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Homo- and Heteronuclear Ruthenium and Osmium Complexes Containing an Asymmetric Pyrazine-Based Bridging Ligand

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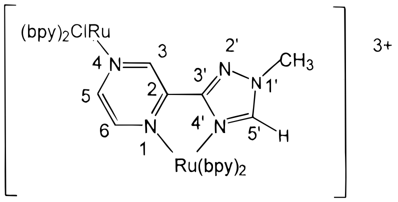
The synthesis, characterization, and electrochemical, photophysical, and photochemical properties of the compounds $[Ru(bpy)_2(L)]^{2+}$ (**Ru**), $[Os(bpy)_2(L)]^{2+}$ (**Os**), $[(L)Os(bpy)_2Cl]^{+}$ (**OsCl**), $[Ru(bpy)_2(L)Ru(bpy)_2Cl]^{3+}$ (**RuRuCl**), $[Os(bpy)_2(L)Os(bpy)_2Cl]^{3+}$ (**OsOsCl**), $[Ru(bpy)_2(L)Os(bpy)_2Cl]^{3+}$ (**RuOsCl**), and $[Os(bpy)_2(L)Ru(bpy)_2Cl]^{3+}$ (**OsRuCl**) are reported (bpy = 2,2′-bipyridine, L = 1-methyl-3-(pyrazin-2-yl)-1,2,4-triazole). The $Os(bpy)_2$ and the $Ru(bpy)_2$ moieties are coordinated to the pyrazyltriazole ligand in two different ways, *i.e.* in a bidentate fashion *via* the triazole ring and N1 of the pyrazine ring and in a monodentate fashion only *via* N4 of the pyrazine ring. In the homonuclear dimers the monodentate bound metal has an oxidation potential that is approximately 400 mV lower than that of the bidentate bound metal. Spectroelectrochemical investigations suggest the presence of a weak interaction between the metal centers in the dinuclear species. The emission properties of the compounds are indicative of efficient energy transfer in the excited state, leading to emission from only one metal unit. In acetone both **RuRuCl** and the **OsRuCl** show photodissociation of the monodentate ruthenium moiety; however, **RuOsCl** and **OsOsCl** were found to be photostable.

Introduction

Extensive investigations have revealed that mononuclear and polynuclear ruthenium compounds exhibit interesting electrochemical, photophysical, and photochemical properties.[1−7] The polynuclear compounds exhibit in many cases photoinduced energy- and electron-transfer processes that are strongly related to the properties of the bridging ligand employed. We have undertaken a systematic study of mononuclear and dinuclear ruthenium−bpy complexes containing various triazole ligands. An interesting feature of triazole ligands is that the position of substituents on the triazole ring determines which coordination mode prevails, *i.e.* N1′ vs N4′ coordination.[8] In addition, triazole-based ligands, being strong σ-donors, have been shown to promote electronic interaction between metal centers.[9] In a previous paper the synthesis and physical properties of a series of ruthenium complexes containing pyrazyltriazoles were presented. We have shown that for 3-(pyrazin-2-yl)-1,2,4-triazole the lowest unoccupied molecular orbital (LUMO) in these complexes can be located on the pyrazinyltriazole ligand or on the bpy ligands, depending on whether the triazole ring is protonated or not.[10] Pyrazines can also act as bidentate ligands. Protons or metal ions may coordinate to the uncoordinated N4 atom of pyrazine-based ligands for example as in $[Ru(bpz)_3]^{2+}$ (bpz = 2,2′-bipyrazine),[11,12] and pyrazine-based dinuclear compounds have been studied in great detail.[13] In this contribution we report the properties of a series of homo- and heteronuclear ruthenium- and osmium-based dinuclear compounds with the pyrazyltriazole ligand 1-methyl-3-(pyrazin-2-yl)-1,2,4-triazole (L), where one metal center is bound in a bidentate fashion and a second *via* N4 of the pyrazine ring shown as follows:



The effect of the asymmetric coordination geometry on the electrochemical, electronic, and photochemical properties will be discussed. The electronic properties of the intervalence compounds are investigated. Emission and electrochemical

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experiments suggest that in these compounds interaction exists between the two metal centers *via* the pyrazine bridge.

