Inorg. Chem. **1982**, *21*, 1023–1026 **1023**

Contribution from the Department of Chemistry and the Chemical Physics Program,
Washington State University, Pullman, Washington 99164

Electronic Spectroscopy of N-Heterocyclic Complexes of Rhodium(I) and Iridium(I)

W. A. FORDYCE and G. A. CROSBY*

Received June 15, 1981

Electronic absorption spectra at room temperature and emission spectra and lifetimes at 77 K are reported for some complexes of the general formula $[M(chel)(diene)]^+$: M = Rh(I), Ir(I); chel = ethylenediamine, 2,2′-bipyridine, 1,10-phenanthroline, 4,7-diphenyl-1,10-phenanthroline, 2,2′-bipyrazine; diene = 1,5-cyclooctadiene, 2,5-norbornadiene, 1,5-hexadiene. When chel = ethylenediamine, the lowest energy transition is mixed metal-to-diolefin charge transfer and $nd_{z^2} \rightarrow (n+1)p_z$. When chel = N-heterocycle, the lowest energy transition is metal-to-chel charge transfer. Low-temperature lifetime vs. temperature results from $[M(bpy)(cod)]ClO_4$ [M = Rh(I), Ir(I)] indicate spin–orbit splitting of the emitting term into two levels. The results from these complexes are compared and contrasted with those from other four-coordinate Rh(I) and Ir(I) d^8 complexes and from six-coordinate d^6 complexes with N-heterocyclic ligands.

Introduction

Investigations of the electronic structures of Rh(I) and Ir(I) complexes have generally dealt with the electronic absorption[1-5] and emission[1,6,7] properties of CO, CN^-, CNR, AsR_3, PR_3, and bidentate diphosphine complexes. Recently, however, Epstein et al.[8] reported the absorption and MCD spectra of some chloro-bridged olefin and diolefin species. They attributed the low-lying bands to metal-to-ligand charge-transfer (MLCT) transitions and inferred that the lowest unoccupied orbital was predominately π^*_{olefin} with some admixture of metal $(n+1)p_z$.

We report here the electronic spectra of the complexes $[M(chel)(diene)]^+$.[9] Cocevar, Mestroni, and Camus first reported complexes of this series in 1972.[10] Since then this same group has synthesized other members of the series[11,12] and studied their catalytic behavior.[12-14] Unlike the Rh(I) and Ir(I) complexes previously investigated spectroscopically, this class of complexes possesses a N-heterocyclic ligand (chel) with an extended π aromatic system. Thus, we were interested in comparing data from this class of molecules both with those of the other Rh(I) and Ir(I) complexes and with the wealth of spectroscopic data available on six-coordinate d^6 complexes possessing N-heterocyclic ligands. In this paper we report the room-temperature absorption spectra, emission spectra at 77 K, and low-temperature emission lifetimes. In the following paper we report cyclic voltammetric studies of these same complexes and the EPR spectra of stable reduced species.[15]

Experimental Section

Materials. Ligand abbreviations are defined in ref 9. All reactions and manipulations with iridium complexes were carried out in an atmosphere of argon with use of Schlenk techniques. $[RhCl(nbd)]_2$,[16] $[RhCl(1,5\text{-hex})]_2$,[17] and bpz[18] were prepared by published procedures. Satisfactory C, H, and N analyses (±0.4%) were obtained in all cases.

$[Rh(bpy)(cod)]ClO_4$, $[Rh(phen)(cod)]ClO_4$, $[Rh(4,7\text{-}Ph_2\text{-}phen)(cod)]ClO_4$, and $[Rh(bpz)(cod)]PF_6$ were prepared by the method of Cocevar et al.[10] $[Rh(bpy)(nbd)]ClO_4$ and $[Rh(phen)(nbd)]ClO_4$ were prepared in the same manner by starting with $[RhCl(nbd)]_2$. $[Rh(bpy)(1,5\text{-hex})]PF_6$ and $[Rh(phen)(1,5\text{-hex})]PF_6$ were synthesized by the method of Mestroni et al.[12] directly from $[RhCl(1,5\text{-hex})]_2$. $[Ir(bpy)(cod)]ClO_4$ and $[Ir(bpy)(nbd)]PF_6$ were obtained by the method of Mestroni et al.[11]

