DALTON
FULL PAPER

The synthesis of the ligand 5-bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine-1,10-phenanthroline and of its ruthenium(II) and rhenium(I) complexes. Binuclear species with Cu(I) and some photophysical properties†

Marianne Riklin, Dat Tran, Xianhui Bu, Leroy E. Laverman and Peter C. Ford *

Department of Chemistry and Biochemistry, University of California, Santa Barbara, CA 93106, USA

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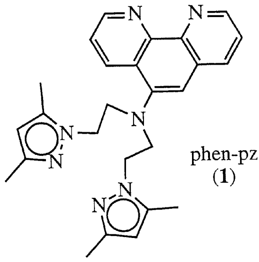
The synthesis and characterization of the new polyfunctional ligand phen-pza (5-bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine-1,10-phenanthroline) are described. Also reported are the preparations and some photophysical properties of the ruthenium(II) and rhenium(I) complexes $[Ru(bpy)_2(phen\text{-}pza)](PF_6)_2$ (bpy = 2,2′-bipyridine) and $[Re(CO)_3Br(phen\text{-}pza)]$, respectively, and the supramolecular copper(I) adducts $[Ru(bpy)_2(phen\text{-}pzaCu^I)](PF_6)_3$ and $[Re(CO)_3Br(phen\text{-}pzaCu^I)](PF_6)$. Limited studies of copper(II) adducts and photophysical changes upon reaction with NO are also described. The synthesis, structural characterization and some redox chemistry of the model copper(II) complex $[Cu(pza)](CF_3SO_3)_2$ (pza = bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine) are reported as are the syntheses and characterizations of 5-diethylamino-1,10-phenanthroline (phen-dea) and rhenium(I) complex $Re(CO)_3Br(phen\text{-}dea)$.

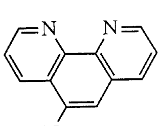
Introduction

The studies described here find their origin in ongoing investigations concerned with the fundamental chemistry of the bioregulatory molecule nitrogen monoxide (a.k.a. "nitric oxide").[1,2] A desirable goal is the development of new photoluminescence systems which may serve as NO sensors.[3,4] With this in mind, the present study sought to examine luminescent polynuclear metal complexes for which NO interaction with one coordination site may influence the photophysical behavior of another chromophore. Studies in this laboratory have shown that NO will reduce certain copper(II) complexes with chelating ligands that constrain the metal ion from attaining planar coordination.[5] Given reported luminescent sensors based on d^9/d^{10} redox switching of metal centers,[6] supramolecular complexes formed by coupling such a copper complex to ruthenium(II) or rhenium(I) luminophors were examined to probe possible NO sensing based on this reaction.

In this context the synthesis and characterization of the new polyfunctional ligand 5-bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine-1,10-phenanthroline (phen-pza, **1**) are described.[7] Also reported are the preparation and some preliminary studies of the photophysical properties of the ruthenium(II) and rhenium(I) complexes $[Ru(bpy)_2(phen\text{-}pza)](PF_6)_2$ (**2**) and $[Re(CO)_3Br(phen\text{-}pza)]$ (**3**), respectively, and the supramolecular Cu(I) adducts $[Ru(bpy)_2(phen\text{-}pzaCu^I)](PF_6)_3$ (**4**, bpy = 2,2′-bipyridine) and $[Re(CO)_3Br(phen\text{-}pzaCu^I)](PF_6)$ (**5**). Also described are limited studies of the Cu(II) adducts and photophysical changes upon reaction with NO. In addition, the synthesis, structure, and some redox chemistry of the model compound $[Cu(pza)(H_2O)_2](CF_3SO_3)_2$ (**6**) (pza = bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine) are described as are the syntheses and characterizations of 5-diethylamino-1,10-phenanthroline (phen-dea, **7**) and the rhenium(I) complex $[Re(CO)_3Br(phen\text{-}dea)]$ (**8**).



phen-pza
(**1**)



phen-dea
(**7**)

Experimental

Materials

THF was dried over Na–benzophenone and CH_2Cl_2 and acetonitrile were dried over CaH_2. Nitric oxide gas was obtained from Matheson Gas Products and was passed through a column of KOH pellets to remove higher nitrogen oxides. NO solubility in methanol was taken as 1.45×10^{-2} M atm^{-1} (25 °C) according to literature values.[8] Bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine (pza) was prepared as reported by Sorrell and Malachowski.[9] The white solid obtained was subsequently dried under vacuum to yield a yellowish oil. $[Re(CO)_5Br]$,[10] $[Re(CO)_3Br(phen)]$ (phen = 1,10-phenantholine),[11] $[Cu(acetonitrile)_4](PF_6)$,[12] $[Ru(bpy)_2Cl_2]\cdot 2H_2O$,[13] and $[Ru(bpy)_2(phen)](PF_6)_2$[13] were prepared according to published methods. 1,10-Phenanthroline-5,6-epoxide was prepared as described,[14] and the crude product was purified by chromatography (silica gel, CH_2Cl_2–hexanes–TEA 80 : 20 : 5) before it was recrystallized. The other reagents were purchased from Aldrich and used without further purification.

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† Electronic supplementary information (ESI) available: Tables of crystallographic data for $[Cu(pza)(H_2O)_2](CF_3SO_3)_2$ including atomic coordinates and equivalent isotropic displacement parameters, anisotropic displacement parameters, bond distances, and bond angles; supplemental figures showing 400 MHz ^{1}H NMR spectra of $[Ru(bpy)_2(phen\text{-}pza)](PF_6)_2$ and $[Ru(bpy)_2(phen\text{-}pzaCu^I)](PF_6)_3$ (aromatic region protons), the unit cell of $[Cu(pza)(H_2O)_2](CF_3SO_3)_2$, and the UV-vis spectrum of $Cu(pza)^{2+}$ in MeOH before and after NO addition. See http://www.rsc.org/suppdata/dt/b0/b009614h/

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Syntheses

[Cu(pza)(H_2O)$_2$](CF_3SO_3)$_2$ (6). Bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine (0.40 g, 1.53 mmol) was dissolved in methanol (20 ml), and copper(II) trifluoromethylsulfonate (Cu(tfl)$_2$, 0.55 g, 1.53 mmol) was then added to give an immediate color change from colorless to blue-green. The resulting solution was concentrated to complete dryness a rotary evaporator then redissolved in acetone. Ether was added and the solution was allowed to cool in the refrigerator to crystallize. X-Ray quality crystals were obtained overnight. The yield of the product after recrystallization was 76%. Analysis: Calculated for $C_{16}H_{27}CuF_6N_5O_8S_2$: C 29.16; H 4.13; N 10.63. Found: C 29.15; H 4.24; N 10.15%.

