

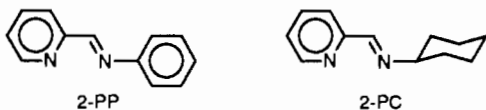
Structural, Spectral, and Charge-Transfer Properties of $\text{ClRe}(\text{CO})_3(2\text{-PP})$ [2-PP = N -(2-Pyridinylmethylene)phenylamine] and $\text{ClRe}(\text{CO})_3(2\text{-PC})$ [2-PC = N -(2-Pyridinylmethylene)cyclohexylamine][†]

Raymond N. Dominey,* Brian Hauser, John Hubbard, and Jennifer Dunham

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The complexes $\text{ClRe}(\text{CO})_3\text{L}$ [L = N -(2-pyridinylmethylene)phenylamine (2-PP), N -(2-pyridinylmethylene)cyclohexylamine (2-PC)] have been prepared and structurally characterized by X-ray diffraction. Their absorption spectra at 298 K, emission spectra and luminescence lifetimes at 77 K, and redox potentials are also reported. The absorption and emission are assigned to MLCT transitions, both of which blue shift upon cooling to 77 K. Increased polarity of the solvent also causes a blue shift in the MLCT absorption. The correlations between the electrochemical properties and both the absorption and emission energies are discussed.

The photophysics, photochemistry, and redox properties of α,α' -diimine complexes of ruthenium¹ have been prolific areas of research over the past 15 years. The $\text{Ru}(\text{d}\pi) \rightarrow \text{diimine}(\pi^*)$ metal-to-ligand charge-transfer (MLCT) excited states usually dominate the photophysics and photochemistry of these complexes. Although much less attention has been given to α,α' -diimine complexes of rhenium and osmium, early studies by Wrighton² and more recent studies by Meyer³ show that they also typically exhibit MLCT absorptions and emission. To date, most studies of $\text{Re}^I(\alpha,\alpha'$ -diimine) complexes have been limited to either complexes of 2,2'-bipyridine or 1,10-phenanthroline or their substituted derivatives.^{2,4-11} The photophysics and photochemistry of these complexes can be "fine-tuned" to some extent by varying the substituents on the bipyridine or phenanthroline ligand. Since the π^* level of the α,α' -diimine ligand is central to the MLCT absorption and emission properties, complexes containing other structural types of α,α' -diimine ligands should be explored. We report here the structural, electrochemical, and spectral properties of two new $\text{ClRe}(\text{CO})_3(\alpha,\alpha'$ -diimine) complexes containing the following α,α' -diimine ligands:



Both $\text{ClRe}(\text{CO})_3(2\text{-PP})$ (**1**) and $\text{ClRe}(\text{CO})_3(2\text{-PC})$ (**2**) show unusually low MLCT transition energies and extremely short emission lifetimes at 77 K. Complex **1** (Figure 1) has the shortest emission lifetime and one of the lowest MLCT energies reported to date for such complexes.

Experimental Section

The ligands 2-PP and 2-PC were synthesized by refluxing 2-pyridinecarboxaldehyde with a stoichiometric amount of the appropriate amine in toluene for about 12 h using a Stark trap. Details on the synthesis, purification, and characterization of the ligands 2-PP and 2-PC and the rhenium complexes **1** and **2** are available as supplementary material. All rhenium complexes $\text{ClRe}(\text{CO})_3\text{L}$, where L = 2-PP, 2-PC, bpy (2,2'-bipyridine), phen (1,10-phenanthroline), and dmphen (4,7-dimethyl-1,10-phenanthroline), were synthesized for this study by the method of Wrighton^{2b} using $\text{ClRe}(\text{CO})_5$ and the appropriate α,α' -diimine ligand. Detailed X-ray diffraction data for **1** and **2** are also included in the supplementary material. Absorption and emission data were obtained using standard techniques as described in the literature.^{6a,7,12} Cyclic voltammograms were obtained on acetonitrile solutions containing 0.1 M tetrabutylammonium hexafluorophosphate using a PAR model 273 potentiostat, a platinum-wire working electrode, and a silver-wire pseudoreference electrode internally referenced to ferrocene.¹³

Results

Structural Studies. A summary of the crystallographic data for compounds **1** and **2** is presented in Table I. The positional

Table I. Crystallographic Data for $\text{ClRe}(\text{CO})_3(2\text{-PP})$ and $\text{ClRe}(\text{CO})_3(2\text{-PC})$