Preparation of $[Rh(en)(cod)]ClO_4$.[19] Ethylenediamine (3 mmol, 180 mg) was added to $[RhCl(cod)]_2$ (1 mmol, 500 mg) in 30 mL of methanol. $NaClO_4$ (3 mL of a saturated methanol solution) was added to the yellow solution. The solution was evaporated to ~20 mL while 5 mL of water was added. The yellow crystals were filtered, washed with water, and recrystallized from 2:1 methanol–water; yield 140 mg.

$[Ir(en)(cod)]ClO_4\cdot H_2O$[20] was prepared analogously to the Rh(I) species except that the mixture was chilled after partial evaporation under an atmosphere of argon. No recrystallization was performed; yield 360 mg.

Spectroscopy. Absorption spectra were recorded on a Cary 14 spectrophotometer. Glasses for obtaining emission spectra and lifetimes were prepared by dissolving the sample in 1 part of dichloromethane and adding the solution to 20 parts of 4:1 ethanol–methanol. Emission spectra and lifetimes were obtained as described previously.[7] All emission spectra were corrected for monochromator and phototube wavelength sensitivity. Spectra were acquired with a Digital PDP 11/34 system and plotted with a Tektronix 4662 digital plotter.

Results

Absorption. The absorption spectra of the Rh(I) complexes were characterized by a single maximum at low energy (Figure 1, Table I). Maxima at energies greater than 28 000 cm^{-1} appeared to be characteristic of $\pi\pi^*$ transitions localized on the N-heterocyclic ligands and are not tabulated. The low-energy maximum of $[Rh(en)(cod)]^+$ was ~6000 cm^{-1} higher in energy than the first maxima of the complexes containing an N-heterocyclic ligand. With the single exception of $[Rh(bpz)(cod)]^+$ variations of chel (when chel = N-heterocycle) and diene produced little change in the low-energy maximum. For the bpz species this first maximum occurred ~3000 cm^{-1}

---

(1) Geoffroy, G. L.; Wrighton, M. S.; Hammond, G. S.; Gray, H. B. *J. Am. Chem. Soc.* **1974**, *96*, 3105.
(2) Isci, H.; Mason, W. R. *Inorg. Chem.* **1975**, *14*, 913.
(3) Brady, R.; Flynn, B. R.; Geoffroy, G. L.; Gray, H. B.; Peone, J.; Vaska, L. *Inorg. Chem.* **1976**, *15*, 1485.
(4) Geoffroy, G. L.; Isci, H.; Litrenti, J.; Mason, W. R. *Inorg. Chem.* **1977**, *16*, 1950.
(5) Andrews, L. J. *Inorg. Chem.* **1978**, *17*, 3180.
(6) Andrews, L. J. *J. Phys. Chem.* **1979**, *83*, 3203.
(7) Fordyce, W. A.; Rau, H.; Stone, M. L.; Crosby, G. A. *Chem. Phys. Lett.* **1981**, *77*, 405.
(8) Epstein, R. A.; Geoffroy, G. L.; Keeney, M. E.; Mason, W. R. *Inorg. Chem.* **1979**, *18*, 478.
(9) Key to abbreviations used in this paper: M = Rh(I), Ir(I); chel = en (ethylenediamine), bpy (2,2′-bipyridine), phen (1,10-phenanthroline), 4,7-Ph_2-phen (4,7-diphenyl-1,10-phenanthroline), bpz (2,2′-bipyrazine); diene = cod (1,5-cyclooctadiene), nbd (2,5-norbornadiene), 1,5-hex (1,5-hexadiene).
(10) Cocevar, C.; Mestroni, G.; Camus, A. *J. Organomet. Chem.* **1972**, *35*, 389.
(11) Mestroni, G.; Camus, A.; Zassinovich, G. *J. Organomet. Chem.* **1974**, *73*, 119.
(12) Mestroni, G.; Zassinovich, G.; Camus, A. *J. Organomet. Chem.* **1977**, *140*, 63.
(13) Zassinovich, G.; Mestroni, G.; Camus, A. *J. Organomet. Chem.* **1979**, *168*, C37.
(14) Mestroni, G.; Zassinovich, G.; Camus, A.; Martinelli, F. *J. Organomet. Chem.* **1980**, *198*, 87.
(15) Fordyce, W. A.; Pool, K. H.; Crosby, G. A. *Inorg. Chem.*, following paper in this issue.
(16) Abel, E. W.; Bennett, M. A.; Wilkinson, G. *J. Chem. Soc.* **1959**, 3178. Modification of this procedure was shown in: Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 2397.
(17) Winkhaus, G.; Singer, H. *Chem. Ber.* **1966**, *99*, 3602.
(18) Lafferty, J. J.; Case, F. H. *J. Org. Chem.* **1967**, *32*, 1591.
(19) Prepared differently by: Uson, R.; Oro, L. A.; Claver, C.; Garralda, M. A. *J. Organomet. Chem.* **1976**, *105*, 365.
(20) Prepared as the BPh_4^- salt by: Louw, W. J.; Singleton, J. E. *Inorg. Chim. Acta* **1978**, *27*, 21.