5-Bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine-5,6-dihydro-6-hydroxy-1,10-phenanthroline (9). Under an argon atmosphere, a 1.9 M toluene solution of triethylaluminium (2.8 ml, 5.32 mmol) was added dropwise to a solution of bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine[8] (1.34 g, 5.13 mmol) dissolved in dry CH_2Cl_2 (30 ml). The resulting solution was stirred at room temperature for 2.5 h, then 1,10-phenanthroline-5,6-epoxide[14] (790 mg, 4.13 mmol) in dry CH_2Cl_2 (20 ml) was added dropwise. The solution was stirred at room temperature for 24 h, then 6 M NaOH (10 ml) was added and the mixture stirred for another hour. The product was isolated by extraction with CH_2Cl_2 (3 × 30 ml) and the organic phase dried (Na_2SO_4) and evaporated. The resulting oil was purified through two successive chromatography columns (silica gel, CH_2Cl_2–hexanes–TEA 80 : 20 : 5 and silica gel, CH_2Cl_2–MeOH–TEA 9 : 1 : 1) to give **9** as a beige solid with a 44% yield (870 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.74–8.70 (m, 2H); 8.25 (ddd, J = 7.9, 1.3, 1.3, 1H); 7.49 (ddd, J = 7.9, 1.3, 1.3, 1H); 7.37 (dd, J = 7.9, 4.8, 1H); 7.22 (dd, J = 7.9, 4.8, 1H); 5.78 (s, 2H); 4.99 (dd, J = 12.2, 2.6, 1H); 4.18 (d, J = 12.1, 1H); 3.89 (ddd, J = 14.0, 6.9, 6.9, 2H); 3.70 (ddd, J = 14.1, 6.1, 6.1, 2H); 3.35 (ddd, J = 14.5, 5.9, 5.9, 2H); 3.26 (ddd, J = 14.2, 5.9, 5.9, 2H); 2.61 (br, 1H); 2.21 (s, 6H); 2.19 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.4 (s); 149.5 (d); 149.3 (d); 149.0 (s); 147.3 (s); 138.7 (s); 135.8 (s); 134.0 (d); 133.9 (d); 131.9 (s); 124.2 (d); 123.5 (d); 105.4 (d); 68.8 (d); 66.8 (d); 53.5 (t); 48.0 (t); 13.4 (q); 11.0 (q). LR-MS (CI/CH_4): m/z (rel. intensity %) 458 (17, MH^+), 440 (100, M − OH), 347 (32), 197 (15), 196 (16). HR-MS: m/z 458.2669 ($C_{26}H_{32}N_7O^+$; calc. 458.2668).

5-Bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine-1,10-phenanthroline (phen-pza) (1). Under an argon atmosphere, a solution of **9** (700 mg, 1.48 mmol) in dry THF (25 ml) was added to a suspension of NaH 95% (370 mg, 14.8 mmol) in dry THF (50 ml). The mixture was refluxed overnight, then methanol (5 ml) followed by water (10 ml) were carefully added and the organic solvents removed by rotary evaporation. The aqueous solution was extracted with CH_2Cl_2 (3 × 30 ml), and the organic phase dried (Na_2SO_4) and evaporated. The resulting oil was finally purified by chromatography (silica gel, CH_2Cl_2–MeOH–TEA 9 : 1 : 1) to give **1** as a beige solid with a 89% yield (600 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.14 (dd, J = 4.2, 1.6, 1H); 9.08 (dd, J = 4.4, 1.6, 1H); 8.09 (dd, J = 7.9, 1.6, 1H); 8.07 (dd, J = 8.2, 1.6, 1H); 7.58 (dd, J = 8.1, 4.2, 1H); 7.51 (dd, J = 8.3, 4.3, 1H); 7.37 (s, 1H); 5.62 (s, 2H); 4.09 (t, J = 6.3, 4H); 3.70 (t, J = 6.3, 4H); 2.13 (s, 6H); 1.85 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.3 (d); 149.3 (d); 147.7 (s); 147.3 (s); 144.3 (s); 143.9 (s); 139.1 (s); 135.1 (d); 132.3 (d); 128.5 (s); 126.9 (s); 123.3 (d); 122.6 (d); 116.4 (d); 105.1 (d); 53.5 (t); 46.1 (t); 13.5 (q); 10.8 (q). LR-MS (CI/CH_4): m/z (rel. intensity %) 440 (100, $MH^{\bullet+}$), 343 (10), 330 (18), 247 (9), 234 (5). HR-MS: m/z 440.2567 ($C_{26}H_{30}N_7^+$; calc. 440.2563). UV-Vis spectrum in acetonitrile (λ_{max} in nm (log ε)): 228 (4.61), 271sh (4.27), 275 (4.28), 322sh (3.64).

5-Diethylamino-5,6-dihydro-6-hydroxy-1,10-phenanthroline (10). 1,10-Phenanthroline-5,6-epoxide (100 mg, 0.51 mmol) was dissolved in a mixture of water (5 ml) and diethylamine (5 ml). The solution was stirred under argon overnight. Water (10 ml) was added and the solution was extracted with dichloromethane (4 × 20 ml). The organic phase was dried over Na_2CO_3 and the solvent eliminated by rotary evaporation. The product was chromatographed (silica gel, THF–TEA 9 : 1) to give **10** as a beige solid with 96% yield (131 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.62 (m, 2H); 7.96 (ddd, J = 7.8, 1.5, 1.5, 1H); 7.71 (ddd, J = 7.9, 1.4, 1.4, 1H); 7.26 (dd, J = 7.7, 4.8, 1H); 7.20 (dd, J = 7.8, 4.7, 1H); 4.87 (d, J = 11.5, 1H); 4.11 (d, J = 11.7, 1H); 2.93 (dq, J = 13.9, 7.0, 2H); 2.88 (dq, J = 13.8, 7.8, 2H); 1.10 (t, J = 7.1, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.95 (s); 149.37 (d); 149.21 (d); 149.18 (s); 135.22 (s); 134.80 (d); 133.32 (d); 133.06 (s); 124.12 (d); 123.48 (d); 67.76 (d); 65.49 (d); 46.01 (t); 16.28 (q). LR-MS (EI): 269 m/z (MH^+), 240, 197, 182, 169. HR-MS: m/z 269.1537, calc. 269.1528 ($C_{16}H_{19}N_3O$).