$\text{ClRe}(\text{CO})_3(2\text{-PP})$	
$\text{ReClO}_3\text{N}_2\text{C}_{15}\text{H}_{10}$	$T = -120\text{ }^\circ\text{C}$
fw = 487.92	$\lambda = 0.71069\text{ \AA}$
$a = 12.481(3)\text{ \AA}$	$d_{\text{calc}} = 2.178\text{ g cm}^{-3}$
$b = 8.987(2)\text{ \AA}$	$\mu = 84.72\text{ cm}^{-1}$
$c = 13.582(2)\text{ \AA}$	transm coeff = 0.91-1.20
$\beta = 102.43(2)^\circ$	2812 unique reflns
$V = 1487.7(5)\text{ \AA}^3$	2101 reflns with $I > 3\sigma(I)$
$Z = 4$	$R(F_o) = 0.024$
$P2_1/n$, No. 14	$R_w(F_o) = 0.031$
$\text{ClRe}(\text{CO})_3(2\text{-PC})$	
$\text{ReClO}_3\text{N}_2\text{C}_{15}\text{H}_{16}$	$T = -120\text{ }^\circ\text{C}$
fw = 493.96	$\lambda = 0.71069\text{ \AA}$
$a = 11.508(2)\text{ \AA}$	$d_{\text{calc}} = 2.026\text{ g cm}^{-3}$
$b = 8.973(2)\text{ \AA}$	$\mu = 77.82\text{ cm}^{-1}$
$c = 16.415(2)\text{ \AA}$	transm coeff = 0.90-1.17
$\beta = 107.14(1)^\circ$	3072 unique reflns
$V = 1619.7(4)\text{ \AA}^3$	2402 reflns with $I > 3\sigma(I)$
$Z = 4$	$R(F_o) = 0.037$
$P2_1/c$, No. 14	$R_w(F_o) = 0.047$

parameters for **1** and **2** are listed in Tables II and III, respectively, with the important bond lengths and bond angles collected in Table

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[†] Presented in part at the 42nd Southeast/46th Southwest Combined Regional Meeting of the American Chemical Society in New Orleans, LA, on Dec 5-7, 1990.

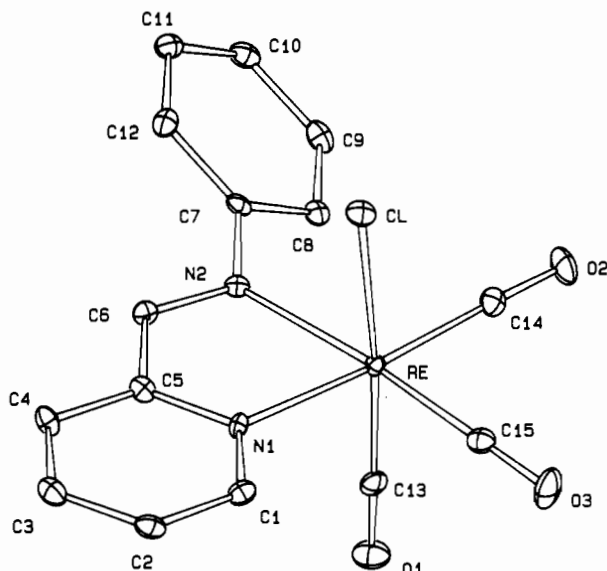


Figure 1. ORTEP diagram for ClRe(CO)₃(2-PP). The structure is arranged so as to show the relative orientation of the phenyl and pyridyl rings and the chlorine atom.

Table II. Atomic Positional Parameters for ClRe(CO)₃(2-PP) According to the Numbering Scheme in Figure 1

atom	x	y	z
Re	0.23586 (2)	0.12158 (3)	-0.01839 (2)
Cl	0.1600 (1)	0.1548 (2)	0.1338 (1)
O(1)	0.3255 (4)	0.1086 (5)	-0.2119 (4)
O(2)	0.4409 (4)	-0.0425 (5)	0.0963 (4)
O(3)	0.1463 (4)	-0.1925 (5)	-0.0679 (4)
N(1)	0.0909 (4)	0.2442 (5)	-0.0907 (4)
N(2)	0.2799 (4)	0.3566 (6)	0.0084 (4)
C(1)	-0.0061 (5)	0.1844 (7)	-0.1364 (5)
C(2)	-0.0955 (5)	0.2719 (7)	-0.1801 (5)
C(3)	-0.0862 (5)	0.4243 (8)	-0.1772 (5)
C(4)	0.0127 (5)	0.4884 (7)	-0.1291 (5)
C(5)	0.0989 (5)	0.3937 (7)	-0.0860 (5)
C(6)	0.2046 (5)	0.4512 (7)	-0.0312 (5)
C(7)	0.3810 (5)	0.4148 (7)	0.0686 (4)
C(8)	0.4781 (5)	0.3381 (7)	0.0675 (5)
C(9)	0.5765 (5)	0.3923 (7)	0.1247 (4)
C(10)	0.5784 (5)	0.5230 (7)	0.1783 (5)
C(11)	0.4828 (5)	0.5972 (7)	0.1800 (5)
C(12)	0.3834 (5)	0.5429 (7)	0.1251 (5)
C(13)	0.2920 (5)	0.1124 (7)	-0.1387 (5)
C(14)	0.3658 (5)	0.0205 (7)	0.0544 (5)
C(15)	0.1788 (5)	-0.0719 (7)	-0.0483 (5)