0020-1669/82/1321-1023$01.25/0

Table I. Spectral Data (<28 000 cm^{-1})

	absorption^a (room temp)				emission^b (77 K)		
complex	band no.^{e}	ν_{max}, cm^{-1} × 10^3	λ_{max}, nm	ϵ_{max}, M^{-1} cm^{-1}	ν_{max}, cm^{-1} × 10^3	λ_{max}, nm	lifetime, μs
[Rh(en)(cod)]ClO$_4$	III	26.4	379	1120			
[Rh(bpy)(cod)]ClO$_4$	I	20.6	485	790	15.6	641	2.2
[Rh(phen)(cod)]ClO$_4$	I	20.4	490	847	15.8	633	2.7
[Rh(4,7-Ph$_2$-phen)(cod)]ClO$_4$	I	20.3	493	887	15.7	637	2.6
[Rh(bpz)(cod)]PF$_6$	I	17.7	565	524	14.1	709	0.6
[Rh(bpy)(nbd)]ClO$_4$	I	20.6	485	976	15.2	658	3.0
[Rh(phen)(nbd)]ClO$_4$	I	20.5	488	1250	15.1	662	4.4
[Rh(bpy)(1,5-hex)]PF$_6$	I	20.5	488	813	13.5 (13.0)^d	741 (769)^d	1.6^d
[Rh(phen)(1,5-hex)]PF$_6$	I	20.2	495	819	12.3^d	813^d	
[Ir(en)(cod)]ClO$_4$^{c}	IIA	21.0	476	196	20.5, 19.7	488, 508	*f*
	IIB	21.7	461	165			
	IIIA	24.2	413	1060			
	IIIB	24.9	402	997			
[Ir(bpy)(cod)]ClO$_4$	I	17.3	578	734	13.9 (14.9, 13.6, 12.3)^d	719 (671, 735, 813)^d	0.5
	III	22.3	448	1080			
[Ir(bpy)(nbd)]PF$_6$	I	17.4	575	484	14.3^d	699^d	
	III	21.5	465	887			

^{a} CH$_2$Cl$_2$ solution unless stated otherwise. ^{b} Ethanol-methanol-CH$_2$Cl$_2$ (16:4:1) glass. ^{c} Absorption and emission spectra obtained in 4:1 ethanol-methanol. ^{d} Solid. ^{e} $I \equiv {}^1A_1 \rightarrow {}^1$CT(chel), II $\equiv {}^1A_1 \rightarrow {}^3$CT(diene), III $\equiv {}^1A_1 \rightarrow {}^1$CT(diene); see text. ^{f} nonexponential decay.

