

Structure and Luminescence Properties of Monomeric and Dimeric Re(I) Complexes with Dicarboxylic Acid-2,2'-Bipyridine Ligands

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Abstract The luminescence properties of Re(I) complexes incorporating the dcbpy ligand (dcbpy=*n,n'*-dicarboxylic acid-2,2'-bipyridine; *n*=3, 4) were investigated as well as their utility as Pb²⁺ sensors. An unusual binuclear complex of the 3,3'- species was isolated. The emission intensity and lifetime for all complexes were found to be highly temperature-dependent, with quantum yields and lifetimes dramatically greater at 77 K than at room temperature. The monomeric 3,3'-dcbpy Re(I) complex demonstrates nearly 1:1 binding with Pb²⁺. The effect of this lead binding on the emission intensity is great, but the low quantum yields allow only for detection of the metal at the micromolar level. The binding of Pb²⁺ to the 4,4'-dcbpy complex is modeled and the interaction is demonstrated to involve two binding sites.

Keywords Rhenium · Luminescence · Lead detection · Bipyridine dicarboxylic acid

Introduction

Luminescent d⁶ transition metal complexes have long been studied for their unique spectral properties and have found widespread applications as molecular and ionic sensors [1]. Specifically, Ru(II) complexes tend to be well-characterized and widely used as probes for a variety of analytes [2–4].

Two ruthenium(II) complexes prepared by Perkovic feature dcbpy ligands; dicarboxylic acid-substituted bipyridines (Fig. 1) demonstrate an affinity for Pb²⁺ ions [5]. Upon complexation with Pb²⁺ in solution, the 3,3'-dcbpy Ru(II) complex shows a measurable increase in quantum yield while the emission of the 4,4'-dcbpy complex decreases in intensity.

It was our desire to further explore the use of these dcbpy ligands on luminescent d⁶ systems and to assess these complexes' ability to detect and quantify lead(II). The luminescence properties of transition metal complexes can be highly unpredictable with sensitivity not only to the metal center but to the ligands as well [6]. Factors such as the bite angle of the bound ligands [7], their structure and conformation [8], and the electron donating or withdrawing nature of the ligands [9] can greatly affect the luminescence properties of a transition metal complex. By substituting dcbpy for bpy in the highly luminescent Re(I) complex Re(bpy)(py)(CO)₃⁺ (py=pyridine), we hoped to produce a new class of lead sensors.

The exact mechanisms by which Pb²⁺ induces changes in quantum yields of transition metal complexes are unknown [5]. However, explanations for this behavior can be inferred from known structural information of related complexes. Crystal structures of the Pb²⁺-bound Re(I) complexes would provide conclusive insight into the structure of these systems.

Experimental

Syntheses and materials

All solvents were reagent grade and used as received. Re(CO)₅Cl was purchased from Strem Chemicals. [Re

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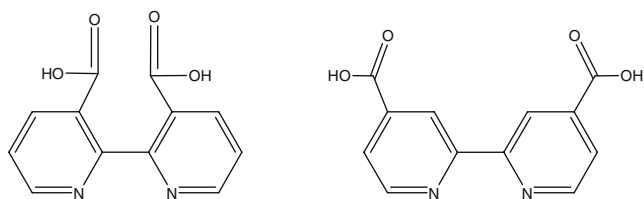


Fig. 1 Structure of ligands: 3,3'-dcbpy (left) and 4,4'-dcbpy (right)

(phen-5-COOH)(CO)₃(*t*Bu-py)]ClO₄ was available from prior work and has been fully characterized [10].

The 4,4'-dcbpy ligand was purchased from Alfa Aesar. The 3,3'-dcbpy ligand was prepared according to a literature procedure [11] and the structure and purity were established by NMR and melting point. ¹H NMR (CD₃OD, 300 MHz): 7.353 (2 H; 5,5'), 7.942 (2 H; 4,4'), 8.370 (2 H; 6,6'). MP=260 °C (lit mp=262 °C).