5-Diethylamino-1,10-phenanthroline (phen-dea) (7). 5-Diethylamino-5,6-dihydro-6-hydroxy-1,10-phenanthroline (130 mg, 0.48 mmol) was added to a suspension of NaH 95% (130 mg) in dry THF (15 ml). The mixture was refluxed under Ar for 4 h then MeOH (5 ml) was carefully added to quench the excess of NaH. The solvents were eliminated by rotary evaporation, water (30 ml) was added, and the product was extracted with dichloromethane (4 × 20 ml). The organic phase was dried over Na_2CO_3 and the solvent removed by rotary evaporation. The product was finally purified by chromatography (silica gel, THF–TEA 9 : 1) to give a brownish oil in nearly quantitative yield (123 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.09 (dd, J = 4.4, 1.8, 1H); 8.98 (dd, J = 4.2, 1.6, 1H); 8.60 (dd, J = 8.4, 1.8, 1H); 8.04 (dd, J = 8.1, 1.5, 1H); 7.55 (dd, J = 8.2, 4.2, 1H); 7.47 (dd, J = 8.1, 4.4, 1H); 7.20 (s, 1H); 3.19 (q, J = 7.0, 4H); 1.03 (t, J = 7.1, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.86 (d); 148.57 (d); 147.30 (s); 145.87 (s); 144.05 (s); 134.82 (d); 132.92 (d); 128.76 (s); 127.76 (s); 123.06 (d); 122.38 (d); 115.80 (d); 47.11 (t); 11.95 (q). LR-MS (EI): m/z 251 (M^+), 236, 222, 208, 179. HR-MS: m/z 251.1420, calc. 251.1422 ($C_{16}H_{17}N_3$). UV-Vis spectrum in acetonitrile (λ_{max} in nm (log ε)): 230 (4.50), 268 (4.07), 277 (4.08), 329 (3.54).

[Re(CO)$_3$Br(5-Bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine-1,10-phenanthroline)] ([Re(CO)$_3$Br(phen-pza)]) (3). A solution of **1** (200 mg, 0.455 mmol) in CH_2Cl_2 (3 ml) was added to a hot solution of [Re(CO)$_5$Br] (184 mg, 0.455 mmol) in toluene (10 ml). The mixture was refluxed for 4 h, then the solvent was partially evaporated. The resulting precipitate was collected by filtration and washed with toluene (2 ml) and diethyl ether (4 × 10 ml). The product was purified by chromatography (neutral alumina, acetone), dissolved in CH_2Cl_2 (3 ml) and finally recrystallized by diffusion of diethyl ether to give **3** as a yellow solid in 78% yield (280 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.32 (dd, J = 5.0, 1.4, 1H); 9.23 (dd, J = 5.0, 1.4, 1H); 8.29 (dd, J = 8.2, 1.3, 1H); 8.14 (dd, J = 8.4, 1.3, 1H); 7.74 (dd, J = 8.2, 5.1, 1H); 7.67 (dd, J = 8.5, 5.0, 1H); 7.42 (s, 1H); 5.57 (s, 2H); 4.14 (t, J = 6.0, 4H); 3.77 (dt, J = 14.1, 5.7, 2H); 3.76 (dt, J = 14.1, 5.7, 2H); 2.04 (s, 6H); 1.92 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.9 (CO); 189.0 (CO); 152.9 (d); 151.5 (d); 148.1 (s); 147.8 (s); 145.9 (s); 144.5 (s); 139.2 (s); 136.8 (d); 135.0 (d); 130.6 (s); 129.4 (s); 125.8 (d); 125.1 (d); 116.3 (d); 105.7 (d); 53.3 (t); 46.3 (t); 13.6 (q); 11.1 (q). LR-MS (FAB/NBA): m/z 790 (MH^+), 789 ($M^{\bullet+}$), 761 (M − CO), 733 (M − 2CO), 710 (M − Br). HR-MS: m/z 787.1082 ($C_{29}H_{29}N_7O_3BrRe^+$; calc. 787.1045). UV-Vis spectrum in acetonitrile (λ_{max} in nm (log ε)): 251 (4.42), 292sh (4.11), 356 (3.88), 415sh (3.48).

[Re(CO)$_3$Br(5-Diethylamino-1,10-phenanthroline)] ([Re(CO)$_3$Br(phen-dea)] (8). This material was prepared from Re(CO)$_5$Br and phen-dea by an experimental procedure similar to that used for the preparation of **3**. ^{1}H NMR (400 MHz, acetone-d_6): δ 9.49 (dd, $J = 5.1$, 1.4, 1H); 9.31 (dd, $J = 5.1$, 1.4, 1H); 9.04 (dd, $J = 8.5$, 1.3, 1H); 8.76 (dd, $J = 8.4$, 1.3, 1H); 8.13 (dd, $J = 8.5$, 5.1, 1H); 8.02 (dd, $J = 8.2$, 5.0, 1H); 7.82 (s, 1H); 3.45 (q, $J = 7.1$, 4H); 1.18 (t, $J = 7.1$, 6H). LR-MS (FAB/NBA): *m*/*z* 601 (M^+), 573 ($[M - CO]^+$), 545 ($[M - 2CO]^+$), 522 ($[M - Br]^+$). HR-MS: *m*/*z* 598.9988, calc. 598.9983 ($C_{19}H_{17}BrN_3O_3Re$). UV-Vis spectrum in acetonitrile (λ_{max} in nm (log ε)): 252 (4.48), 296 (4.14), 355 (3.92), 413sh (3.52).