IV. Complex 1 crystallizes in the $P2_1/n$ space group. The structure, shown in Figure 1, shows the complex to have a facial arrangement of the carbonyl ligands. The chloride ligand is displaced toward the α, α' -diimine functionality. Notably, the phenyl and pyridyl rings are not coplanar. The dihedral angle between the phenyl ring and the planar (pyridinylmethylene)amino functionality is 34.1° . The phenyl C-N bond distance is 1.446 Å, which is intermediate between a typical C-N single and double bond. Complex 2 crystallizes in the $P2_1/c$ space group, and its structure is qualitatively similar to that of 1. The only notable differences between the structures of 2 and 1 are the longer cyclohexyl C-N bond distance (1.52 Å) and larger thermal disorder in the cyclohexyl ring. Several attempts to model this disorder failed to produce an acceptable geometry for the cyclohexyl ring.

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Table III. Atomic Positional Parameters for ClRe(CO)₃(2-PC)

atom	x	y	z
Re	0.23066 (3)	0.35817 (3)	0.94909 (2)
Cl	0.0189 (2)	0.3293 (2)	0.8561 (1)
O(1)	0.4931 (6)	0.3697 (7)	1.0627 (4)
O(2)	0.3050 (6)	0.4895 (8)	0.7989 (4)
O(3)	0.2021 (7)	0.6772 (7)	1.0063 (4)
N(1)	0.1611 (5)	0.2460 (7)	1.0412 (4)
N(2)	0.2506 (7)	0.1235 (7)	0.9263 (5)
C(1)	0.1059 (7)	0.309 (1)	1.0943 (5)
C(2)	0.0607 (7)	0.226 (1)	1.1487 (5)
C(3)	0.0698 (7)	0.074 (1)	1.1488 (5)
C(4)	0.1221 (7)	0.005 (1)	1.0928 (5)
C(5)	0.1655 (7)	0.0952 (9)	1.0401 (5)
C(6)	0.2177 (8)	0.032 (1)	0.9755 (6)
C(7)	0.297 (1)	0.065 (1)	0.855 (1)
C(8)	0.437 (1)	0.109 (1)	0.8784 (7)
C(9)	0.484 (2)	0.059 (2)	0.802 (1)
C(10)	0.443 (1)	-0.069 (2)	0.762 (1)
C(11)	0.311 (1)	-0.115 (1)	0.7466 (7)
C(12)	0.264 (1)	-0.073 (2)	0.823 (1)
C(13)	0.3963 (8)	0.3664 (8)	1.0233 (6)
C(14)	0.2792 (7)	0.4422 (9)	0.8561 (5)
C(15)	0.2111 (7)	0.5570 (9)	0.9835 (5)

Table IV. Selected Bond Lengths (Å) and Angles (deg) for Compounds 1 and 2

	ClRe(CO) ₃ (2-PP)	ClRe(CO) ₃ (2-PC)
Re-Cl	2.471 (2)	2.478 (2)
Re-N(1)	2.165 (5)	2.157 (5)
Re-N(2)	2.193 (5)	2.163 (7)
Re-C(13)	1.914 (7)	1.94 (1)
Re-C(14)	1.934 (6)	1.927 (8)
Re-C(15)	1.890 (7)	1.905 (8)
N(1)-C(5)	1.348 (7)	1.35 (1)
N(2)-C(6)	1.296 (8)	1.29 (1)
N(2)-C(7)	1.446 (8)	1.52 (1)
C(5)-C(6)	1.462 (8)	1.48 (1)
N(1)-Re-N(2)	75.0 (2)	75.4 (2)
N(1)-Re-Cl	83.4 (1)	83.2 (2)
N(2)-Re-Cl	82.7 (1)	85.8 (2)
N(1)-Re-C(13)	93.4 (2)	94.4 (3)
N(1)-Re-C(15)	97.6 (2)	97.4 (3)
N(2)-Re-C(13)	93.3 (2)	90.6 (3)
N(2)-Re-C(14)	102.4 (2)	100.0 (3)
Cl-Re-C(13)	175.4 (2)	176.1 (2)
Re-N(1)-C(5)	116.1 (4)	115.7 (5)
Re-N(2)-C(6)	115.4 (4)	116.7 (6)
N(1)-C(5)-C(6)	115.2 (5)	114.8 (7)
N(2)-C(6)-C(5)	118.3 (5)	117.4 (8)
C(6)-N(2)-C(7)	117.7 (5)	120.1 (8)

