



Crystallography and luminescence of divalent osmium complexes green osmium emitters and possible evidence for d-orbital backbonding

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Dedicated to Professor Tobin J. Marks on the occasion of his 60th birthday

Abstract

The preparation, photophysics, and solid-state structures of three osmium cored complexes are reported. The osmium complexes take the general form of $[\text{OsCl}(\text{N-N})(\text{L-L})(\text{CO})]^+$ hexafluorophosphate where N stands for a derivative of 1,10-phenanthroline and L stands for a phosphine type ligand. The emission of the complexes is shown to be blue shifted to the osmium emission of $\text{Os}(\text{bpy})_3^{2+}$. The emissions of the various complexes range from yellow (560 nm) to yellow-green (550 nm) to green (520 nm). The quantum yields vary between 60% and 75%. The complexes show lifetimes that are much longer than expected with ranges of 6.5–38 μs . Crystallographic results show that the carbonyl is *trans* to a phenanthroline nitrogen and the chloro ligand is *trans* to phosphorus. A discussion will be presented as to the nature of the bonding in these complexes based upon the data from the crystallography.

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1. Introduction

There is considerable interest in using metal complexes in a variety of applications including light sources in organic light emitting devices (OLEDs) [1]. Using metals such as iridium [2], ruthenium [3], or osmium [4] it is possible to design complexes that can emit light ranging in color from blue through red making them ideal candidates for this technology [2a]. The resulting luminophores could be part of an OLED in optical displays.

Another possible application of these materials is in solid-state light sources [3a]. To achieve a true white color emission from these materials it is necessary to combine complexes that have emissions that are blue, green and red and controlling the amounts of each until the desired white is achieved. We have shown the syn-

thesis of $[\text{Os}(\text{N-N})_2\text{L-L}]^{2+}2\text{X}^-$ (N-N = a pyridyl and L-L = phosphine or arsine) complexes that have a strong red emission in our previous work. In this work, we show the tunability of the osmium complexes (Fig. 1) by shifting their emission resulting in a green emitting complex.

The bonding in phosphine (arsine, antimony) ligand containing metal complexes may be thought of as having two major components (Fig. 2). There is σ donation of the lone pair contained in the s orbital on the phosphorus (arsine, antimony) ligand to an empty d orbital on the metal [5]. For complexes in octahedral coordination, as in the case for the osmium complexes being discussed here, the donation of the ligand lone pair is to the d_{z^2} and the $d_{x^2-y^2}$ [5]. The other component is called backbonding. This occurs by backdonation from a filled d orbital on the metal (d_{xy} , d_{xz} , d_{yz}) to an empty orbital on the phosphorus [5]. The question of what kind of orbital on the phosphorus is responsible for accepting the back donation from the metal. This empty phosphorus orbital has been described as being either a

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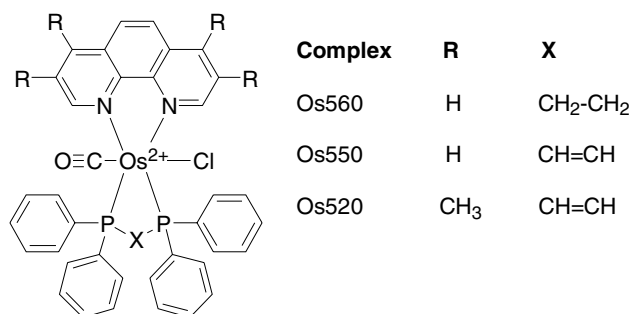


Fig. 1. Chemical structures of the complexes being presented.