Synthesis of ReCl(CO)₃(3,3'-dcbpy)

Re(CO)₅Cl (722 mg, 2 mmol) and 3,3'-dcbpy (488 mg, 2 mmol) were refluxed in 200 ml methanol for 3 h under N₂. Solvent was removed via rotary evaporation and the residue was purified by flash column chromatography. A 50:50 (v/v) solution of acetone and hexanes was used as eluant, with several percent of methanol gradually added to recover the orange band. The complex gave a single spot on TLC. Yield, 60%. ¹H NMR (CD₃OD, 300 MHz): δ7.809 (2 H; 5,5'), 8.623 (2 H; 4,4'), 9.167 (2 H; 6,6'). ESI-MS: *m/z* 551 (M⁺). IR (KBr): ν_{-OH}=3,434 cm⁻¹; ν_{C=O}=2,028 cm⁻¹, 1,908 cm⁻¹; ν_{C=O}=1,637 cm⁻¹.

Synthesis of Re(3,3'-dcbpy)(CO)₃(py) and [Re(μ-3,3'-dcbpy)(CO)₃]₂

ReCl(CO)₃(3,3'-dcbpy) (110 mg, 0.2 mmol) was dissolved in 24 ml methanol and the solution heated to 50 °C. Pyridine (200 mg, 2.5 mmol) was added and the solution was heated for 24 h under N₂, during which time the orange solution turned to yellow. The solution was cooled to room temperature and evaporated to half-volume by rotary evaporation. The solid portion was collected and thoroughly washed with hexanes and ether. The product was separated on a Sephadex LH-20 column (methanol) to obtain the pure monomeric Re⁺ complex as a yellow, luminescent solid. Elemental analysis and the charge balance indicate the complex to be in a zwitterionic form, with one carboxylic acid deprotonated in solution to form a neutral Re(I) species. Yield, 20%. Slow evaporation of the remaining reaction solution resulted in precipitation of the Re⁺ dimer as orange crystals that were characterized by X-ray diffraction. Monomer ¹H NMR (CD₃OD, 300 MHz):

7.384 (2 H; 3,5 py), 7.739 (2 H; 5,5' dcbpy), 7.914 (1 H; 4 py), 8.413 (4 H; 4,4' dcbpy, 2,6 py), 9.179 (2 H; 6,6' dcbpy). ESI-MS: *m/z* 594 (M⁺). IR (KBr): ν_{-OH}=3,431 cm⁻¹; ν_{C=O}=2,023 cm⁻¹, 1,912 cm⁻¹; ν_{C=O}=1,625 cm⁻¹. Dimer ESI-MS: *m/z* 1,027 (M⁺). IR (KBr): ν_{-OH}=3,431 cm⁻¹; ν_{C=O}=2,024 cm⁻¹, 1,902 cm⁻¹; ν_{C=O}=1,627 cm⁻¹.

Synthesis of 4,4'-complex proceeded by an analogous procedure with the substitution of the 4,4'-dicarboxylic-2,2'-bipyridine ligand. ¹H NMR (DMSO, 300 MHz): 7.451 (2 H; 3,5 py), 7.753 (2 H; 5,5' dcbpy), 8.174 (1 H; 4 py), 8.708 (2 H; 2,6 py), 9.140 (2 H; 6,6' dcbpy), 9.378 (2 H; 3,3' dcbpy). ESI-MS: *m/z* 594 (M⁺), IR (KBr): ν_{-OH}=3,426 cm⁻¹; ν_{C=O}=2,030 cm⁻¹, 1,907 cm⁻¹; ν_{C=O}=1,606 cm⁻¹.

Methods and instrumentation

UV-visible absorption spectra were obtained on a Perkin-Elmer Lambda 25 spectrophotometer. Luminescence measurements were carried out on a Spex Fluorolog 2+2 spectrofluorometer with 360 nm excitation for both complexes. The instrument was equipped with a Dewar flask filled with liquid nitrogen for low temperature measurements. Acetonitrile was the solvent for room temperature measurements, while low-temperature spectra were obtained in a 4:1 methanol/ethanol glass.

Lead titrations were carried out by adding successive additions of a Pb(NO₃)₂ solution into the Re⁺ monomer solution. The lead(II) solution was prepared such that the Re⁺ concentration and the solvent composition remained the same throughout the titration. A 90:10 acetonitrile/water mixture was found to be the optimum solvent system for solubility of all species and maximum sensitivity. Binding constants for both monomeric complexes were obtained by a data fitting routine in Mathcad.