Table V. Solvent Dependence of MLCT Absorption at 289 K

solvent	λ_{\max} , nm ($10^{-3}\epsilon$)	
	ClRe(CO) ₃ (2-PC)	ClRe(CO) ₃ (2-PP)
PhCH ₃	429 (3.69)	443 (3.68)
THF ^a	414 (4.99)	435 (3.29)
CH ₂ Cl ₂	412 (3.47)	435 (3.80)
EtOH	399 (6.15)	414 (4.60)
DMF ^b	398 (4.42)	410 (3.48)
CH ₃ CN	393 (3.66)	412 (2.73)

^a Tetrahydrofuran. ^b Dimethylformamide.

Absorption Spectra. The absorption spectra of 1 and 2 are qualitatively similar to those published^{2,5,9} for similar rhenium complexes. Typical spectra in EtOH/MeOH solution are shown in Figure 2. Although the complexes retain fairly intense intraligand absorption bands in the UV region, the key feature is the lower energy band that is unique to the complexes. It is reasonable to assign this low-energy absorption (390–420 nm) to a Re(d π) \rightarrow ligand(π^*)¹ MLCT transition.

The position of the low-energy MLCT absorption band, for both 1 and 2, is quite sensitive to solvent. The absorption maximum blue-shifts with increased solvent polarity (Table V). Similar

Table VI. Absorption, Luminescence, and Electrochemical^a Properties of $\text{ClRe}(\text{CO})_3\text{L}$ Complexes

complex	E_{abs} , eV ^b (λ_{max} , nm)	E_{em} , eV ^c	τ , μs ^c	$\ln(1/\tau)$	redn $E_{1/2}$, V ^d	oxidn $E_{\text{p,a}}$, V	ΔE , V
2-PP	3.010 (412)	1.748	0.077	16.4	-0.94	1.39	2.33
2-PC	3.155 (393)	1.934	0.377	14.8	-1.21	1.41	2.62
bpy ^e	3.351 (370)	2.257	3.8 ^f	12.5	-1.33	1.40	2.73
phen ^g	3.324 (373)	2.263	7.2	11.8	-1.32	1.39	2.73
dmphen ^h	3.464 (358)	2.356	15.0	11.1	-1.44	1.38	2.82

^a 298 K acetonitrile solution; V vs SCE.¹³ ^b 298 K acetonitrile solution. ^c 77 K EtOH/MeOH (4:1 v/v). ^d $E_{1/2} = (E_{\text{p,a}} + E_{\text{p,c}})/2$. ^e 2,2'-Bipyridine. ^f 1,10-Phenanthroline. ^g Reference 2a. ^h 4,7-Dimethyl-1,10-phenanthroline.

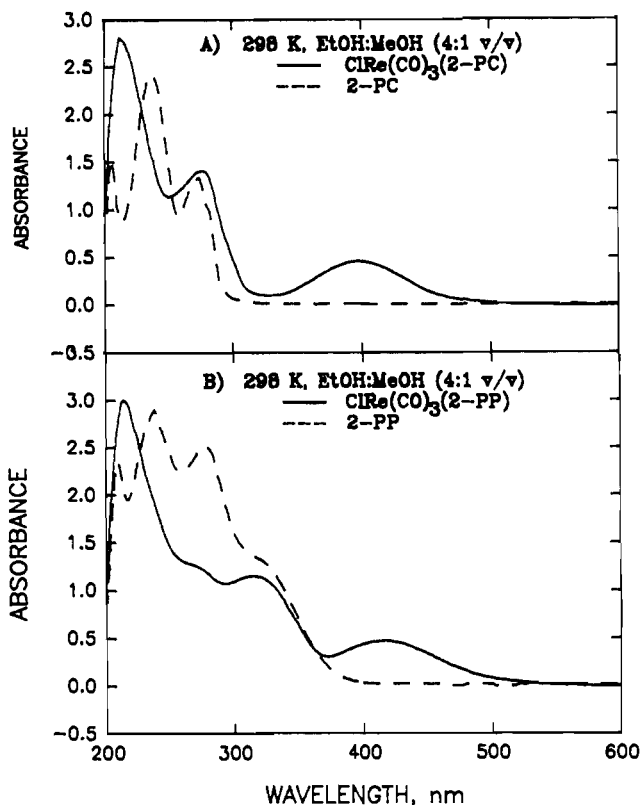


Figure 2. Room-temperature absorption spectra in EtOH/MeOH (4:1 v/v) solution: (A) 7.4×10^{-5} M $\text{ClRe}(\text{CO})_3(2\text{-PC})$ (—), 2.5×10^{-4} M 2-PC (---); (B) 9.8×10^{-5} M $\text{ClRe}(\text{CO})_3(2\text{-PP})$ (—), 2.4×10^{-4} M 2-PP (---).

effects have been reported for MLCT absorptions of bipyridine and phenanthroline complexes of rhenium.^{2b,4e,9} In addition, the MLCT absorption band shows a small blue shift upon cooling from 298 to 77 K. This effect also has been reported for MLCT absorptions of Re complexes.^{2b,e,7} This phenomenon most likely is due to the fact that the energy of the highly dipolar MLCT state is affected by differences in the microstructural ordering of the solvent in low-temperature glasses versus room-temperature fluid solutions.