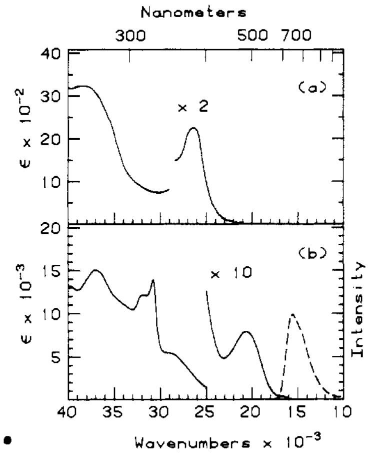

Figure 1. (a) Room-temperature absorption spectrum of [Rh(en)(cod)]ClO$_4$ in CH$_2$Cl$_2$. (b) Room-temperature absorption spectrum in CH$_2$Cl$_2$ (—) and 77 K emission spectrum in 16:4:1 ethanol–methanol–CH$_2$Cl$_2$ (- - -) of [Rh(bpy)(cod)]ClO$_4$.

lower in energy (17 700 cm^{-1} in dichloromethane). The band blue shifted 600 cm^{-1} when the solvent was switched to methanol (18 300 cm^{-1}). The low-lying band of [Rh(en)(cod)]$^+$ blue shifted only 200 cm^{-1} when the solvent was changed to methanol. Low solubilities prevented our making further solvent studies.

The absorption spectra of the Ir(I) complexes were characterized by two low-energy maxima (Figure 2, Table I). The lower energy band (~21 000 cm^{-1}) in [Ir(en)(cod)]$^+$ contained two peaks separated by ~700 cm^{-1}. Two peaks separated by the same amount also appeared in the much more intense higher energy band (24 000 cm^{-1}). In molecules containing an N-heterocycle the low-energy peak (17 000 cm^{-1}) was significantly red shifted relative to that of the en complex. The slightly more intense higher energy peak (22 000 cm^{-1}) lay midway between the first two bands of the en complex.

Emission. Emission bands of the Rh(I) complexes at 77 K (Figure 1, Table I) both in glasses and in the solid state were broad and unstructured. The en complex did not emit light. Emissions from the complexes containing 1,5-hex were significantly less intense than the emissions observed from the other species. In addition, the energy separation between the first absorption and the emission maxima (typically 4000–5000 cm^{-1}) was greater for the 1,5-hex complexes (7000 cm^{-1}).

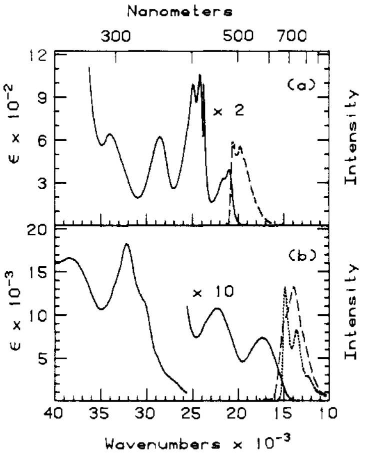

Figure 2. (a) Room-temperature absorption (—) and 77 K emission (- - -) spectra of [Ir(en)(cod)]ClO$_4$ in 4:1 ethanol–methanol. (b) Room-temperature absorption spectrum in CH$_2$Cl$_2$ (—), 77 K emission spectrum in 16:4:1 ethanol–methanol–CH$_2$Cl$_2$ (- - -), and 77 K emission spectrum in the solid state (···) of [Ir(bpy)(cod)]ClO$_4$.

The emission spectrum of [Ir(en)(cod)]$^+$ both in a glass (Figure 2) and in the solid state was a mirror image of the low-energy absorption band and showed a small Stokes shift. In contrast, the weak and relatively unstructured emission of [Ir(bpy)(cod)]$^+$ in a glass sharpened drastically in the solid state, revealing a 1300-cm^{-1} progression. The Stokes shift was substantially larger than for the en complex. [Ir(bpy)(nbd)]$^+$ displayed an intense band in the solid state but did not emit light in glassy solution.