[Ru(bpy)$_2$(5-Bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine-1,10-phenanthroline)](PF$_6$)$_2$ ([Ru(bpy)$_2$(phen-pza)](PF$_6$)$_2$) (2). [Ru(bpy)$_2$Cl$_2$]·2H$_2$O (100 mg, 0.192 mmol) and phen-pza (84 mg, 0.191 mmol) were refluxed for 3 h in ethanol–water 9 : 1 (20 ml). The solvent was eliminated by rotary evaporation and the residue dissolved in water (10 ml). The resulting solution was filtered and ammonium hexafluorophosphate (500 mg) in water (3 ml) was added to precipitate the product. The complex was filtered, washed with cold water (2 ml) and diethyl ether (30 ml), and purified by chromatography (neutral alumina–water 200 : 8, acetone–water 98 : 2). The product was finally dissolved in CH_2Cl_2 (3 ml) and precipitated by diffusion of diethyl ether to give **2** as a red solid in 87% yield (190 mg). ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 8.85 (2d, $J = 8.2$, 2H); 8.82 (2d, $J = 8.1$, 2H); 8.55 (dd, $J = 8.3$, 1.3, 1H); 8.33 (dd, $J = 5.2$, 1.2, 1H); 8.27 (dd, $J = 8.5$, 1.3, 1H); 8.25(3) (ddd, $J = 7.9$, 7.9, 1.7, 1H); 8.24(9) (ddd, $J = 7.9$, 7.9, 1.7, 1H); 8.20–8.13 (m, 5H); 7.83 (d, $J = 4.9$, 2H); 7.80 (dd, $J = 8.2$, 5.3, 1H); 7.78 (s, 1H); 7.76 (dd, $J = 8.5$, 5.3, 1H); 7.63 (ddd, $J = 7.6$, 5.6, 1.3, 1H); 7.62 (ddd, $J = 7.6$, 5.6, 1.3, 1H); 7.48 (ddd, $J = 7.6$, 5.7, 1.3, 1H); 7.45 (ddd, $J = 7.6$, 5.7, 1.3, 1H); 5.51 (s, 2H); 4.23 (t, $J = 6.0$, 4H); 3.87 (t, $J = 6.0$, 4H); 1.95 (s, 6H); 1.89 (s, 6H). ^{13}C NMR (125 MHz, $(CD_3)_2CO$, *J*/Hz): δ 158.64 (s); 158.52 (s); 153.24 (d); 152.81 (d); 151.54 (d); 149.75 (s); 147.77 (s); 147.63 (s); 145.86 (s); 140.02 (s); 139.24 (d); 139.18 (d); 136.87 (d); 135.13 (d); 132.23 (s); 130.50 (s); 129.04 (d); 129.01 (d); 128.90 (d); 128.83 (d); 127.39 (d); 126.55 (d); 125.63 (d); 125.59 (d); 118.06 (d); 105.77 (d); 54.03 (t); 47.16 (t); 13.94 (q); 11.13 (q). LR-MS (FAB): *m*/*z* 998 ($[M - PF_6]^+$), 853 ($[M - 2PF_6]^+$), 697 ($[M - bpy - 2PF_6]^+$). UV-Vis spectrum in acetonitrile (λ_{max} in nm (log ε)): 246 (4.61), 287 (4.80), 349 (3.99), 374 (4.00), 430sh (4.15), 453 (4.21).

[Re(CO)$_3$Br(5-Cu(I)Bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]-amine-1,10-phenanthroline)](PF$_6$) ([Re(CO)$_3$Br(phen-pzaCu^I)]-(PF$_6$)) (5). To a solution of [Re(CO)$_3$Br(phen-pza)] (50 mg, 0.063 mmol) in degassed acetonitrile (15 ml) was added [Cu(CH$_3$CN)$_4$](PF$_6$) (24 mg, 0.064 mmol). The resulting solution was condensed under vacuum to 2–3 ml and **5** was finally precipitated as a yellow solid by slow diffusion of degassed diethyl ether. ^{1}H NMR (400 MHz, $(CD_3)_2CO$, *J*/Hz): δ 9.39(4) (dd, $J = 5.1$, 1.1, 1H); 9.39(1) (dd, $J = 5.2$, 1.3, 1H); 8.80 (dd, $J = 8.4$, 1.3, 1H); 8.28 (s, 1H); 8.09 (dd, $J = 8.2$, 5.2, 1H); 7.75 (dd, $J = 8.5$, 5.2, 1H); 7.65 (br d, $J = 8.5$, 1H); 6.34 (s, 2H); 4.85–4.70 (br m, 4H); 4.10 (dt, $J = 15.0$, 4.9, 2H); 4.05 (dt, $J = 15.2$, 4.9, 2H); 2.53 (s, 6H); 2.39 (s, 6H). LR-MS (ESI/MeOH): *m*/*z* 852 ($[M - PF_6]^+$). UV-Vis spectrum in acetonitrile (λ_{max} in nm (log ε)): 246 (4.44), 291sh (4.12), 356 (3.88).

[Ru(bpy)$_2$(5-Cu(I)Bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]-amine-1,10-phenanthroline)](PF$_6$)$_3$ ([Ru(bpy)$_2$(phen-pzaCu^I)]-(PF$_6$)$_3$) (4). To a degassed solution of [Ru(bpy)$_2$(phen-pza)]-(PF$_6$)$_2$ (**2**, 60 mg, 0.052 mmol) in acetonitrile (10 ml) was added solid [Cu(CH$_3$CN)$_4$](PF$_6$) (20 mg, 0.052 mmol). Acetonitrile was removed under vacuum and the residue dissolved in degassed dichloromethane (3 ml). The product **4** was precipitated as a red solid by addition of degassed diethyl ether (10 ml). ^{1}H NMR (400 MHz, $(CD_3)_2CO$, *J*/Hz): δ 8.84 (d, $J = 8.4$, 2H); 8.80 (d, $J = 8.3$, 2H); 8.65 (dd, $J = 8.4$, 1.2, 1H); 8.30–8.21 (m, 5H); 8.17–8.11 (m, 4H); 7.85 (dd, $J = 8.3$, 5.2, 1H); 7.82 (ddd, $J = 5.6$, 1.5, 0.7, 1H); 7.78 (ddd, $J = 5.6$, 1.5, 0.7, 1H); 7.62 (ddd, $J = 7.8$, 5.5, 1.3, 1H); 7.61 (ddd, $J = 7.7$, 5.4, 1.3, 1H); 7.55–7.48 (br m, 2H); 7.41 (ddd, $J = 7.6$, 5.7, 1.3, 1H); 7.36 (ddd, $J = 7.6$, 5.6, 1.3, 1H); 6.28 (s, 2H); 4.82–4.62 (br m, 4 H); 4.04 (dt, $J = 15.3$, 4.8, 2H); 4.03 (dt, $J = 15.2$, 4.8, 2H); 2.46 (s, 6H); 2.35 (s, 6H). UV-Vis spectrum in acetonitrile (λ_{max} in nm (log ε)): 245 (4.61), 287 (4.79), 350 (3.97), 375 (3.99), 433sh (4.14), 453 (4.20).