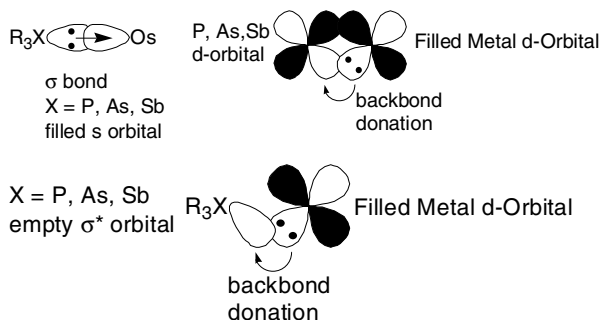
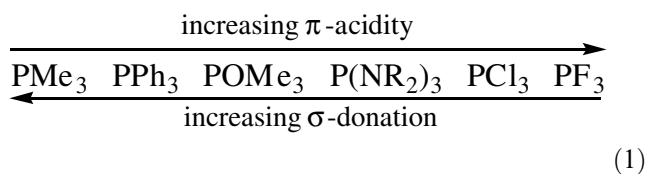


Fig. 2. Sketch of possible bonding scenarios involving phosphine (arsine, antimony) ligands.

d-orbital or an antibonding σ orbital; current consensus is that the latter is more appropriate [6]. Some crystallographic reports it has been shown that the bond lengths between phosphorus and the R groups attached to it lengthen, which supports the notion that a σ^* is responsible for backbonding with the metal [6,7]. It has been generally accepted that the phosphine ligands backbond strongly when based upon strongly electron withdrawing groups such as fluorine. Those with more electron donating groups such as methyl are more likely to be σ donors and backbond more weakly. This establishes a series of σ donors versus π acceptors.



2. Synthesis

2.1. General procedure for synthesis of osmium complexes of form $[OsCl(N-N)(L-L)(CO)]^+$

Potassium hexachloroosmate (1.000 g, 2.08 mmol) was reacted with 2.05 equivalents of either *cis*-1,2-bis(diphenylphosphino)ethene or 1,2-bis(diphenylphosphino)ethane in deoxygenated DMF (by a nitrogen purge) for 30 min. The solution was then precipitated in

250 ml of water with 3.5 g of sodium hydrosulfite dissolved at 0 °C. A colorless to off-white precipitate formed, which was filtered and dried under vacuum. The dried colorless solid was dissolved into a mixture of 2,2'-ethoxyethoxyethanol (Aldrich) and glycerol (75:25 by volume) with a 1,10-phenanthroline ligand. The solution was deoxygenated by nitrogen purge and refluxed for 45 min. The resulting solution was then precipitated into a solution containing potassium hexafluorophosphate. The solids were filtered and dried under vacuum. The solids were dissolved into methylene chloride and placed onto a column of basic activated alumina. The target band had a green to yellow luminescence was collected. The solvents were removed by rotary evaporation and the resulting solids were crystallized from 50/50 mixtures of methylene chloride and hexanes.

2.2. Chloro osmium carbonyl *cis*-1,2-bis(diphenylphosphino)ethylene 3,4,7,8-tetramethyl-1,10-phenanthroline hexafluorophosphate (**Os520** abbreviation refers to the emission wavelength)

A pale yellow crystalline material was obtained in 53% yield. The crystal structure is shown in Fig. 3. Elemental analysis and mass spectrometry data are summarized in Table 1. FT-IR $\nu(CO) = 1966\text{ cm}^{-1}$.

2.3. Chloro osmium carbonyl *cis*-1,2-bis(diphenylphosphino)ethylene 1,10-phenanthroline hexafluorophosphate (**Os550**)

A yellow crystalline material was obtained in 55% yield. The crystal structure is shown in Fig. 4. Elemental