Lifetime measurements were done on a Laser Science VSL 337 pulsed N₂ (337 nm) laser decay system. Data fitting was achieved using a nonlinear least-squares routine in Mathcad.

All diffraction data were collected on a Bruker SMART APEX CCD diffractometer at -120 °C using graphite-monochromated Mo K radiation (λ=0.710 73 Å). Empirical absorption corrections were applied using the Bruker SADABS program [12], with the transmission factors ranging 0.67–1.00. The structures were solved by direct methods within the Bruker SHELXTL program suite [13]. Full-matrix least-squares refinement on |F|² yielded the final R1 and wR2 values of 0.032 and 0.082, respectively. Hydrogen atoms were found in difference maps and refined with isotropic displacement parameters. The highest peak in the final difference Fourier map was 2.39 e/Å³ and was located near one of the Re atoms.

Results and discussion

The absorption spectra for the 3,3' monomer and dimer are shown in Fig. 2. Both complexes exhibit typical broad MLCT bands in the 350–450 nm range and intense bpy localized π – π^* transitions in the further UV (<300 nm). The binuclear Re^+ complex has the potential for two dcbpy-centered MLCT transitions and two π – π^* transitions per molecule; accordingly, the extinction coefficients in the dimer are roughly twice those of the monomeric 3,3'-dcbpy Re^+ complex. The monomeric Re^+ complex bearing the strong-field pyridine moiety has an MLCT band at higher energy than the dimer, which is consistent with known spectra of Re(I) complexes. Extinction coefficients and absorption maxima of the 4,4'-dcbpy complex are virtually identical to those of analogous 3,3'-dcbpy complex and are not reproduced here.

$\text{Re}(3,3'\text{-dcbpy})(\text{py})(\text{CO})_3$ gave a weak 610 nm emission at room temperature, and the dimer had no detectable emission. The low quantum yields (<0.005) for these systems are consistent with strained bipyridine complexes. It has been demonstrated that the quantum yield of a transition metal complex incorporating bipyridine or a related analog is affected by the torsion angle along the 2,2' axis of this ligand [14]. Bipyridines substituted at the 3,3' position tend to have relatively low quantum yields, as steric effects act to distort the geometry of the ligand out of the planar conformation that characterizes the unsubstituted ligand [15, 16].

In some cases, the conformation of these ligands can be affected by factors such as heavy metals in solution. In this way, changes in a ligand's dihedral angle can result in measurable emission changes in emission properties that can be used to measure a target analyte [5, 15].

Figure 3 shows the titration of the Re^+ monomer with Pb^{2+} , which yields a fairly linear increase in emission

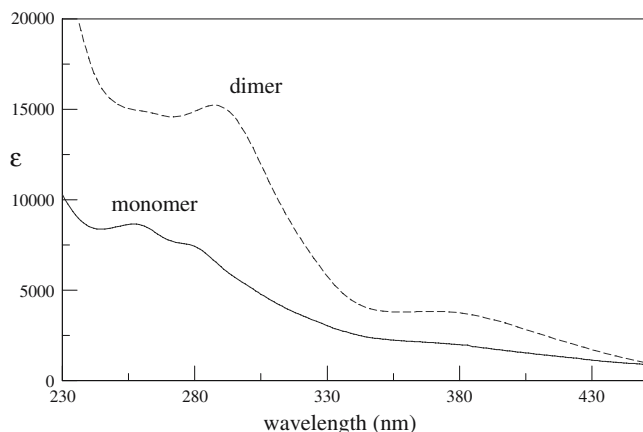


Fig. 2 UV-visible absorption spectra of $\text{Re}(3,3'\text{-dcbpy})(\text{CO})_3(\text{py})$ and $[\text{Re}(\mu\text{-}3,3'\text{-dcbpy})(\text{CO})_3]_2$ in CH_3CN