Instrumentation

NMR spectra were recorded on a Varian Inova 400 or a Varian Inova 500 MHz NMR spectrometer. Coupling constants are given in hertz and chemical shifts expressed in ppm relative to $SiMe_4$ using the solvent as an internal reference. Absorption spectra were recorded using a Hewlett Packard 8452A diode array spectrophotometer and corrected by subtracting solvent background. Emission spectra were collected on a SPEX Fluorolog II spectrofluorimeter equipped with a Hamamatsu R928A water-cooled PMT. Emission lifetimes were measured using the third harmonic of a Continuum NY60 Nd/YAG laser (355 nm, pulse width 10 ns) as an excitation source. The emission decay was followed at 600 nm by using an RCA 8852 PMT mounted on a SPEX double monochromator. The analog output was recorded by a Tektronix TDS 540 digital oscilloscope, and the resulting digital data was transferred to a computer. The waveforms collected were signal-averaged (500 points per waveform) and analyzed using the exponential fitting routine of Igor Pro software on a Macintosh computer. Cyclic voltammograms were obtained using a BAS 100B/W voltammetric analyzer, with tetra-n-butylammonium hexafluorophosphate (0.1 M) as base electrolyte.

X-Ray structure determination of 6

A 0.40 mm × 0.40 mm × 0.10 mm prism was mounted on a thin glass fiber with epoxy glue and mounted on a Siemens Smart-CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Mo-Kα radiation, $\lambda = 0.71073$ Å) operating at 50 kV and 40 mA. About 1.3 hemispheres of intensity data were collected in 1321 frames with ω scans (width of 0.30° and exposure time of 30 s per frame). Unit cell dimensions were determined by a least-squares fit of 8192 reflections with $I > 10\sigma(I)$. The empirical absorption correction was based on the equivalent reflections. Other effects such as absorption by the glass fiber were simultaneously corrected. The structure was solved by Patterson methods followed by difference Fourier methods. All calculations were performed using SHELXTL[28] running on a Silicon Graphics Indy 5000. Final full-matrix refinements were against F^2 and included secondary extinction correction and anisotropic thermal parameters for all non-hydrogen atoms. Parameter shifts in the final least-squares cycle were smaller than 0.03σ. Relevant crystallographic parameters are listed in Table 1.

CCDC reference number 159776.

See http://www.rsc.org/suppdata/dt/b0/b009614h/ for crystallographic data in CIF or other electronic format.

Results and discussion

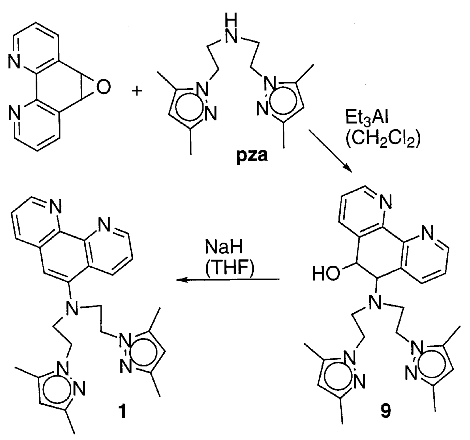
Syntheses

The synthesis of the new ligand phen-pza (**1**) was achieved following Scheme 1. The amino-dihydro-hydroxy-1,10-phenanthroline **9** was prepared through the transformation of pza to a diethylaluminium amide salt by addition of one equivalent of triethylaluminium. The addition of this diethylaluminium amide to 1,10-phenanthroline-5,6-epoxide occurred at room temperature to give **9**.[15] The dehydration of **9** occurred easily in the presence of NaH in refluxing THF to give the strongly emissive amino-phenanthroline ligand phen-pza. The simpler ligand phen-dea (**7**) was prepared according to prescriptions

Table 1 Crystallographic parameters for [Cu(pza)(H_2O)$_2$](CF_3SO_3)$_2$

Structural formula	$C_{16}H_{27}CuF_6N_5O_8S_2$
Formula weight	659.1
Color and habit	Turquoise and prism
Crystal size/mm	0.40 × 0.40 × 0.10
Crystal system	Monoclinic
Space group	$P2_1/c$ (no. 14)
a/Å	13.2155(2)
b/Å	24.1634(3)
c/Å	17.2183(3)
β/°	90.8
V/Å^3	5497.78(14)
Z	8
ρ_{calc}/g cm^{-3}	1.593
Temperature/K	293
μ(Mo-Kα)/mm^{-1}	1.035
No. of total reflections	45503
No. of unique reflections	9661 [R(int) = 0.0486]
R^a	0.0655
$R_w{}^b$	0.165

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ with $F_o > 4.0\sigma(F)$. [b] $R_w = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o)^2]]^{1/2}]$ with $F_o > 4.0\sigma(F)$.



Scheme 1 Synthesis route to phen-pza.

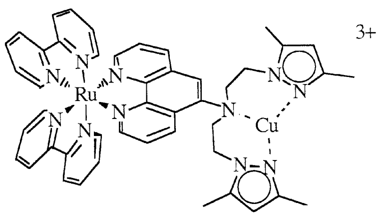
reported by Shen and Sullivan[14] for the similar compound 5-dimethylamino-1,10-phenanthroline. A sample of 1,10-phenanthroline-5,6-epoxide was simply stirred overnight in a mixture of water and diethylamine to give the dihydro-hydroxy species **10**. Dehydration of **10** to give **7** was effected by reaction with NaH in refluxing THF.

The yellow rhenium complexes [Re(CO)$_3$Br(phen-pza)] (**3**) and [Re(CO)$_3$Br(phen-dea)] (**8**) were prepared by reaction of the respective phenanthroline ligands with [Re(CO)$_5$Br].[16] In each case, no complexation of the pyrazole part of the ligand to rhenium was observed, and only one product was formed. [Re(CO)$_3$Br(phen-pzaCu^{I})](PF$_6$) (**5**) was prepared by adding one equivalent of [Cu(CH$_3$CN)$_4$](PF$_6$) to an argon deaerated solution of **3** in acetonitrile. Complexation of Cu(I) to the phen-pza ligand was confirmed by examining the ^{1}H NMR spectrum (acetone-d$_6$) and the ESI-mass spectrum. The Cu(II) analog (**11**) was prepared by reaction of **3** with equimolar Cu(tfl)$_2$ in methanol. FAB-MS of the resulting solid confirmed the formation of a dinuclear complex, but NMR analysis was prevented by the paramagnetic character of Cu(II) and the compound was not further characterized.