Emission Spectral Data. Room-Temperature Emission. In room-temperature solution both **1** and **2** exhibit very weak emission with maxima near or greater than 800 nm. The emission is clearly detectable; however, detailed luminescence data are not reported for **1** and **2** at 298 K because the weak emission have maxima in a region where the detector response is uncalibrated.

Low-Temperature Emission. The emission spectrum in EtOH/MeOH glass at 77 K, for both **1** ($\lambda_{\text{em}}^{\text{max}} = 694$ nm) and **2** ($\lambda_{\text{em}}^{\text{max}} = 628$ nm), shows a broad structureless emission band. Although the shapes of the emission bands are similar to those reported for similar complexes, the emission energies for **1**, and for **2**, at 77 K are much lower. It is noteworthy that only one other $\text{Re}^{\text{I}}(\alpha, \alpha'\text{-diimine})$ complex, $\text{ClRe}(\text{CO})_3(\text{biquinoline})$, has an emission energy ($\lambda_{\text{em}}^{\text{max}} = 686$ nm) at 77 K¹⁴ that is comparable

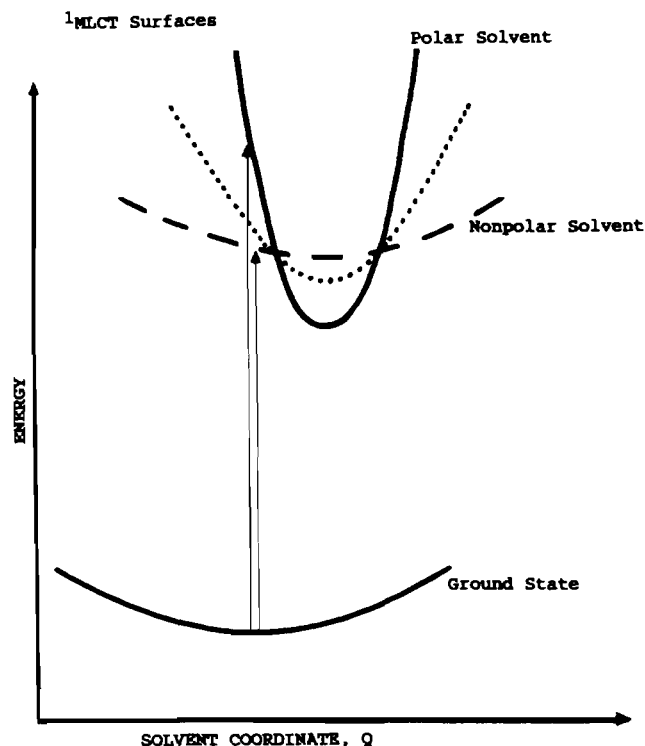


Figure 3. Representation of the effect of solvent polarity on the potential energy surfaces and absorption energies for $\text{ClRe}(\text{CO})_3(\alpha, \alpha'\text{-diimine})$.

to those of **1** or **2**. For both complexes, the emission is more intense and occurs at higher energy at 77 K than that detected at room temperature. Several studies^{2b,5,7} report such a blue shift of ³MLCT emission for analogous bipyridine and phenanthroline rhenium complexes upon cooling to 77 K. This so called "rigidochromic" effect^{2b} arises from the fact that in low-temperature glasses solvent dipoles cannot reorient around and stabilize the excited-state dipole. On the basis of these facts, we assign the emission to a $d\pi(\text{Re}) \leftarrow \pi^*(2\text{-PP or } 2\text{-PC})$ ³MLCT transition.