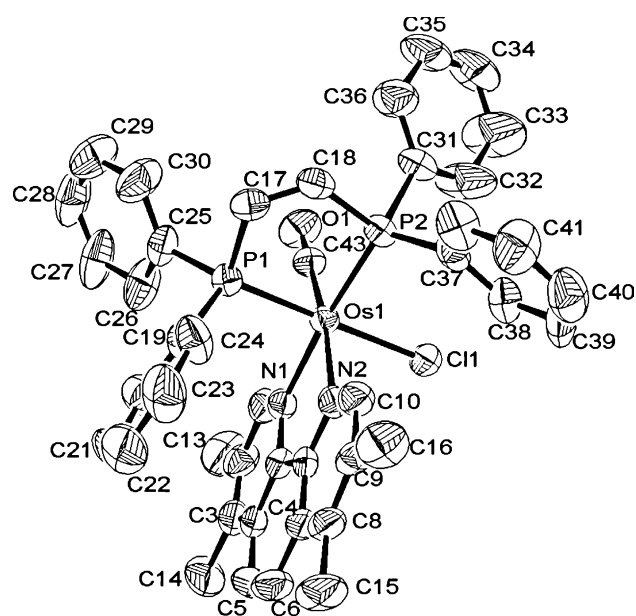
Fig. 3. Structure of **Os520** with ellipsoids at 50%. Hydrogen, hexafluorophosphate and solvent removed for clarity.

Table 1
Elemental analysis, mass spectrometry (m/z) and yield data

Compound	Calculated (%)			Found (%)			Mass	Yield (%)
	C	H	N	C	H	N		
Os520	50.08	3.71	2.72	49.96	3.76	2.81	887.2	53
Os550	48.03	3.10	2.87	48.10	3.23	2.76	831.1	55
Os560	47.93	3.30	2.87	48.03	3.27	2.88	833.1	45

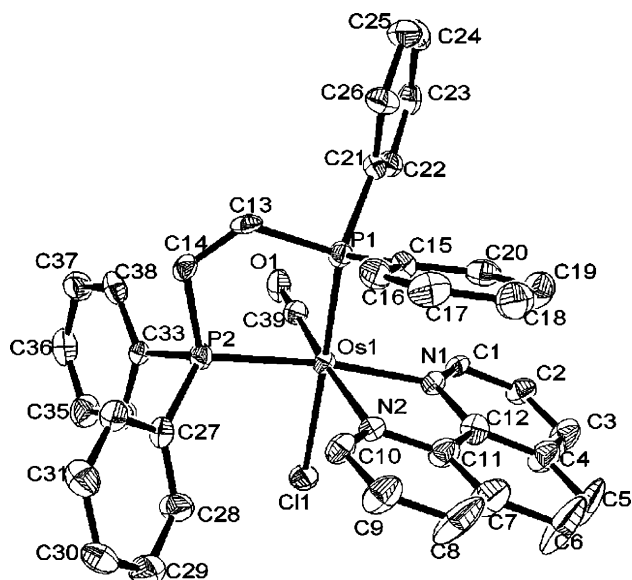


Fig. 4. Structure of **Os545** with ellipsoids at 50%. Hydrogen, hexafluorophosphate and solvent removed for clarity.

analysis and mass spectrometry data are summarized in Table 1. FT-IR $\nu(\text{CO}) = 1972 \text{ cm}^{-1}$.

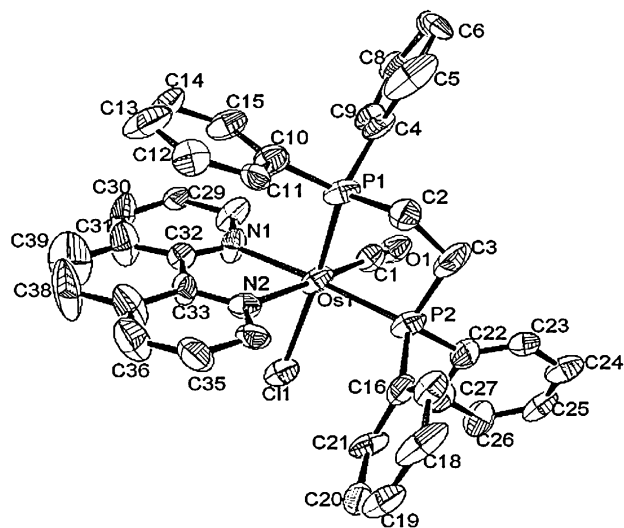


Fig. 5. Structure of **Os560** with ellipsoids at 50%. Hydrogen, hexafluorophosphate and solvent removed for clarity.