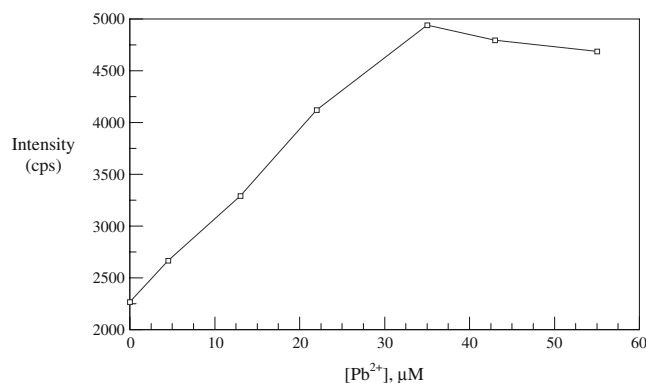


Fig. 3 Titration of $\text{Re}(3,3'\text{-dcbpy})(\text{CO})_3(\text{py})$ ($27 \mu\text{M}$) with Pb^{2+} in 90:10 acetonitrile/ H_2O monitored by emission intensity

intensity up to approximately 1:1 binding. This trend supports an interaction between the two carboxylates of the dcbpy ligand and Pb^{2+} . While the exact binding mechanism of Pb^{2+} to the complex is unknown, the increase in quantum yield suggests that a conformational change occurs upon complexation with lead(II) [5]. This leads to increased planarity of bipyridine rings and enhances luminescence. It seems plausible that bidentate coordination of the lead by the two carboxylates pulls the bipyridine into a more planar configuration. Unfortunately, the quantum yield is very low, which allows only for detection of Pb^{2+} at the micromolar level.

The increase in intensity continues until the Pb^{2+} concentration slightly exceeds that of the Re^+ complex. This is indicative of a nearly 1:1 association between Pb^{2+} and the Re^+ complex and a relatively high K_b for the formation of the lead species. Fitting the data using a 1:1 model results in a binding constant K_1 of $1 \mu\text{M}^{-1}$. Incremental addition of $\text{Pb}(\text{II})$ to $\text{Re}(3,3'\text{-dcbpy})(\text{CO})_3(\text{py})$ results in a continuous red shift reaching a maximum of 8 nm at the peak of the titration curve.

Another noteworthy result is the decline in intensity after the saturation point. Tests on the unsubstituted bipyridine analog of the Re^+ complex showed no response to Pb^{2+} , even at concentrations far exceeding 1:1, indicating that there is no bimolecular quenching of the complex with lead (II). Thus, it seems likely that the complex's association with the carboxylic acid-bound Pb^{2+} is affected by the addition of lead beyond the saturation point. A second, weaker binding between the two carboxylates and free lead (II) may disrupt the more nearly planar structure and consequently decrease the quantum yield.

Emission spectra taken at 77 K of the 3,3'-dcbpy monomer and the dimer in a rigid glass are shown in Fig. 4. The monomer shows a blue shift of 50 nm and an increase in quantum yield of two orders of magnitude with respect to the room temperature data. The dimer at 77 K also shows enhancement of luminescence and demonstrates a similar structureless emission.

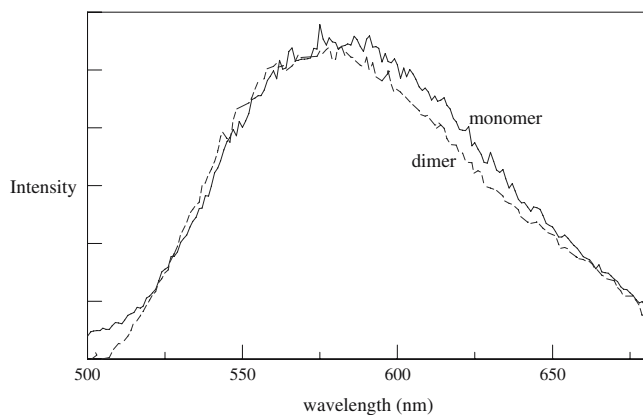


Fig. 4 Emission spectra of $\text{Re}(3,3'\text{-dcbpy})(\text{CO})_3(\text{py})$ and $[\text{Re}(\mu\text{-}3,3'\text{-dcbpy})(\text{CO})_3]_2$ at 77 K in 4:1 methanol/ethanol

The room temperature lifetime of this monomer was 16 ns and the dimer's negligible emission precluded lifetime measurement with our instrumentation. At 77 K, the monomer and dimer decay curves were fit with double exponentials. These multi-exponential fits can be attributed to the differences in the solvent matrix as well as possible existence of protonated and deprotonated forms of each species. The lifetimes (intensity fractions) are as follows: monomer: 947 ns (0.902), 236 ns (0.098); dimer: 638 ns (0.944), 54 ns (0.056). The preexponential weighted lifetimes for the monomer and dimer are 732 ns and 400 ns, respectively.