Low-Temperature Lifetimes. For both **1** and **2** in EtOH/MeOH at 77 K, the luminescence exhibits a single exponential decay. The lifetime of **2** is 377 ns; but, for **1**, the lifetime is only 77 ns. These low-temperature emission lifetimes are very short. Typically, ³MLCT emission lifetimes for $\text{XRe}(\text{CO})_3(\alpha, \alpha'\text{-diimine})$ complexes in low-temperature glasses are in the 1–50- μs range.^{2b,5}

Electrochemistry. The redox potentials for **1** and **2** as well as several other $\text{Re}(\alpha, \alpha'\text{-diimine})$ complexes were measured by cyclic voltammetry and are presented in Table VI. They all show a reversible diimine ligand-based reduction; these reflect the differences in the energy of the π^* level of the different ligands. Anodic scans reveal a single irreversible oxidation at about 1.4 V vs SCE for all the complexes in CH_3CN . This is assigned to the $\text{Re}(\text{II})/\text{Re}(\text{I})$ redox couple. The fact that the potentials for oxidation of Re are very similar for all the complexes is reasonable

(14) Reference 2b reports the emission energy but not the emission lifetime for $\text{ClRe}(\text{CO})_3(\text{biquinoline})$ at both room temperature and 77 K.

(15) (a) Dodsworth, E. E.; Lever, A. B. P. *Chem. Phys. Lett.* **1986**, *124*, 152. (b) Barigelletti, F.; Juris, A.; Balzani, V.; Belser, P.; Von Zelewsky, A. *Inorg. Chem.* **1987**, *26*, 4115.

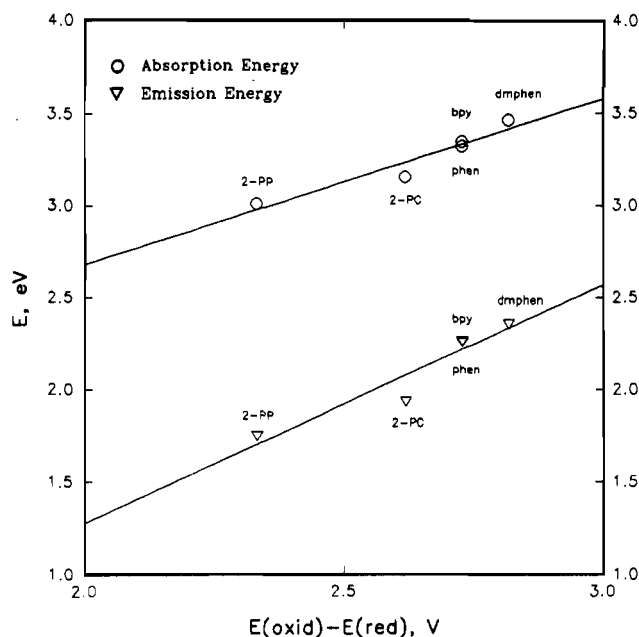


Figure 4. Correlations between the ¹MLCT absorption energy maxima at 298 K (O), and the ³MLCT emission energy maxima at 77 K (▽) and ΔE (the difference between the Re(II)/Re(I) and the α,α' -diimine redox potentials) for the complexes listed in Table VI (see text).

in view of the fact that the diimine ligands should all have very similar positions within the spectrochemical series. This strongly suggests that any differences in the MLCT absorption and emission energies between the complexes are primarily due to differences in the π^* level of the α,α' -diimine ligands.

Discussion

According to dielectric continuum theory^{4c} there are two major factors that determine solvatochromism for MLCT transitions. One is the effect of solvent on the outer-sphere reorganization energy. A larger outer-sphere reorganization energy can be envisioned as an excited-state surface whose energy is much more strongly dependent on the solvent coordinate, as depicted for the more polar solvent in Figure 3. The second factor is the effect of solvent on the energy difference between the thermally equilibrated excited state and ground state. The energy of the thermally equilibrated excited state of **1**, and of **2**, is expected to be lower in more polar solvents. Nevertheless, if the outer-sphere reorganization energy for excitation dramatically increases with solvent polarity, then a blue-shift in MLCT absorption similar to that observed (Table V) is expected. This situation can be represented by excited-state potential energy surfaces with respect to a solvent coordinate as shown in Figure 3. This model also predicts that the emission maximum should red-shift with increased solvent polarity as has been reported for both [XRe(CO)₃(L)₂]^{2c} and [Ru(bpy)₃]²⁺.^{1c}

For Ru(α,α' -diimine) complexes, MLCT absorption and emission energies correlate directly with ΔE (where $\Delta E = E_{p,a}\{\text{Re(II/I)}\} - E_{1/2}\{\text{ligand(0/-1)}\}$).^{1b,15} Consistent with our assignment of MLCT transitions for **1** and **2**, we find that both the 298 K absorption and 77 K emission energies show good correlation with ΔE when compared with other Re(α,α' -diimine) complexes (Figure 4; Table VI). Together with the fact that the potential for Re oxidation is ≈ 1.4 V SCE for all the complexes used, this correlation confirms that the major reason for the unusually low energy for the MLCT excited states of **1** and **2** is the low π^* level of 2-PC and especially of 2-PP. Further examination of Figure 4 reveals that the slope for the absorption energy correlation is about 0.9 and for the emission energy correlation about 1.2. Deviation of the slopes from unity probably results from differences in solvent interactions with the neutral ground state and the dipolar excited state relative to that with the charged oxidized and reduced ground states.^{15a}