Lifetimes. When a glassy sample of [Rh(bpy)(cod)]ClO$_4$ was cooled, the emission lifetime increased dramatically (Figure 3a). Lifetimes of [Ir(bpy)(cod)]ClO$_4$ were also observed to increase as the temperature was lowered (Figure 3b), although the rapid decay taxed the operation of the detection system. Our method of analysis of these data, which assumed two emitting levels in Boltzmann equilibrium, was identical with that described previously,[7] and the computer-generated fits and resultant level schemes are shown in Figure 3. The degeneracy factor of 2 for the higher level in the emitting manifold is not derivable from the experimental data but is consistent with the proposed term assignments (vide infra). Note that the lifetime of the higher level is for depopulation of the entire level.

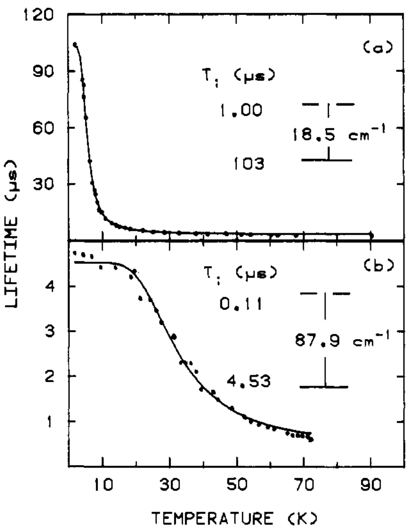

Figure 3. Temperature dependence of the lifetimes and computer-generated fits with resultant level schemes for (a) $[Rh(bpy)(cod)]ClO_4$ and (b) $[Ir(bpy)(cod)]ClO_4$ in 16:4:1 ethanol–methanol–CH_2Cl_2: (●) experimental values; (—) "best fit" computer-generated curve.

Discussion

Assignments. Due to the absence of an extended aromatic system we would expect the low-energy transitions of the en complexes to involve the –M(diene) chromophore. Indeed, the absorption spectra of $[M(en)(cod)]^+$ closely resemble the absorption spectra of $MCl(cod)(CH_3CN)$ [M = Rh(I), Ir(I), respectively] reported by Epstein et al. We assign the transitions in the en complexes accordingly. The low-energy peak in the Rh(I) complex is assigned to an allowed charge-transfer-to-diolefin [$^1A_1 \rightarrow {}^1CT$(diene)] transition. The similarity in the band shapes of the two low-energy bands in the Ir(I) complex suggests assignments of $^1A_1 \rightarrow {}^3CT$(diene) for the weak band at 21 000 cm^{-1} and $^1A_1 \rightarrow {}^1CT$(diene) for the more intense band at 24 200 cm^{-1}. The peaks at 21 700 and 24 900 cm^{-1} may be vibronic transitions associated with the triplet and singlet, respectively, although it seems odd that more components of the vibrational progression cannot be observed. These assignments indicate a singlet–triplet splitting of 3200 cm^{-1} for the $^1A_1 \rightarrow$ CT(diene) excited configuration. As noted by Epstein et al.[8] the lowest unoccupied molecular orbital contains some $(n + 1)p_z$ character. We emphasize that the amount of $(n + 1)p_z$ admixture is unknown, but it may be substantial (vide infra).