Based on synthetic challenges and the spectroscopic behavior of the monomeric 3,3'-dcbpy Re(I) complex, it can be inferred that there is considerable conformational strain on the bound dcbpy ligand. Despite the chelate effect, efforts to carry out the synthesis at higher temperature led to the surprising result of dcbpy being replaced by pyridine. While it is possible that the electron-withdrawing carboxylic acid groups on dcbpy weaken this ligand's interaction with the metal to some extent, this phenomenon must also suggest a strain that causes the system to be more labile.

While the exact conformation of this monomeric Re^+ complex is not known, the similar, weak emission of the monomeric and dimeric species indicate that the ligands of both complexes are distorted in a comparable fashion. Surprisingly, it appears that the neutral dimer is the thermodynamically more stable product and that there is conversion from the monomeric to the dimeric form in solution, even under ambient conditions. This was observed after attempts to grow crystals of the monomer consistently resulted in those of the dimeric species. It is unknown how the carboxylic acid groups can replace another ligand on the Re^+ complex so readily; attempts to replicate this type of binding using other carboxylic acids (e.g., benzoic acid) and Re^+ complexes failed completely. The formation of a dimeric Re^+ species does, however, give evidence for a

highly distorted torsion angle around the 2,2' axis of the rhenium-bound dcbpy. This ligand is forced out of planarity to such a degree that it is able to form a bridging interaction with another Re^+ .

The crystal structure of the dimeric species exhibits some unique features (Fig. 5). The 2,2' axes of the bipyridine rings are twisted at 25° and 26°, respectively, and the planes including each dcbpy's rings are offset with respect to one another by 30°. This is a considerable deviation from the normally planar unsubstituted bipyridine in highly luminescent d^6 complexes. Even among substituted bipyridine complexes, the 2,2' torsion angles are high compared with 19.3° for the analogous 2,2'-bipyridine-3,3'-dicarboxylic acid Ru(II) complex [5]. Altered geometry and steric effects in 3,3' substituted bipyridines have been demonstrated to reduce the quantum yield of Ru(II) systems [14, 15], and our findings validate this trend in Re(I) systems as well.

In order to assess the role of the steric interactions between the two carboxylates in the 3,3' complex we examined the 4,4' complex. The emission intensity of the 4,4'-dcbpy complex provides further evidence that the weak room temperature luminescence properties of the 3,3'-dcbpy complexes can be ascribed to the steric strain on the substituted bipyridine ligand. It is presumed that the electronics of the two ligands are similar enough so that the only significant contrast is the sterics and consequently the torsion angle around the 2,2' axis of the bipyridine. Therefore, any divergence between the emission characteristics can be diagnostic of the cause of the 3,3'-dcbpy complex's low quantum yield.

The room temperature emission of the 4,4'-dcbpy complex peaks at 564 nm (Fig. 6). The emission at 77 K exhibits a blue shift of 50 nm with respect to the room temperature emission, as was seen in the 3,3'-dcbpy

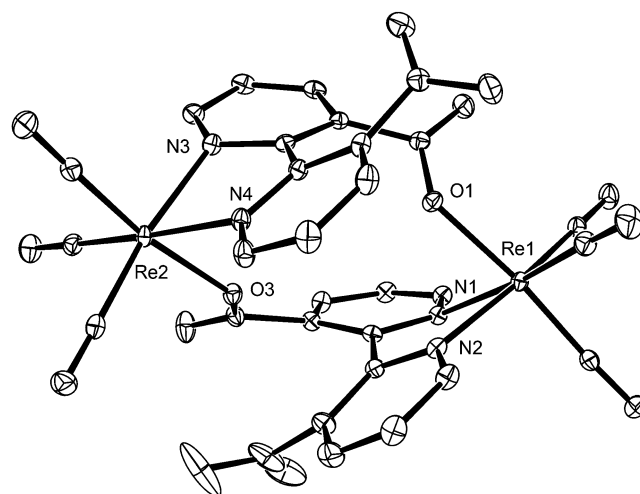


Fig. 5 Crystal structure of $[\text{Re}(\mu\text{-}3,3'\text{-dcbpy})(\text{CO})_3]_2$