2.4. Chloro osmium carbonyl 1,2-diphenylphosphino ethane 1,10-phenanthroline hexafluorophosphate (**Os560**)

A yellow crystalline material was obtained in 45% yield. The crystal structure is shown in Fig. 5. Elemental analysis and mass spectrometry data are summarized in Table 1. FT-IR $\nu(\text{CO}) = 1969 \text{ cm}^{-1}$.

3. Methods

The crystals of each of the complexes were obtained by first dissolving the compound in methylene chloride and then adding hexanes until the cloud point has been reached and finally by adding a small amount of methylene chloride to redissolve the compound. Crystals were obtained through the slow evaporation of solvent within a day at $20 \text{ }^\circ\text{C}$. The crystals were mounted with oil in random orientation on a glass fiber on a KAPPA CCD Diffractometer, Mo $\text{K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$). Measurements were performed at $130 \pm 2 \text{ K}$. Cell constants and an orientation matrix for data collections were obtained by least squares refinements of the diffraction data from up to 14019 full and partial reflections. The structures were solved by direct methods using SIR-97 and DIRDIFF, provided by the refinement package MaXus [8]. Missing atoms were found by difference-Fourier synthesis. The non-hydrogen atoms were refined with anisotropic temperature factors. Scattering factors are from Waasmaier and Kirfel [9]. The structures were refined with SHELXL-97 and ORTEP plots were generated with Oak ridge thermal ellipsoid program (ORTEP-32) [10]. Table 2 summarize the crystal data, collection information, and refinement data for these structures.

UV-Vis absorption spectra were measured on a Shimadzu UV-1601 spectrophotometer. Quantitative measurements were obtained by using 1.000 cm path length quartz cells with absolute ethanol as the solvent. Electro-spray mass spectrometry was measured on either an Esquire-LC ion trap mass spectrometer (Bruker and Hewlett-Packard) or an Applied Biosystems Mariner ESI-TOF mass spectrometer. The FT-IR data were collected using a Nicolet Nexus 470 FT-IR.

Emission spectra of ethanol solutions were collected on a Perkin-Elmer LS50B fluorescence spectrophotometer. The wavelength sensitivity of the instrument was calibrated prior to measurements using a standard

20 W tungsten lamp of known output. All emission spectra were corrected to the calibration curve calculated from the known lamp output. The solutions were degassed using argon for 30 min before the measurement. Photoluminescence (PL) quantum yields to $\pm 10\%$ of the Os complexes (Φ_{Os}) in ethanol solutions were obtained using Ru(II) tris(4,7-diphenyl-1,10-phenanthroline) dichloride as the standard, which has a known quantum yield of 0.366 [11] using the following equation [12]:

$$\Phi_{\text{Os}} = \frac{\text{abs Ru}}{\text{area Ru}} \times \frac{\text{area Os}}{\text{abs Os}} \times 0.366, \quad (2)$$

where abs is the absorbance of the sample and area is the integration of the emission curve. Samples were excited through the LC state at 280 nm with absorption of 0.050. Temperature for the measurements was 25 ± 2 °C.

4. Discussion of the X-ray structures

The three crystal structures for osmium complexes containing phosphine ligands are shown in Figs. 3–5. The crystallographic data and structural refinement data are shown in Table 2. The complexes contain *cis*-1,2-bis(diphenylphosphino)ethane (dppene), or 1,2-bis(diphenylphosphino)ethane. The crystal structure for free dppene has been reported previously [13]. In this report, the bond lengths around the phosphorus were: P–C bridge 181.5 pm, P–C phenyl 182.9 pm, and P–C phenyl 183.9 pm. The complex **Os520** has phosphorus–carbon bond lengths of P–C (bridge, 181.6(7) and 181.9(7) pm) and P–C (phenyl, 181.8(7), 182.4(7), 182.1(7), 183.4(7) pm) as shown Table 3. The phosphorus–osmium bond