When en is replaced by an N-heterocycle, low-lying CT-to-chel [$^1A_1 \rightarrow$ CT(chel)] transitions become possible. Since only a single emission band is observed from any Rh(I) or Ir(I) complex containing N-heterocyclic ligands, we assign the luminescence to a $^1A_1 \leftarrow {}^3CT$(chel) transition. This triplet CT assignment is corroborated by the observed microsecond emission lifetimes[21,22] and, for $[Ir(bpy)(cod)]^+$, by the 1300-cm^{-1} progression on the band envelope.[23] The lowest absorption band in both the Rh(I) and the Ir(I) series is assigned to a $^1A_1 \rightarrow {}^1CT$(chel) transition. Although the energy of this lowest band in the Rh(I) series is relatively insensitive to changes of the N-heterocyclic ligand compared to those of ^1CT transitions of Ru(II) six-coordinate complexes containing these same ligands,[24] the CT assignment is reinforced by the significant red shift that occurs when bipyrazine is incorporated into the system. One expects the strong electron-withdrawing nature of the additional nitrogens in the bpz ligand to stabilize the π^*_{chel} orbital and thus reduce the energy of the CT-to-chel transition, as observed. The blue shift of this low-lying absorption band of the bpz complex upon a change of the solvent from dichloromethane to more polar methanol is also typical of ^1CT transitions to N-heterocycles.[25]

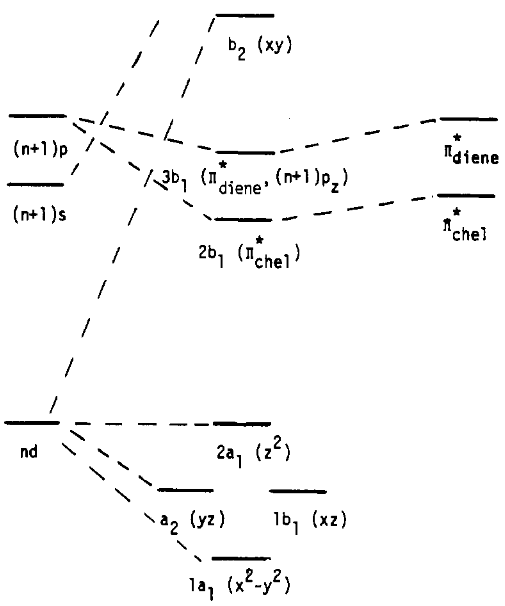

Figure 4. Molecular orbital energy level diagram for C_{2v} complexes $[M(chel)(diene)]^+$ (chel = N-heterocycle).

For the iridium species containing an N-heterocycle, assignment of the lowest absorption bands (~17 000 and ~22 000 cm^{-1}) to triplet and singlet transitions, respectively, of the same configuration is inconsistent with the strong relative intensity of the lower energy band. In addition, such assignments would indicate a $^1A_1 \rightarrow {}^1CT$(chel) transition that lay higher in energy in an Ir(I) complex than in the corresponding Rh(I) species, a situation contrary to expectations. Furthermore, Epstein et al.[8] observed a distinct singlet–triplet splitting of the low-lying CT-to-diene transition only for $[IrCl(cod)(CH_3CN)]$. For $[IrCl(cod)]_2$ the $^1A_1 \rightarrow {}^{1,3}CT$(diene) bands appeared as a single peak at 22 000 cm^{-1}. We therefore assign the band at ~22 000 cm^{-1} in the Ir(I) complexes reported here to $^1A_1 \rightarrow {}^1CT$(diene) and the peak at ~17 000 cm^{-1} to $^1A_1 \rightarrow {}^1CT$(chel). These absorption band assignments are summarized in Table I.