The ruthenium(II) analog [Ru(bpy)$_2$(phen-pza)](PF$_6$)$_2$ (**2**) was prepared by heating phen-pza in the presence of one equivalent of Ru(bpy)$_2$Cl$_2$ in ethanol containing water (10%). Again, only one product was formed. The cuprous complex [Ru(bpy)$_2$-(phen-pzaCu^{I})](PF$_6$)$_3$ (**4**) was prepared by adding one equivalent of [Cu(CH$_3$CN)$_4$](PF$_6$) to a solution of **2** in argon entrained acetonitrile. Complex formation was demonstrated by deshielding of pza protons upon Cu(I) coordination (^{1}H NMR spectrum in acetone-d$_6$) (Supplemental Fig. S-1).† The

Table 2 Selected bond distances (Å) and angles (°) of forms **A** and **B** of [Cu(pza)(H_2O)$_2$]$^{2+}$

Form **A**		Form **B**	
Cu–O(1)	2.094(4)	Cu–O(3)	2.108(5)
Cu–O(2)	2.082(4)	Cu–O(4)	2.076(4)
Cu–N(1)	2.083(4)	Cu–N(2)	2.088(4)
Cu–N(12)	1.955(4)	Cu–N(42)	1.963(4)
Cu–N(22)	1.967(4)	Cu–N(32)	1.968(4)
N(12)–Cu–N(22)	170.8(2)	N(42)–Cu–N(32)	170.6(2)
N(12)–Cu–N(1)	92.7(2)	N(42)–Cu–N(2)	93.3(2)
N(22)–Cu–N(1)	96.1(2)	N(32)–Cu–N(2)	95.7(2)
N(12)–Cu–O(2)	90.6(2)	N(42)–Cu–O(4)	89.9(2)
N(22)–Cu–O(2)	88.0(2)	N(32)–Cu–O(4)	88.8(2)
N(1)–Cu–O(2)	114.3(2)	N(2)–Cu–O(4)	114.5(2)
N(12)–Cu–O(1)	87.0(2)	N(42)–Cu–O(3)	86.4(2)
N(22)–Cu–O(1)	87.9(2)	N(32)–Cu–O(3)	88.4(2)
N(1)–Cu–O(1)	107.4(2)	N(2)–Cu–O(3)	106.9(2)
O(2)–Cu–O(1)	138.3(2)	O(4)–Cu–O(3)	138.5(2)



(**4**)

Cu(II) adduct [Ru(bpy)$_2$(phen-pzaCu^{II})(tfl)$_2$] (**12**) was prepared by adding equimolar Cu(tfl)$_2$ in acetonitrile leading to a color change from red to red-brown upon mixing. This material was not well characterized, since the paramagnetic Cu(II) broadened proton resonances and FAB and ES ionization induced the decomplexation of copper, so the measured MS for both **4** and **12** was the same as that of **2**.

The copper(II) model complex Cu(pza)$^{2+}$

X-Ray diffraction quality crystals of triflate salt **6** were prepared by adding solid Cu(tfl)$_2$ to dissolved pza in equimolar quantities and recrystallizing the resulting salt from an acetone–ether mixture. The crystallographic parameters for [Cu(pza)(H_2O)$_2$](CF_3SO_3)$_2$ are listed in Table 1. The asymmetric unit (Supplemental Fig. S-2)† has two unique cations (**A** and **B**) with slight differences in bond distances and angles (Table 2). ORTEP[29] diagrams of **A** and **B** are shown in Fig. 1. The geometry of the five-coordinate cations can be described as distorted trigonal bipyramid with Cu, N(1/2), O(1/3), and O(2/4) atoms defining the trigonal plane and the remaining N atoms (N(12)/N(42), N(22)/N(32)) occupying the axial positions. Trigonal plane Cu–ligand bond distances are essentially identical (2.08 Å) while the axial Cu–N bond distances are shorter (1.97 Å). The sum of the bond angles of the trigonal plane is 360°, consistent with the trigonal bipyramid geometry.

In solution Cu(pza)$^{2+}$ is pale blue, typical of cupric complexes. The UV-Vis absorption spectrum of Cu(pza)$^{2+}$ in methanol shows a ligand field transition at ~650 nm and two higher energy bands centered at ~300 and 350 nm (Fig. 2). Given that the extinction coefficients are >10^3 M^{-1} cm^{-1}, the latter are likely to be ligand to metal charge transfer transitions.[17]

The cyclic voltammogram of [Cu(pza)](tfl)$_2$ in acetone–0.1 M Bu$_4$NPF$_6$ solution shows one reversible reduction at an $E_{1/2}$(Cu$^{II/I}$) value of 0.57 V (*vs.* SCE) with a peak to peak separation of ~80 mV. Thus Cu(pza)$^{2+}$ is a much stronger oxidant than most cupric amine complexes. One can rationalize this behavior by suggesting that the coordination sphere of this

Table 3 Photophysical properties of the ligands and complexes in deaerated 298 K acetonitrile (except where noted)

Compound	$\lambda_{max}{}^{abs}$/nm (ε in 10^3 M^{-1} cm^{-1})	$\lambda_{max}{}^{em}$/nm	τ_0/µs
phen-pza (**1**)	228 (40.4), 271sh (18.8), 275 (19.0), 322sh (4.4)	478[a] (490)[b]	
phen-dea (**7**)	230 (31.3), 268 (11.7), 277 (11.9), 329 (3.5)	515[a]	
[Re(CO)$_3$Br(phen-pza)] (**3**)	251 (26.4), 292sh (12.9), 356 (7.6), 415sh (3.0)	595 (608)[a,b] (606)[a,d]	≈18[c]
[Re(CO)$_3$Br(phen-dea)] (**8**)	252 (30.2), 296 (13.7), 355 (8.3), 413sh (3.3)	610	34 ± 5
[Re(CO)$_3$Br(phen)]	222 (39.6), 266 (23.9), 290sh (11.3), 370 (3.4)	617	0.35 ± 0.04
[Ru(bpy)$_2$(phen-pza)](PF$_6$)$_2$ (**2**)	246 (40.3), 287 (63.6), 349 (9.7), 374 (10.0), 430sh (14.1), 453 (16.3)	617	1.0 ± 0.1
[Ru(bpy)$_2$(phen)](PF$_6$)$_2$ (**13**)	265 (49.0), 287 (55.0), 387sh (6.7), 430sh (12.9), 449 (14.5)	616	0.85 ± 0.1

[a] Aerated solutions. [b] Methanol solution. [c] See ref. 23. [d] Dichloromethane solution.