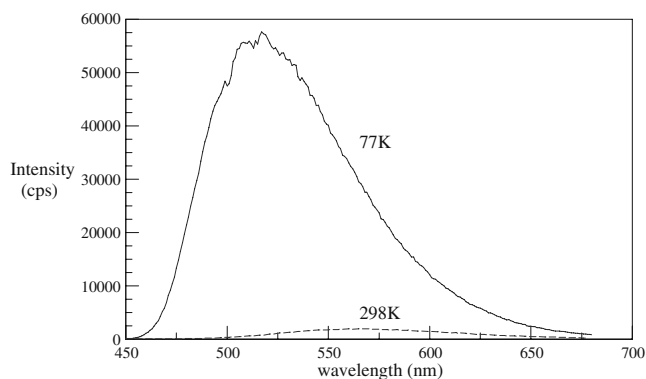


Fig. 6 Emission spectra of $\text{Re}(4,4'\text{-dcbpy})(\text{CO})_3(\text{py})^+$ at 77 and 298 K

complex. Also similar between the two complexes is the increase in quantum yield on cooling; however, the 4,4'-dcbpy complex's increase is roughly 30 times that of the room temperature value while that of the 3,3'-dcbpy complex is over two orders of magnitude. Thus, it is concluded that the 4,4'-dcbpy complex has stronger-field d-d splitting due to the tighter interaction of the dcbpy ligand to the metal. Figure 7 shows our proposed energy level scheme. The higher energy of the e_g level in the 4,4'-dcbpy complex inhibits thermal deactivation via this non-radiative state.

The lead(II) response of the 4,4'-dcbpy Re^+ complex was also examined (Fig. 8). In marked contrast to the response of the 3,3'-dcbpy complex, Pb^{2+} induces a decrease in quantum yield of this complex as monitored by emission intensity. There is a substantial red shift with increasing Pb^{2+} concentration; the decreasing quantum yield may be due to the energy gap law where lower energy excited states tend to have higher radiationless decay rates and, thus, lower quantum yields.

Figure 9 shows the emission intensity versus lead concentration monitored at 565 nm. Clearly these data are not consistent with a simple one-to-one binding. This is not surprising as the distance between the two carboxylic acids in the 4,4'-dcbpy complex would not permit bidentate

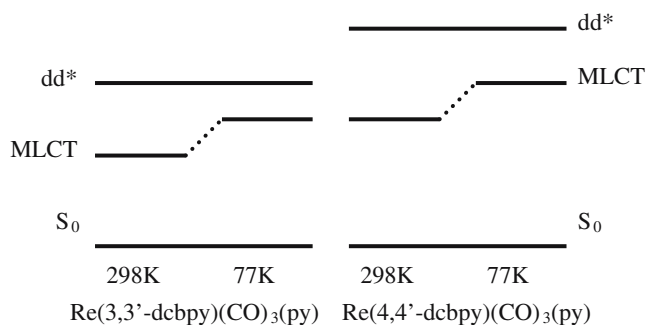


Fig. 7 Schematic of energy levels of 3,3'-dcbpy and 4,4'-dcbpy Re^+ complexes

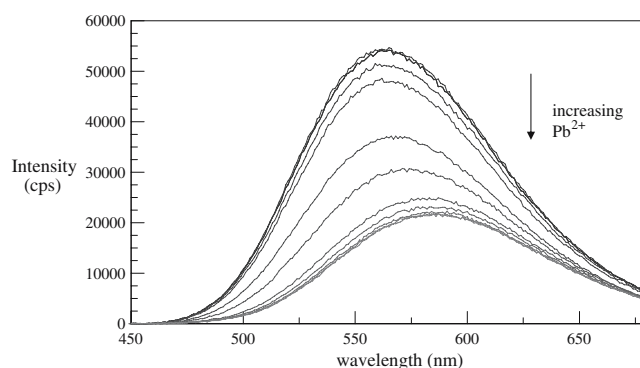
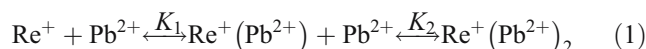