From these assignments an orbital scheme can be constructed. The one-electron orbital diagram for a planar C_{2v} system is shown in Figure 4; we have chosen the same coordinate system as Epstein et al.,[8] namely, the x axis as the molecular symmetry axis and the z axis perpendicular to the molecular plane. The ordering of the d orbitals, with the d_{z^2} orbital as the highest occupied, is in accord with previous studies.[1-4,8] When chel = N-heterocycle, the lowest unfilled molecular orbital is the lowest energy π^* orbital on chel. Simple Hückel molecular orbital calculations indicate that this orbital has b_1 symmetry. The next unfilled molecular orbital is shown to be mixed π^*_{diene} and $(n + 1)p_z$. It also has b_1 symmetry. In this scheme the π^*_{chel} orbital mixes with the $(n + 1)p_z$ orbital but to a lesser extent than the π^*_{diene}. From the diagram the following assignments are made: $^1A_1 \rightarrow {}^1CT$(chel) (band I) arises from $^1A_1 \rightarrow {}^1B_1$ ($2a_1 \rightarrow 2b_1$), $^1A_1 \rightarrow {}^3CT$(diene) (band II) arises from $^1A_1 \rightarrow {}^3B_1$ ($2a_1 \rightarrow 3b_1$), and $^1A_1 \rightarrow {}^1CT$(diene) (band III) arises from $^1A_1 \rightarrow {}^1B_1$ ($2a_1 \rightarrow 3b_1$). Emission from the complexes containing an N-heterocycle arises from $^1A_1 \leftarrow {}^3B_1$ ($2a_1 \leftarrow 2b_1$). All the transitions are dipole allowed.

---

(21) Demas, J. N.; Crosby, G. A. *J. Mol. Spectrosc.* **1968**, *26*, 72.
(22) Crosby, G. A.; Watts, R. J.; Carstens, D. H. W. *Science (Washington, D.C.)* **1970**, *170*, 1195.
(23) Klassen, D. M.; Crosby, G. A. *J. Chem. Phys.* **1968**, *48*, 1853.
(24) Watts, R. J.; Crosby, G. A. *J. Am. Chem. Soc.* **1971**, *93*, 3184.
(25) Demas, J. N.; Turner, T. F.; Crosby, G. A. *Inorg. Chem.* **1969**, *8*, 674.

Nature of States. Attempts to locate $^1A_1 \rightarrow {}^3CT$(chel) transitions by low-temperature absorption and emission excitation experiments failed. Triplet bands have been observed in the spectra of numerous Rh(I) and Ir(I) complexes,[1-4] although only in those with ligands without extended π aromatic structures. The reported singlet-triplet splitting was $\sim$3500 cm^{-1}, the same as we observe for $[Ir(en)cod)]^+$. In the chel = N-heterocycle complexes either the triplet absorption intensity is particularly weak relative to the singlet or the singlet–triplet splitting is small. From the measured lifetimes and emission intensities of our $[M(chel)(diene)]^+$ ions we predict extinction coefficients for the triplet absorptions of 50 M^{-1} cm^{-1}. Bands of this intensity should be visible if separated from the ^{1}CT-to-chel transition ($\epsilon \cong 800$ M^{-1} cm^{-1}) by 3500 cm^{-1}. We therefore opt for a singlet–triplet splitting in these complexes that is considerably less than 3500 cm^{-1}. This conclusion seems justified in light of the delocalization of the excited electron in the π^*_{chel} orbital that should decrease the effective exchange integral. In the complexes studied previously the localization of the excited electron on the atoms adjacent to the metal and the mixing of the p_z metal orbital in the highest unfilled molecular orbital may be responsible for the substantial singlet–triplet splittings that are observed.

The weak emissions and apparently large Stokes shifts observed from complexes containing 1,5-hexadiene may be attributed to the flexibility of this ligand, a property that would facilitate distortion in the excited state and enhance nonradiative decay rates. The demonstrated greater chemical lability of this ligand relative to that of other diolefins further corroborates the flexibility argument.[12] The weak emissions of the Ir(I) complexes in glasses are not so easily explained. We offer no simple explanation for the dramatic decrease in emission intensity of the N-heterocyclic complexes of Ir(I) from glasses relative to that observed from the solid state.

The emission band shape of the $[Ir(en)(cod)]^+$ complex stands out as unusual. The mirror-image relationship of the band with the corresponding absorption and the similarity of the band shape in glassy solution to that of the solid-state emission indicate that the luminescence does not originate from impurities or decomposition products. To our knowledge this is the first example of a CT from an olefin emission. We are unable to explain the observed nonexponential decay.