for this complex was 229.04(16) and 231.48(17) pm, with the phosphorus *trans* to the pyridyl being the slightly longer bond, and the phosphorus *trans* to chloro being shorter. The complex **Os550** had phosphorus–carbon bond lengths of P–C (bridge, 182.5(7) and 181.9(7) pm) and P–C (phenyl, 181.8(8), 183.6(7), 180.2(7), 182.4(8) pm) as shown Table 3. The phosphorus–osmium bond for this complex was very similar to the previous complex and were 229.2(2) and 231.28(18) pm. The phosphorus *trans* to phenanthroline was the longer of the two bonds and the phosphorus *trans* to chloro being shorter. **Os560** had P–C bond lengths of P–C (bridge, 186.4(14), 179.9(18) pm) and P–C(phenyl, 181.7(14), 185.6(15), 180.1(14) and 184.2(15) pm) as shown in Table 3. The P–Os bond lengths were 231.3(4) and 232.8(4) pm with the phosphorus *trans* to nitrogen being the longer of the two. Between these complexes there are not many significant deviations of the ligand complexed to osmium and the free ligand. The covalent radii of phosphorus and osmium are 110 and 133 pm, respectively [14]. Using these figures, the expected covalent single bond length between phosphorus and osmium would be 243 pm. The single bonded metallic radii of osmium has been reported to be 126 pm [14], thus, using this value, a single bond would be expected to be 136 pm. The measured values in the crystal structures were shorter than either of these two values. The N–Os bond lengths of the phenanthroline ligands were similar in length *trans* to carbonyl or *trans* to phosphorus; thus, it can be concluded that backbonding is indeed taking place between the phosphine ligand and osmium. With the similar *trans* effect on the phenanthroline, the Os–P backbonding may be similar in strength to that of the Os–carbonyl backbonding.

Table 2
Crystallographic data and structural refinement for the osmium complexes

Property	Os560	Os520	Os550
Empirical formula	C ₄₁ H ₃₈ Cl ₃ F ₆ N ₂ O ₂ OsP ₃	C ₄₅ H ₄₂ Cl ₅ F ₆ N ₂ O ₂ OsP ₃	C ₄₀ H ₃₃ Cl ₄ F ₆ N ₂ O ₂ OsP ₃
Formula weight	1094.19	1201.17	1102.6
<i>T</i> (K)	130(2)	130(2)	130(2)
λ (Å)	0.71073	0.71073	0.71073
Crystal	needle	prism	plate
Color	yellow	yellow	yellow
Crystal system	monoclinic	triclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> 2 ₁ / <i>c</i> (No. 14)
<i>Unit cell dimensions</i>			
<i>a</i> (Å)	14.337(2)	11.9990(3)	13.4450(4)
<i>b</i> (Å)	13.2720(15)	14.6130(4)	14.5810(5)
<i>c</i> (Å)	22.965(4)	14.6720(6)	21.5790(6)
α (°)	90	91.6220(11)	90
β (°)	104.567(5)	110.2630(13)	99.2620(19)
γ (°)	90	91.1140(11)	90
<i>V</i> (Å ³)	4229.3(11)	2411.26(13)	4175.2(2)
<i>D</i> _{calc} (Mg/m ³)	1.718	1.654	1.754
Reflections collected/unique	9369/5053	13472/9592	14019/8371
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0687, <i>wR</i> ₂ = 0.1228	<i>R</i> ₁ = 0.0530, <i>wR</i> ₂ = 0.1270	<i>R</i> ₁ = 0.0508, <i>wR</i> ₂ = 0.1067
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1353, <i>wR</i> ₂ = 0.1404	<i>R</i> ₁ = 0.0733, <i>wR</i> ₂ = 0.1382	<i>R</i> ₁ = 0.0949, <i>wR</i> ₂ = 0.1214

Table 3
Bond lengths (Å) for the complexes

Complex	N1	N2	C	Cl	P1	P2
520	2.139(5)	2.156(5)	1.838(6)	2.4448(16)	2.2904(16)	2.3148(17)
550	2.151(5)	2.142(6)	1.861(8)	2.4361(19)	2.292(2)	2.3128(18)
560	2.162(9)	2.196(10)	1.920(16)	2.438(4)	2.313(4)	2.328(4)
P	C(br)	C(Ph)	C(Ph)	C=C(br)		
dppene ¹³	1.815	1.829	1.839			
520	1.819(7)	1.821(7)	1.834(7)	1.293(10)		
550	1.819(7)	1.825(7)	1.824(8)	1.332(9)		
560	1.799(18)	1.801(14)	1.842(15)	1.598(18) ^a		

br, bridge; Ph, phenyl.