Fig. 8 Decrease in quantum yield seen in emission intensity during lead(II) titration of $\text{Re}(4,4'\text{-dcbpy})(\text{CO})_3(\text{py})$ in 90:10 acetonitrile/ H_2O

coordination to one lead(II). Therefore a two binding-site model is presented to account for binding of the heavy metal to each carboxylic acid:



where Re^+ represents $\text{Re}(4,4'\text{-dcbpy})(\text{CO})_3(\text{py})$. This model is seen to satisfactorily fit the intensity data and results in binding constants of $K_1=7 \mu\text{M}^{-1}$ and $K_2=3.5 \mu\text{M}^{-1}$. The best fit seems to be with K_2 nearly half of K_1 . If the two binding sites are far enough apart to be independent, this would be the expected behavior since the second lead would be presented half the number of binding sites of the first lead.

To test the proposed energy gap law mechanism of lead (II) quenching, an identical titration was performed on the complex $\text{Re}(\text{phen-5-COOH})(\text{CO})_3(t\text{Bu-py})^+$. The data were fit well with a single binding site model and $K_1=0.3 \mu\text{M}^{-1}$.

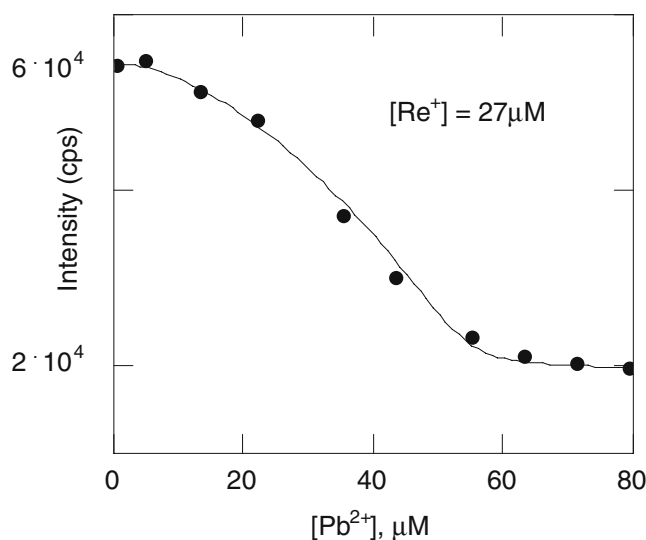


Fig. 9 Fitting of intensity data from the titration of $\text{Re}(4,4'\text{-dcbpy})(\text{CO})_3(\text{py})$ ($27 \mu\text{M}$) with Pb^{2+}

The rigidity of the phenanthroline ligand rather than the bipyridine confirms that the change in quantum yield is not due to geometry of the ligand, and the presence of only one carboxylic acid ensures a monodentate interaction. Lead(II) was seen to decrease both emission energy and intensity of this complex in the same manner as the Re(4,4'-dcbpy)(CO)₃(py). Therefore, the energy gap law mechanism is supported for Re(4,4'-dcbpy)(CO)₃(py).

It is interesting that K_1 for the bidentate 3,3'-dcbpy complex is less than that for the monodentate 4,4'. This may be due to a stabilization of the mono protonated form of the 3,3' complex by formation of a hydrogen-bonded bridge between the two carboxylic acids (C–O–H–O–C). This bridge would make it more difficult for the ligand to bind a Pb²⁺ ion. Due to the position of the carboxylic acids on the 4,4'-dcbpy complex, this hydrogen bridge would not be possible.