Experimental Section

Synthesis and Materials. 1-Methyl-3-(pyrazin-2-yl)-1,2,4-triazole (L) was obtained as reported elsewhere.[10] *cis*-[Ru(bpy)$_2$Cl$_2$]·2H$_2$O and *cis*-[Os(bpy)$_2$Cl$_2$] were prepared according to literature methods.[14,15]

[Ru(bpy)$_2$(L)](PF$_6$)$_2$·H$_2$O (Ru). L (0.5 mmol, 80 mg) was dissolved in 400 mL of hot ethanol/water (1/1 v/v). *cis*-[Ru(bpy)$_2$Cl$_2$]·2H$_2$O (0.5 mmol, 240 mg) was added in small portions to the dissolved ligand, and the mixture was heated at reflux for 24 h. The solution was filtered, evaporated to dryness, and dissolved in 20 mL of water. The complex was purified using a Sephadex SP-25 cation exchange column. Elution took place with a 0.6 M NaCl solution. The complex was isolated as the PF$_6^-$ salt, further purified using neutral alumina as column material and acetone as eluent, and finally recrystallized from an acetone/water mixture (1/1 v/v) Yield: 240 mg (55%). Anal. Found: C, 36.41; H, 2.51; N, 14.03. Calcd for $C_{27}H_{25}F_{12}N_9P_2ORu$: C, 36.75; H, 2.86; N, 14.28.

^{1}H NMR [(CD)$_3$CO] for L: 9.46 (d; H3 L), 8.06 (q; H6 L), 8.59 (d; H5 L), 8.71 (s; H5′), 4.09 ppm (s; CH$_3$). The chemical shifts of the bpy ligands are in the range found for other Ru(bpy)$_2$ compounds.[10]

[Os(bpy)$_2$(L)](PF$_6$)$_2$ (Os) and [(L)Os(bpy)$_2$Cl]PF$_6$·H$_2$O (OsCl). These compounds were prepared as **Ru** except that the monopositively charged **OsCl** complex was collected after elution with a 0.08 M NaCl solution and **Os** was collected after elution with a 0.6 M NaCl solution. Yield for **Os**: 180 mg (38%). Anal. Found: C, 33.93; H, 2.40; N, 13.43. Calcd for $C_{27}H_{23}F_{12}N_9P_2Os$: C, 34.01; H, 2.43; N, 13.22. Yield for **OsCl**: 30 mg (6%). Anal. Found: C, 38.16; H, 2.91; N, 14.05. Calcd for $C_{27}H_{25}ClF_6N_9OPOs$: C, 37.61; H, 2.92; N 14.62.

^{1}H NMR for L in **Os** [(CD)$_3$CO]: 9.41 (d; H3 L), 8.06 (q; H6 L), 8.38 (d; H5 L), 8.71 (s; H5′), 4.08 ppm (s; CH$_3$). ^{1}H NMR for L in **OsCl** [(CD)$_3$CO, 298 K]: 9.73 (d; H6 bpy), 8.42 (s; H5′ L), 8.32 (br H6, L), 4.05 ppm (s; CH$_3$). The chemical shifts of the protons of the bpy ligands are in the range as found for the analogous ruthenium complex.

[Ru(bpy)$_2$(L)Ru(bpy)$_2$Cl](PF$_6$)$_3$·4H$_2$O (RuRuCl). L (0.25 mmol, 40 mg) and an excess of *cis*-[Ru(bpy)$_2$Cl$_2$]·2H$_2$O were heated at reflux in 50 mL of ethanol/water (1/1 v/v) for 24 h. The compound was purified and isolated as described for **Ru**, except that elution took place with a 3 M NaCl solution. Yield: 300 mg (82%). Anal. Found: C, 37.12; H, 2.59; N, 11.90. Calcd for $C_{47}H_{47}ClF_{18}N_{13}O_4P_3Ru_2$: C, 36.89; H, 3.10; N, 11.90. MS (*m/e*): [(M − PF$_6^-$)]$^+$, 1313 (calcd, 1312.5).

[Os(bpy)$_2$(L)Os(bpy)$_2$Cl](PF$_6$)$_3$·H$_2$O (OsOsCl). This complex was prepared as for **RuRuCl**, except that the solution containing *cis*-[Os(bpy)$_2$Cl$_2$] and ligand was refluxed for 3 days. Yield: 180 mg (44%). Anal. Found: C, 34.20; H, 2.53; N, 10.80. Calcd for $C_{47}H_{41}ClF_{18}N_{13}OP_3Os_2$: C, 34.12; H, 2.50; N, 11.00. MS (*m/e*): [(M − PF$_6^-$)]$^+$, 1491 (calcd, 1490.5).