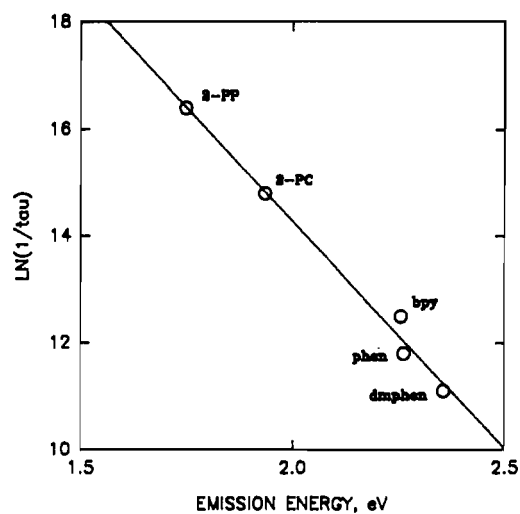


Figure 5. Correlation between $\ln \tau^{-1}$ and the ³MLCT emission energy maxima at 77 K for the complexes listed in Table VI.

Several studies^{1a-c,e,f,3,16} have demonstrated the applicability of the "energy gap law" to ³MLCT emitters, in particular Meyer's work with (bpy)Re(CO)₃L⁺ complexes.^{4a,b} According to the energy gap law^{1a} the nonradiative decay rate should decrease logarithmically as the emitter state energy increases. The lifetime data in Table VI shows such a trend. The quantum yields for **1** and **2** at 77 K are much less than 1% relative to Ru(bpy)₃²⁺ at room temperature. We also assume that the dominant decay paths for the bpy and phen complexes are nonradiative.¹⁷ Thus, using the assumption that $\ln \tau^{-1} \approx \ln k_{nr}$, we can approximate an energy gap law plot as shown in Figure 5. Indeed, the plot shows a good fit to a straight line ($r = 0.99$) with a slope of -8.50 eV^{-1} and an intercept of 31.27. These values are similar to those previously reported for a series of Os(II)- and Ru(II)-bpy MLCT excited states (slopes = -7.4 to -8.1 eV^{-1} ; intercepts = 28–31)^{1f} and for a series of (bpy)Re(CO)₃L⁺ MLCT excited states (slope = -11.8 eV^{-1} ; intercept = 40.2).^{4a} The main conclusions from this are that the dominant decay processes for compounds **1** and **2** are nonradiative, and thus, their unusually short lifetimes are understandable in terms of their low ³MLCT energies and the energy gap law.

The spectroscopic properties of **1** and **2** reflect a relatively low energy for their MLCT excited states. This, in turn, appears to be a direct consequence of comparatively low π^* energy levels for 2-PP and 2-PC. Why 2-PP and 2-PC are better at accepting charge than bpy or phen is an intriguing question. We are continuing to study this by performing extended Huckel molecular orbital (EHMO) calculations on the ligands, complexes, and methylated analogues. Preliminary EHMO results suggest that addition of a methyl to the imine carbon should push the π^* levels up in energy. We are proceeding with the synthesis of a variety of methylated versions of 2-PP and 2-PC, and with a more thorough computational study, in order to fully explore this possibility.

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(17) The low-temperature quantum yields for these complexes were not measured; however, the room-temperature quantum yields are all less than 0.04 (refs 2b and 4a). In any event, Figure 5 is based on lifetimes at 77 K and is not based on a precisely homologous set of complexes. Due to these factors the agreement with theory suggested by Figure 5 may be partly fortuitous.

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Registry No. 1, 136847-07-9; 2, 136847-08-0; 2-PP, 7032-25-9; 2-PC, 7166-35-0; ClRe(CO)₅, 14099-01-5; 2-pyridinecarboxaldehyde, 1121-

60-4; aniline, 62-53-3; cyclohexylamine, 108-91-8.

Supplementary Material Available: Text containing preparational details and analytical data for 1 and 2, tables of X-ray diffraction data, thermal parameters, and bond lengths and angles for 1 and 2, and an ORTEP diagram of 2 (15 pages); tables of structure factors (32 pages). Ordering information is given on any current masthead page.