Conclusion

Re(3,3'-dcbpy)(CO)₃(py) and [Re(μ-3,3'-dcbpy)(CO)₃]₂ have been observed to be weak and non-emitters at room temperature respectively; this is due, in large measure, to conformational strain on the dcbpy ligand. Lead(II) is shown to bind nearly 1:1 to the monomeric complex, causing an increase in quantum yield that allows for quantification of micromolar concentrations of the heavy metal. Both complexes demonstrate highly temperature-dependent emissions, with great enhancement of emission at 77 K. Low temperature lifetime measurements result in multi-exponential fits for both species and demonstrate that both are longer-lived at 77 K. Re(4,4'-dcbpy)(CO)₃(py) exhibits a higher relative quantum yield at room temperature compared to the 3,3'-dcbpy complex. This complex undergoes a decrease in quantum yield in the presence of Pb²⁺ and is demonstrated to bind these ions at two sites.

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References

1. Demas JN, DeGraff BA (1991) Design and applications of highly luminescent transition metal complexes. *Anal Chem* 63(17):830A–836A
2. Anzenbacher P Jr, Tyson DS, Jursikova K, Castellano FN (2002) Luminescence lifetime-based sensor for cyanide and related anions. *J Am Chem Soc* 124(22):6232–6233
3. Jain A, Xu W, Demas JN, DeGraff BA (1998) Binding of luminescent ruthenium(II) molecular probes to vesicles. *Inorg Chem* 37(8):1876–1879
4. Hagerman ME, Salamone SJ, Herbst RW, Payeur AL (2002) Tris (2,2'-bipyridine)ruthenium(II) cations as photoprobes of clay tactoid architecture within hectorite and laponite films. *Chem Mater* 15(2):443–450
5. Perkovic MW (2000) Allosteric manipulation of photoexcited state relaxation in (bpy)₂Ru(II)(binicotinic acid). *Inorg Chem* 39(21):4962–4968
6. Sacksteder L, Zipp AP, Brown EA, Streich J, Demas JN, DeGraff BA (1990) Luminescence studies of pyridine a-diimine rhenium(I) tricarbonyl complexes. *Inorg Chem* 29(21):4335–4340
7. Hung C-Y, Wang T-L, Jang Y, Kim WY, Schmehl RH, Thummel RP (1996) Dipyrido[4,3-b;5,6-b]acridine derivatives and their ruthenium(II) complexes. *Inorg Chem* 35(20):5953–5956
8. Zipp AP, Sacksteder L, Streich J, Cook A, Demas JN, DeGraff BA (1993) Luminescence of rhenium(I) complexes with highly sterically hindered a-diimine ligands. *Inorg Chem* 32(24):5629–5632
9. Liu Q, Mudadu MS, Schmider H, Thummel R, Tao Y, Wang S (2002) Tuning the luminescence and electroluminescence of diphenylboron complexes of 5-substituted 2-(2'-Pyridyl)indoles. *Organometallics* 21(22):4743–4749
10. Higgins B, DeGraff BA, Demas JN (2005) Luminescent transition metal complexes as sensors: structural effects on pH response. *Inorg Chem* 44(19):6662–6669
11. Dholakia S, Gillard RD, Wimmer FL (1985) 3,3'-Dicarbomethoxy-2,2'-bipyridyl complexes of palladium(II), platinum(II) and rhodium(III). *Polyhedron* 4(5):791–795
12. Sheldrick GM (1996) SADABS: program for empirical absorption of area detector data. University of Gottingen, Gottingen, Germany
13. Sheldrick GM (1997) SHELXTL Version 5.1 reference manual. Bruker AXS, Madison, WI
14. Wu F, Riesgo E, Pavalova A, Kipp RA, Schmehl RH, Thummel RP (1999) Ruthenium(II) complexes of 2-Aryl-1,10-phenanthrolines: synthesis, structure, and photophysical properties. *Inorg Chem* 38(24):5620–5628
15. McFarland SA, Magde D, Finney NS (2005) Conformational control of excited-state dynamics in highly distorted Ru(II) polypyridyl complexes. *Inorg Chem* 44(11):4066–4076
16. Lai RY, Chiba M, Kitamura N, Bard AJ (2001) Electrogenerated chemiluminescence. 68. Detection of sodium ion with a ruthenium (II) complex with crown ether moiety at the 3,3'-positions on the 2,2'-bipyridine ligand. *Anal Chem* 74(3):551–553