^a Single bond.

Since backbonding is observed, the question is what method of backbonding is responsible? There have been two proposed methods of backbonding for phosphine (arsine and antimony) type ligands, one method involves donation from filled metal orbitals to empty σ^* orbitals on the ligand, the other method involves donation from filled metal orbitals to empty d-orbitals on the phosphorus. In the case of σ^* backbonding, a C–P bond is lengthened around the phosphorus. This bond lengthening has been observed before, which has led to the conclusion that backbonding between phosphine ligands and metals take place through σ^* overlap [6,7]; however, this is not compatible with the structures of these complexes. It is clear from the data that there is no change in the C–P bond lengths between those on the free ligand and those on the complexes. Some bond lengths are shorter and a couple of bonds are longer, but the deviation is no greater than 0.5%. The bond angles around the phosphorus have changed between the free ligand and the complexes as listed Table 4. While not a 2 σ difference, there seems to be a broadening of bond angles when the dppene ligand is complexed to osmium. Such increase in bond angles has been reported for arsine [4a] and antimony ligands [15]. In the case of the antimony ligand complexes it was concluded that the increase in bond angles in conjunction with a decrease in the σ bonds was evidence for d-orbital backbonding [14]. We propose that the crystallographic data suggests

that this is evidence of overlap between the empty 3d of the phosphorus and the filled 5d of osmium.

The N–Os bond lengths for each of the complexes were longer than expected [4a]. For **Os520** N1–Os was 213.9(5) pm and N2–Os was 215.6(5) pm; for **Os550** these bond lengths were 215.1(5) and 214.2(6) pm, and for **Os560** these bond lengths were 216.2(9) and 219.20(16) pm. This could be explained by the *trans* effect of the strongly backbonding carbonyl ligand. The bond lengths of the two nitrogen atoms in each of the complexes are roughly equivalent, which may show that phosphorus is backbonding equally as well as the carbonyl. A Ru–N bond in Ru(1,10-phenanthroline)₃ has been reported at 206.3(4) pm [16] and in previous osmium reports the Os–N bond lengths were typically 207 pm [4a]. In other reports where 1,10-phenanthroline is *trans* to carbonyl, the reported bond lengths were typically over 220 pm [17]. Here, the bond lengths are shorter than 220 pm, typically 215.6(5) pm. There are two possibilities to explain why the bond length of the presented complexes are shorter than that of other complexes with the pyridyl *trans* to the carbonyl. One possibility is that there is only one carbonyl *trans* to the pyridyl. The other is that there is still a measure of backbonding taking place between the pyridyl ligand and osmium even though the bond length would suggest a bond order of less than one. The absorption and luminescence spectra of these molecules suggest that

Table 4
C–P–C bond angles (°) for complexes

Complex	C(Ph)–P–C(br)	C(Ph)–P–C(Ph)	C(Ph)–P–C(Ph)
dppene ¹³	101.4	102.2	102.4
520	103.5(3)	103.8(3)	106.8(3)
550	105.8(3)	104.9(3)	104.2(3)
560	107.1(7)	102.7(7)	107.0(6)
Complex	C(Ph)–P–Os	C(Ph)–P–Os	C(br)–P–Os
520	116.9(2)	116.1(2)	108.3(2)
550	114.2(2)	118.1(2)	108.5(2)
560	112.5(5)	117.5(5)	109.2(4)

br, bridge; Ph, phenyl.

MLCT to phenanthroline occurs. This is a transition that takes place through backbonding.