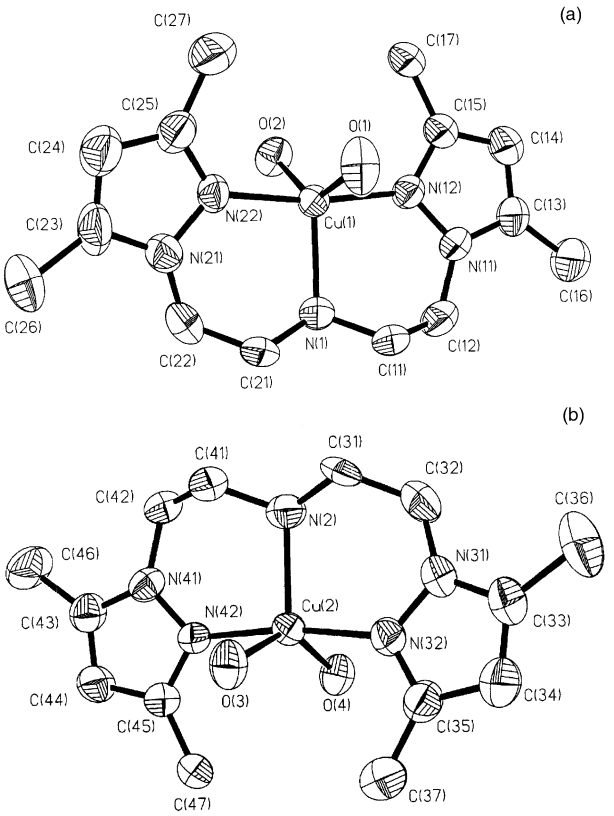


Fig. 1 Structure and numbering of atoms of the $[Cu(pza)(H_2O)_2]^{2+}$ cation: (a, top) form **A**; (b, bottom) form **B**. Thermal ellipsoids shown at 50% probability level.

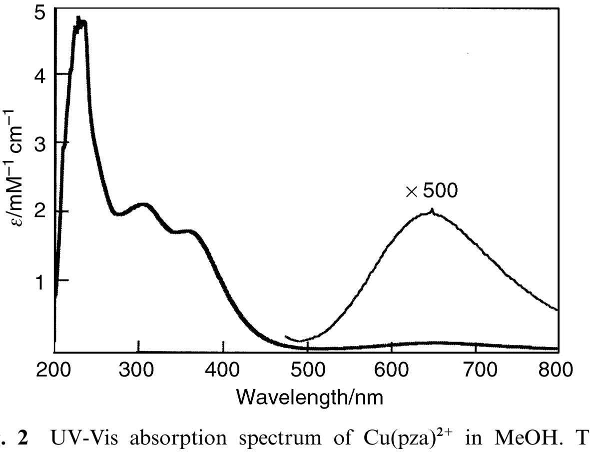


Fig. 2 UV-Vis absorption spectrum of $Cu(pza)^{2+}$ in MeOH. The ligand field band is magnified for clarity.

cation may match that of the cuprous analog $Cu(pza)^+$ more closely than is typical for Cu(II)/Cu(I) couples. Although the structure for $Cu(pza)^+$ is unknown, the related cuprous complex $Cu(pze)^+$ (pze = bis[2-(3,5-dimethyl-1-pyrazolyl)-ethyl]-ether) has been shown to be a three-coordinate cation with a T-shape geometry with bond angles 94.0°, 95.9°, and 169.1°.[9] The analogous bond angles for $Cu(pza)^{2+}$ are remarkably similar, 92.7°, 96.2°, and 170.8°, respectively. Although pze and pza are not identical (the difference is simply the replacement of the central NH of pza with an O in pze), the comparison suggests that structural changes in the Cu(pza) unit upon reduction of Cu(II) to Cu(I) may be small. Similar structural arguments have been offered to account for the relatively high reduction potentials of Cu(II) complexes such as $Cu(dmp)_2^{2+}$ ($E_{1/2}(Cu^{II/I})$ = 0.34 V *vs.* SCE in water) (dmp = 2,9-dimethyl-1,10-phenanthroline),[5b] other sterically crowded bis(phenanthroline)copper(II) derivatives[18] and blue copper proteins.[19,20]

The highly positive reduction potential for $Cu(pza)^{2+}$ suggested that this species would react with NO as was observed for the $Cu(dmp)_2^{2+}$ ion.[5] Indeed exposure of a methanol solution of **6** to NO (1 atm) led to spectral changes consistent with reduction of $Cu(pza)^{2+}$ to $Cu(pza)^+$ (Supplemental Fig. S-3).†[21] Similar NO reduction of $Cu(pza)^{2+}$ was observed in aqueous solution but not when the solvents were dry CH_3CN or CH_2Cl_2. This behavior follows that seen for the NO reduction of $Cu(dmp)_2^{2+}$ which occurred only when hydroxylic solvents (ROH) were present and gave RONO plus $Cu(dmp)_2^+$ as products.[5]

Photophysical properties

Rhenium(I) complexes. $Re(CO)_3Br$(phen-dea) (**8**) and $Re(CO)_3Br$(phen-pza) (**3**) each show an absorption band at ~355 nm not apparent in the free ligand spectra (Table 3). This can be assigned as metal-to-ligand charge-transfer (MLCT) bands, although the extinction coefficients are about twice as large as seen for the $Re(CO)_3Br$(phen) analog. Similar observations were made for related phen-amine complexes.[22] Both **3** and **8** are emissive in room temperature deaerated solution, but the emission is strongly quenched in the presence of O_2. For example, the luminescence spectrum of **3** in deaerated acetonitrile shows a moderately strong emission band centered at $\lambda_{max}{}^{em}$ = 595 nm ($\tau \approx$ 18 µs).[23] This emission was quenched by an intensity factor of 225 in aerated solution (Fig. 3), while deaerating the solution restored the emission intensity. Thus, O_2 quenching is nearly diffusion limited (k_q estimated as ~10^{10} M^{-1} s^{-1} from the Stern–Volmer relationship $I_0/I = 1 + k_q\tau_0[Q]$ and $[O_2]$ ~10^{-3} M in aerated acetonitrile). The emission spectrum and relaxation dynamics of **8** were similar to those for **3**. In both cases the $\lambda_{max}{}^{em}$ are blue shifted relative to that for $Re(CO)_3Br$(phen) (617 nm), which also displays a much shorter lifetime (0.35 µs) (Table 3).

