent E_u band. *P* for the analogous transition in [Ir(P—P)$_2$]Cl becomes slightly negative (−0.02) near its maximum. Semiempirical calculations by Geoffroy et al.[10] show that the various E_u and A_{2u} states are thoroughly mixed so that absorption intensities among these transitions should be roughly the same. This expectation is realized in low-temperature absorption spectra.[11]

The situation in Rh(P=P)$_2$Cl is less clear. *P* values for the 352- and 338-nm bands clearly indicate that they are E_u in character, whereas the 321-nm band has somewhat diminished positive polarization. The corresponding transitions in [Rh(P—P)$_2$]Cl all show *P* = 0.10. It appears that none of these bands can be clearly associated with the A_{2u} component of ^3E_u ($a_{2u} \leftarrow e_g$). This, perhaps, is not too surprising in view of calculations on [Rh(P=P)$_2$]Cl which predict the intensities of transitions to states of triplet origin should be more than a factor of 10 less intense than transitions to states of singlet origin.[10] The low-temperature absorption spectra show the intensities of these bands (321, 338, 352, and 410 nm) to vary less than a factor of 2.[11] It seems certain that E_u (^1E_u) $\leftarrow$ $^1A_{1g}$ ($a_{2u} \leftarrow e_g$) must lie in this region and perhaps also E_u (^1E_u) $\leftarrow$ $^1A_{1g}$ ($e_u \leftarrow a_{1g}$), but detailed assignments must await a more refined theoretical model than presently available.

Acknowledgment. We thank the Air Force Office of Scientific Research for support of this work under Contract No. F49620-77-C-0015.

Registry No. [Ir(P=P)$_2$]Cl, 36390-37-1; [Ir(P—P)$_2$]Cl, 15390-38-2; [Rh(P=P)$_2$]Cl, 22754-44-5; [Rh(P—P)$_2$]Cl, 15043-47-7.

References and Notes

(1) H. B. Gray and C. J. Ballhausen, *J. Am. Chem. Soc.*, **85**, 260 (1963).
(2) W. R. Mason, III, and H. B. Gray, *J. Am. Chem. Soc.*, **90**, 5721 (1968).
(3) S. B. Piepho, P. N. Schatz, and A. J. McCaffery, *J. Am. Chem. Soc.*, **91**, 5994 (1969).
(4) C. D. Cowman, C. J. Ballhausen, and H. B. Gray, *J. Am. Chem. Soc.*, **95**, 7873 (1973).
(5) H. Isci and W. R. Mason, *Inorg. Chem.*, **14**, 905, 913 (1975).
(6) L. V. Interrante and R. P. Messmer, *Chem. Phys. Lett.*, **26**, 225 (1974).
(7) D. G. Marsh and J. S. Miller, *Inorg. Chem.*, **15**, 720 (1976).
(8) R. Brady, B. R. Flynn, G. L. Geoffroy, H. B. Gray, J. Peone, Jr., and L. Vaska, *Inorg. Chem.*, **15**, 1485 (1976).
(9) C. D. Cowman and H. B. Gray, *Inorg. Chem.*, **15**, 2823 (1976).
(10) G. L. Geoffroy, H. Isci, J. Litrenti, and W. R. Mason, *Inorg. Chem.*, **16**, 1950 (1977).
(11) G. L. Geoffroy, M. S. Wrighton, G. S. Hammond, and H. B. Gray, *J. Am. Chem. Soc.*, **96**, 3105 (1974).
(12) A. C. Albrecht, *J. Mol. Spectrosc.*, **6**, 84 (1961).
(13) T. Azumi and S. P. McGlynn, *J. Chem. Phys.*, **37**, 2413 (1962).
(14) L. Vaska and D. L. Catone, *J. Am. Chem. Soc.*, **88**, 5324 (1966).