One unusual feature of these complexes is that the carbonyl is *trans* to nitrogen rather than being *trans* to phosphorus. Usually, the *trans* effect would favor the carbonyl being *trans* to phosphorus. Previously published compounds similar to the complexes of this work found the carbonyl *trans* to phosphorus [18]. Here, the carbonyl is *trans* to nitrogen. The carbon osmium bond length was 183.8(6) pm for Os520 and 186.1(8) pm for Os550, and 192.0(16) pm for Os560. The C–O bond lengths of the carbonyl ligands were 115.5 and 115.3 pm. Both the C–O bond lengths and the C–Os bond lengths are not unusual for what is observed for carbonyl complexes of third row metals [17].

5. Luminescence properties

Divalent osmium complexes that emit at 561, 553 and 522 nm have been created as shown in Table 5 and Fig. 6. The carbonyl stretching frequency was observed to be 1969 cm^{-1} for Os560, 1972 cm^{-1} for Os550 and 1966 cm^{-1} for Os520. Another unusual feature is that they contain a LMCT entity bonded to osmium, the chloride ligand, yet these complexes are emissive. Usually, LMCT entities on these types of complexes have very low to non-existent quantum yields. Each of these complexes exhibits strong emission. This may be due to the fact that the chloride is *trans* to the phosphine ligand and not to the pyridyl ligand. The quantum yield for Os560 was measured at 63%, Os550 at 70%, and Os520 at 75%. The quantum yields for these complexes are much stronger than those for the red and orange emitting complexes, which is in accordance with the energy gap law. However, though strongly emitting, these complexes feature little to no conjugation between the ligands through the osmium core. While many of the red emitting compounds feature ligand centered (LC) absorption bands with ϵ in excess of 100 000 $\text{l cm}^{-1} \text{mol}^{-1}$ [4a], and metal-to-ligand charge transfer (MLCT) ϵ in excess of 40 000 $\text{l cm}^{-1} \text{mol}^{-1}$, these blue shifted emitters have LC ϵ of 30 000 $\text{l cm}^{-1} \text{mol}^{-1}$ and MLCT ϵ of 3000 $\text{l cm}^{-1} \text{mol}^{-1}$. The LC transition appears between 272

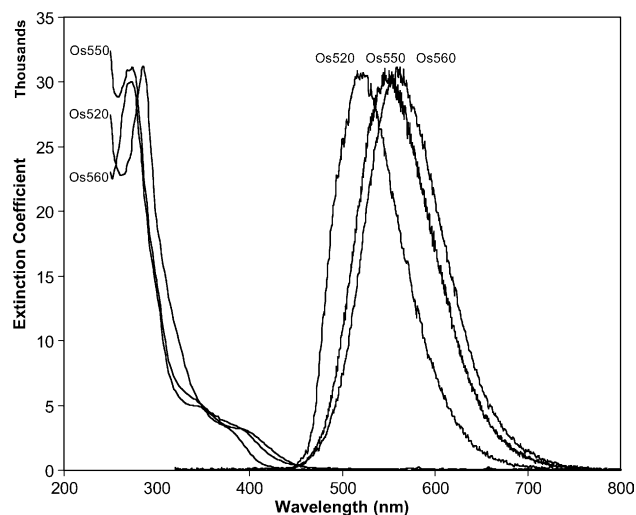


Fig. 6. Absorption and emission of Os520, Os550, and Os560.

and 286 nm and is largely the result of the $\pi-\pi^*$ of the phenanthroline, while the MLCT bands appear at lower energy with triplet charge transfer bands ranging from 378 nm for Os520 to 398 nm for Os560.