From the perspective of developing a luminactive NO sensor, the Re(I) phen-pza complexes proved undesirable, since they decomposed when probed by laser flash photolysis. Degradation of **3** was also seen upon continuous photolysis in acetonitrile with a 325–375 nm band pass filter, and the ^{1}H NMR spectrum of the solution suggested formation of multiple products. In contrast, $Re(CO)_3Br$(phen) was unchanged under similar photolysis conditions. Furthermore, NO quenched the photoluminescence from both **3** and $Re(CO)_3Br$(phen). For example, the emission intensity of a

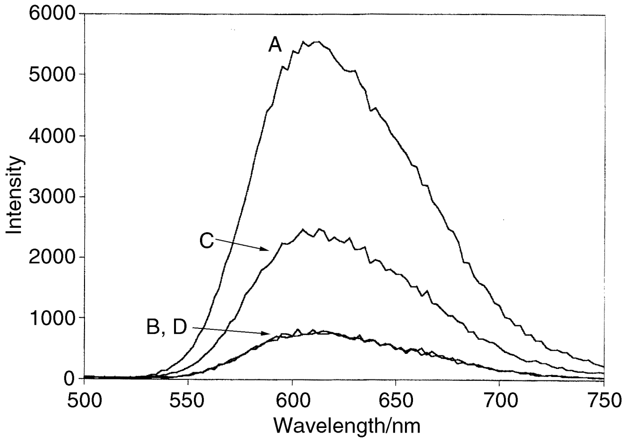


Fig. 3 Emission spectrum ($\lambda_{exc} = 452$ nm) of a methanol solution of $[Ru(bpy)_2(phen\text{-}pza)](PF_6)_2$ (36 μM) and $Cu(PF_6)_2$ (1.8 mM): A: degassed by freeze–pump–thaw techniques. B: under NO (760 Torr). C: after evacuation to remove NO. D: after reintroduction of NO (760 Torr).

degassed methanol solution of **3** (10^{-4} M) was quenched by a factor of 33 when equilibrated with NO (400 Torr, 0.0076 M). This may be the result of redox quenching ($k_q \approx 10^8$ M^{-1} s^{-1}) but was not probed further.

Ruthenium(II) complexes. In this context, attention turned to the $Ru^{II}(bpy)_2L$ luminophor, which has been the synthetic platform for related systems designed as luminactive sensors.[24,25] Acetonitrile solutions of $[Ru(bpy)_2(phen\text{-}pza)](PF_6)_2$ (**2**) proved to be strongly luminescent with a λ_{max}^{em} at 617 nm with monoexponential decay giving $\tau = 1.0$ μs at 298 K. Long term photolysis and repeated laser excitation led to no obvious degradation of the solutions, and NO addition (~1 atm) did not diminish the luminescence intensity. The parent complex $[Ru(bpy)_2(phen)](PF_6)_2$ (**13**) displays nearly identical photophysical properties ($\lambda_{max}^{em} = 616$ nm, $\tau = 0.85$ μs), so the absence of a substituent effect on these parameters may indicate a luminactive MLCT state largely localized on a bpy rather than the phen ligands. The photophysical properties of **2** and **13** were not affected by added NO.

In acetonitrile, the emission spectra of **2** and of 1 : 1 solutions of **2** and $Cu(PF_6)_2$ (30 μM) showed the same λ_{max}^{em} (617 nm); however, the intensity of the latter was about 35% that of the former. The luminescence intensity of $[Ru(bpy)_2(phen\text{-}pza)](PF_6)_2$ decreased to about 3% at higher Cu(II) concentrations (3.0×10^{-4} M). We interpret this in terms of intermolecular quenching by dissociated Cu^{2+} given that the MLCT excited state of $[Ru(bpy)_2(phen)](PF_6)_2$ (3.0×10^{-4} M) is 88% quenched by adding free $Cu(PF_6)_2$ (3.0×10^{-4} M) ($k_q \approx 2.8 \times 10^{10}$ M^{-1} s^{-1}).

In methanol, the effect of Cu(II) was much smaller. For example, the emission intensities of analogous solutions of **2** and **12** (69 μM) in degassed methanol differed by less than 10%. On the other hand a similar solution of **4** (69 μM) had a relative intensity 4× smaller than that of **12**. Similarly, the 617 nm MLCT emission from **2** (36 μM) showed only moderate quenching as $Cu(PF_6)_2$ was added, the intensity being only about 15% lower at 1.8 mM Cu(II). One would expect the pza moiety of the ligand **1** to compete effectively with MeOH for Cu(I) but not for Cu(II), so that luminescence behavior appears to be dominated by the dinuclear species. The less efficient luminescence of **4** then might be attributed to quenching by inner sphere electron transfer from Cu(I) to a "Ru(III)" center of a metal-to-bipyridine charge transfer excited state. Similar quenching of luminescence from ruthenium tris(diimine) centers in supramolecular complexes after complexation of Cu(I) has been reported by Sauvage and Chambrion[26] and by Ziessel and Grossenhenny.[27] The minimal quenching by Cu(II) in MeOH is puzzling given its relative effectiveness in CH_3CN.

When degassed methanol solutions of **2** (36 μM) were treated with NO (760 Torr) the luminescence efficiency was not affected. The same observation was made when the much more weakly emitting solutions of **4** were treated with NO. However, NO treatment of methanolic **2** (36 μM) in the presence of various concentrations of $Cu(PF_6)_2$ (0.18–1.8 mM) led to significant quenching of the MLCT emission, the extent of quenching being a non-linear function of the copper concentration. Removing NO by evacuating the system led to partial regeneration of the emission (to about half that seen originally); however, reintroduction of NO led to diminished emission intensity again (Fig. 3). We propose that these observations are the consequence of reversible NO reduction of Cu(II) to give **4** (eqn. 1).

$$Ru(bpy)_2(phen\text{-}pza)^{3+} + Cu^{II} + NO + MeOH \rightleftharpoons Ru(bpy)_2(phen\text{-}pzaCu^{I}) + MeONO \quad (1)$$

This finds analogy in the reaction of NO with the Cu(II) complex $Cu(dmp)_2^{2+}$ in methanol[5] and the NO reduction of methanolic $Cu(pza)^{2+}$ described above. Since NO addition to a 1 : 1 methanolic solution of **2** and $Cu(tfl)_2$ (each at 69 μM) did not induce further change in the observed luminescence of that mixture, one may conclude that the pza functionality is necessary to effect Cu(II) reduction by NO or to provide for formation of a stable inner sphere Cu(I) complex in this medium (or both).

In summary, the synthesis of a phenanthroline derivatized with the pendant chelating group bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine (pza) is described as well as the use of this ligand to prepare phen-pza complexes of Re(I) and Ru(II). Binuclear complexes with Cu(I) and Cu(II) are formed by reaction of the Re(I) and Ru(II) phen-pza species with the appropriate cuprous and cupric precursors. Limited photophysical data accumulated for the various species are also described. The system prepared from $Cu(tfl)_2$ and $[Ru(bpy)_2(phen\text{-}pza)](PF_6)_2$ displayed changes in photophysical behavior upon exposure to NO consistent with the goal of designing a luminactive NO sensor. However, while such behavior provides a promising "proof of concept", Cu(I) and Cu(II) coordinated at the pza centers are apparently too labile for practical applications of the present systems.

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