Nature of the Emitting Manifold. Upon a lowering of the temperature below 77 K the emission intensity of $[M(bpy)(cod)]ClO_4$ [M = Rh(I), Ir(I)] decreased but no significant changes in band shape were observed. The lifetime vs. temperature results, $\tau_H = 1.00$ μs, $\tau_L = 103$ μs and $\tau_H = 0.11$ μs, $\tau_L = 4.53$ μs (H = higher, L = lower), respectively, indicate that emission from the higher level is partially allowed, whereas emission from the lower level is forbidden. This is identical with the situation observed for the D_{4h} symmetry complexes $[M(2{=}phos)_2]^+$ [M = Rh(I), Ir(I);[7] 2=phos is *cis*-1,2-bis(diphenylphosphino)ethylene] and other Rh(I) and Ir(I) complexes.[26] In the 2=phos complexes the assumed emitting $^3A_{2u}$ term was split by spin–orbit coupling into E_u (dipole allowed) and A_{1u} (dipole forbidden) components. In C_{2v} symmetry and the coordinate system we have used, the emitting $^3B_1$ term is spin–orbit split into A_1 and B_2 (both dipole allowed) and A_2 (dipole forbidden) states. The A_1 and B_2 components correlate with E_u, and the A_2 state correlates with A_{1u} in D_{4h}. On the basis of the satisfactory fit of the lifetime vs. temperature data to only two levels we assign the shorter lived higher energy emitting level to accidentally degenerate A_1 and B_2 states and lower energy emitting level to the A_2 state.

The energy of the splitting between the two levels of $[M(bpy)(cod)]ClO_4$ [M = Rh(I), 18.5 cm^{-1}; M = Ir(I), 87.9 cm^{-1}] is substantially less than that of $[M(2{=}phos)_2]ClO_4$ [M = Rh(I), 37.8 cm^{-1}; M = Ir(I), 143 cm^{-1}][7] and other Rh(I) and Ir(I) diphosphine and diarsine complexes[26] we have studied by similar methods. The decreased splitting is indicative of a greater CT character in the triplet state and consequently less metal $(n + 1)p_z$ character in the excited configuration than in the diphosphine and diarsine species. The splitting for $[Ir(bpy)(cod)]ClO_4$ is a factor of 5 greater than for the corresponding Rh(I) complex. The level splittings observed for the Rh(I) and Ir(I) 2=phos complexes were related by a similar factor.[7]

As a final observation we note that the appearance of well-resolved low-energy CT transitions to two different chromophores in the Ir(I) complexes with chel = N-heterocycle is unique. These complexes may possess wavelength-dependent photoredox properties associated with two different CT excited states.

Acknowledgment. This research was supported by Air Force Office of Scientific Research Grant AFOSR-80-0038. We also thank Matthey Bishop, Inc., for a generous loan of rhodium and iridium chlorides.

Registry No. $[Rh(en)(cod)]ClO_4$, 59329-62-3; $[Rh(bpy)(cod)]ClO_4$, 37685-01-1; $[Rh(phen)(cod)]ClO_4$, 37685-03-3; $[Rh(4,7\text{-}Ph_2\text{-}phen)(cod)]ClO_4$, 80263-28-1; $[Rh(bpz)(cod)]PF_6$, 80263-29-2; $[Rh(bpy)(nbd)]ClO_4$, 52445-04-2; $[Rh(phen)(nbd)]ClO_4$, 52445-07-5; $[Rh(bpy)(1,5\text{-}hex)]PF_6$, 62630-26-6; $[Rh(phen)(1,5\text{-}hex)]PF_6$, 62630-28-8; $[Ir(en)(cod)]ClO_4$, 80287-58-7; $[Ir(bpy)(cod)]ClO_4$, 41444-85-3; $[Ir(bpy)(nbd)]PF_6$, 53505-25-2; $[RhCl(cod)]_2$, 12092-47-6.

---

(26) Fordyce, W. A.; Crosby, G. A. *Inorg. Chem.*, in press.