The emission lifetime of these complexes is exceeding long; Os520 has a lifetime of 38 μs , thirty times longer than its red counterparts! The long lived excited state usually suggests a ligand-centered state; however, the gaussian emission band clearly is that of charge transfer character. Other evidence for the MLCT transition is the difference between Os520 and Os550. The only difference between these two structures is that Os550 uses 1,10-phenanthroline and Os520 uses 3,4,7,8-tetramethyl-1,10-phenanthroline. The change in phenanthroline results in over a 20 nm blue shift in emission. This shows that the phenanthroline ligand is involved in the transition. If the emission was from the LC state, the 3,4,7,8-tetramethyl-1,10-phenanthroline complex (Os520) would have emission shifted to the red of the 1,10-phenanthroline complex (Os550) as its absorption is to the red (286 nm for Os520 versus 273 nm for Os550). The long excited state lifetimes for these MLCT complexes is unusual because of the significant spin orbit coupling parameter of osmium. The lifetime of Ru tris(bathophenanthroline) (one of the longer lived ruthenium

Table 5

Absorption maxima for the various ligand and charge transfer bands, extinction coefficients (ϵ), and emission properties of the Os(II) complexes being reported

Complex	LC (nm) (ϵ)	¹ MLCT (nm)	³ MLCT (nm) (ϵ)	Emission ^a	τ (ns) ^b	Φ^c
Os520	286 (31 000)		378 (3200)	522	38 000	0.75
Os550	273 (31 000)	shoulder	393 (2000)	553	7500	0.70
Os560	272 (30 000)	345 (3500)	398 (2000)	561	6500	0.63

All measurements were made in ethanol at 298 K.

^aEmission peak.

^bLuminescence lifetime.

^cLuminescence quantum yield.

complexes) is at most 7 μs [19] yet ruthenium's spin orbit coupling parameter ($\sim 900\text{ cm}^{-1}$) is less than a third of that of osmium ($\sim 3400\text{ cm}^{-1}$). There are two structural aspects to the complexes that may contribute to the long-lived excited state: the chloride ligand and the rather long N–Os bond lengths. A MLCT transition is much like an internal reduction–oxidation system. When the complex is excited, an electron is transferred from the metal core to the pyridyl ligand. Thus the osmium is oxidized from +2 to the +3 state and the pyridyl is reduced from the 0 state to –1. The longer excited state lifetimes of these complexes may be due to the stabilization of the Os^{3+} by LMCT effects. There are four pairs of electrons around the chloride anion. One pair is used for σ donation to osmium. The other three are able to back donate into empty or partially filled d-orbitals on the osmium. Thus, while the pyridyl is reduced in the MLCT, the Cl is partially oxidized by LMCT thereby offsetting the oxidation of the osmium from 2+ to 3+. This would reduce the osmium's need to get the charge back from the pyridyl, and thus, extend the lifetime of the complex.

As discussed in the crystallography section, the N–Os bond lengths are longer than what would be expected for polypyridyl ligands to osmium. The π^* of the phenanthroline is lower in energy than the carbonyl π^* or either the σ^* or 3d of the phosphorus, so it is likely that the primary charge transfer transition would be $\text{Os} \rightarrow \pi^*$ of the phenanthroline. This agrees with what is observed in the absorption and emission properties. Due to the longer bond length between osmium and the phenanthroline, the backbonding, while it still exists, is not as strong. The charge transfer is dependent upon backbonding as that is the pathway through which the charge is transferred from the metal to the phenanthroline ligand. Thus, it would be expected that any changes to the nature of this bond would have consequences on the MLCT luminescence behavior. By lengthening this bond, the transition may be slowed, which is observed in the longer lifetime of the phosphorescence. We believe that the longer lifetime of these species is due to both the participation of the chloro ligand and the longer bond lengths between osmium and the phenanthroline.

6. Conclusion

In conclusion, we have synthesized a variety of osmium complexes that emit in the green to yellow regions of the visible spectrum. These complexes have very long lived charge transfer emissions. The crystal structures show that the carbonyl is *trans* to nitrogen and the chloro ligand is *trans* to phosphorus. There is very little change in P–C bond lengths between the free dppe ligand and when dppe is coordinated to the metal. However, there is a change in bond angles with the

phosphorus adopting a more tetrahedral arrangement when coordinated to the metal. We conclude from the data that there is evidence for backbonding due to overlap of d-orbitals.

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