Contribution from the Departments of Chemistry, Oregon State University, Corvallis, Oregon 97331, and University of Reading, Whiteknights Park, Reading, England

Gas-Phase Electron-Diffraction Studies of the Molecular Structures of Tetrabromo(sulfido)tungsten(VI), WBr₄, and Tetrabromo(seleno)tungsten(VI), WSeBr₄

Elizabeth M. Page,^{1a} David A. Rice,^{1a} Kolbjørn Hagen,^{1b} Lise Hedberg,^{1c} and Kenneth Hedberg*,^{1c}

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The molecular structures of WBr₄ and WSeBr₄ at 220 and 250 °C, respectively, have been determined by gas-phase electron diffraction. The experimental data for both compounds are fitted by square-pyramidal models of C_{4v} symmetry in which the tungsten atom is above the plane of the bromine atoms. The bond lengths (*r*_a/Å) and bond angles (*∠*/deg) with estimated 2σ uncertainties are as follows. WBr₄: *r*(W=S) = 2.109 (11), *r*(W—Br) = 2.433 (3), *∠*(S=W—Br) = 103.5 (7), *∠*(Br—W—Br)_{cis} = 86.9 (3), and *∠*(Br—W—Br)_{trans} = 153.0 (14). WSeBr₄: *r*(W=Se) = 2.220 (22), *r*(W—Br) = 2.427 (9), *∠*(Se=W—Br) = 102.5 (9), *∠*(Br—W—Br)_{cis} = 87.3 (4), and *∠*(Br—W—Br)_{trans} = 154.9 (19). The structures of the series of nine WYX₄ molecules (Y = O, S, Se; X = F, Cl, Br) are discussed.

Introduction

We have previously determined the structures of WOF₄,² WSF₄,³ WSeF₄,⁴ WSeCl₄,⁵ and WOBr₄,^{6,7} by gas-phase electron diffraction; other workers have measured WOCl₄.^{8,9} In each case the data have been consistent with C_{4v} symmetry for the free molecules, although the experimental uncertainties would also allow small distortions from that symmetry. There are only limited single-crystal X-ray data for the compounds^{10,11} because the crystals tend to be twinned or the structures disordered. Tetrabromo(sulfido)tungsten(VI) (WBr₄) and tetrabromo(seleno)tungsten(VI) (WSeBr₄) remain the only compounds in the WYX₄ (X = F, Cl, Br; Y = O, S, Se) series for which gas-phase structures have not yet been reported. This article is an account of our electron-diffraction investigation.

Experimental Section

Samples of WBr₄ and WSeBr₄ were prepared at Reading University as previously described.¹² Small quantities were loaded under an inert

atmosphere into glass ampules fitted with break-seals. The ampules were evacuated, sealed, and taken to Oregon State University for the diffraction experiments. For an experiment an ampule was connected via glass tubing and a Swagelok coupling to the diffraction apparatus. The tubing between the break-seal and the apparatus was heated to ca. 150 °C under vacuum for 1.5 h before the break-seal was opened. At the end of the experiments no evidence for the formation of tungsten blue (an indication that the compounds had reacted or decomposed) was observed.

The diffraction photographs were made at nozzle temperatures of 220 °C (WBr₄) and 250 °C (WSeBr₄). Other experimental conditions, the various analytical procedures, and the source of the electron-scattering amplitudes and phases were similar to those adopted for WSF₄.³ The scattered intensity data (four plates each from the long and intermediate camera distances for both compounds) covered the ranges 2.00 ≤ *s*/Å⁻¹ ≤ 13.75 (long) and 6.00 ≤ *s*/Å⁻¹ ≤ 33.75 (intermediate) at intervals Δ*s* = 0.25 Å⁻¹. The total intensity curves (*s*⁴*I*), the calculated backgrounds, the average intensity curves (*sI*_m(*s*)), the theoretical curve that gives the best fit to the data, and the difference curves for the compounds are shown in Figures 1 and 2. The total and averaged intensity data and the calculated backgrounds are available as supplementary material.

Experimental radial distribution curves, calculated in the usual manner from *I*'(*s*) = *sI*_m(*s*)Z_WZ_{Br}(A_WA_{Br})⁻¹ exp(-0.0025*s*²), are shown in Figure 3. These curves are consistent with C_{4v} symmetry for the molecules, as is the case for the other WYX₄ compounds.

Results from preliminary refinements of the structures of both compounds suggested that the samples of each contained an impurity. In view of the known propensity of sulfido and seleno halides to react with oxygenated species, the most likely impurity was judged to be WOBr₄. This conclusion is supported by IR matrix studies carried out on samples of WBr₄ and WSeBr₄,¹³ from the same preparations used for the electron-diffraction experiments. Accordingly, models that allowed for the presence of WOBr₄ in each of our materials were formulated. In each case the parameters chosen to define the system were the bond lengths *r*(W=Y) and *r*(W—Br), the bond angle *∠*(Y=W—Br) (Y = S, Se), the five vibrational amplitudes corresponding to the interatomic distances in molecules of assumed C_{4v} symmetry, and a composition parameter to represent the presumed WOBr₄ impurity (which was assigned the structure and vibrational amplitudes previously determined⁶). The

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