[Ru(bpy)$_2$(L)Os(bpy)$_2$Cl](PF$_6$)$_3$·4H$_2$O (RuOsCl). A 0.125 mmol amount of [Ru(bpy)$_2$(L)]$^{2+}$ and 0.125 mmol of *cis*-[Os(bpy)$_2$Cl$_2$] were heated at reflux in 50 mL of ethanol/water (1/1 v/v) for 3 days. The complex was purified as described for **RuRuCl**. Yield: 125 mg (64%). Anal. Found: C, 34.96; H, 2.32; N, 11.15. Calcd for $C_{47}H_{47}ClF_{18}N_{13}O_4P_3OsRu$: C, 34.86; H, 2.93; N, 11.24. MS (*m/e*): [(M − PF$_6^-$)]$^+$, 1402 (calcd, 1401.5).

[Os(bpy)$_2$(L)Ru(bpy)$_2$Cl](PF$_6$)$_3$·HPF$_6$·2H$_2$O (OsRuCl). A 0.125 mmol amount of [Os(bpy)$_2$(L)]$^{2+}$ and 0.125 mmol of *cis*-[Ru(bpy)$_2$Cl$_2$]·2H$_2$O were heated at reflux in 50 mL of ethanol/water (1/1 v/v) for 24 h. The complex was purified as described for **RuRuCl**. Yield: 100 mg (51%). Anal. Found: C, 32.98; H, 2.43; N, 10.19. Calcd for $C_{47}H_{44}ClF_{24}N_{13}O_2P_4OsRu$: C, 32.64; H, 2.56; N, 10.53.

Scheme 1

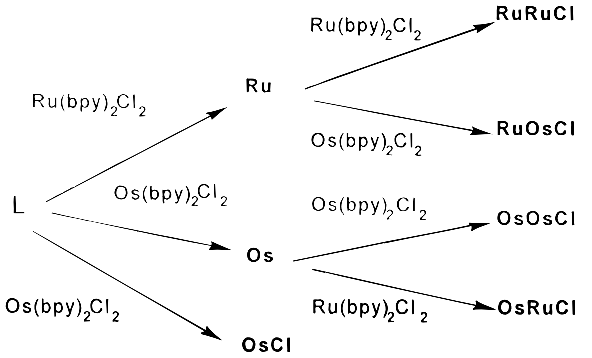

Table 1. Electrochemical Data for Mononuclear and Dinuclear Pyrazyltriazole Complexes

compd	metal-based oxidn potential		ligand-based redn potential^a			
OsCl	0.45		−1.44	−1.68	−1.90^b	
Os	0.86		−1.20	−1.48	−1.60^b	
Ru	1.32		−1.27	−1.54	−1.81	
RuRuCl	0.92	1.41	−0.97	−1.51	−1.57	−1.76^b
OsOsCl	0.50	1.00	−0.80	−1.53	−1.74^b	−1.89^b
RuOsCl	0.53	1.41	−0.95	−1.51	−1.75^b	−1.89^b
OsRuCl	0.86	1.04	−0.87	−1.49	−1.70^b	−1.87^b

[a] Measurements were carried out in acetonitrile containing 0.1 M TBAP using differential pulse polarography. Potentials are listed in volt *versus* SCE. [b] Irreversible wave.

Physical Measurements. ^{1}H-NMR and COSY ^{1}H-NMR were recorded on a Bruker WM 300 spectrometer. UV−vis measurements were obtained on 10^{-5}−10^{-4} M solutions on a Perkin-Elmer 330 or a Shimadzu UV-240 spectrophotometer by using 1 cm quartz cells. Emission spectra were recorded on a Perkin-Elmer LS5 and on a Perkin-Elmer LS50 luminescence spectrometer. Room-temperature measurements were carried out in acetonitrile, while measurements at 77 K were carried out in methanol (approximately 10^{-5} M solutions). Spectra were not corrected for photomultiplier response. Photolysis experiments were carried out at room temperature in acetone using visible light with a 400 W light source.

The differential pulse voltammetry (DPV) experiments (4 mV/s, pulse height 20 mV) and the cyclic voltammograms (CV) (100 mV/s) were carried out on a EG & G Par C Model 303 instrument with an EG & G 384 B polarographic analyzer. A saturated calomel electrode (SCE) was used as a reference electrode. The electrolyte used for all electrochemical experiments was acetonitrile, containing 0.1 M tetrabutylammonium perchlorate (TBAP). Spectroelectrochemical experiments were carried out using a Shimadzu UV-3100 UV−vis−NIR spectrophotometer and an EG & G Princeton Applied Research (PAR) Mode 362 scanning potentiostat. Platinum-mesh working, platinum-wire counter, and anodized silver-wire quasi-reference electrodes were used for the electrolysis experiments. Experiments in the UV−vis and near-infrared regions were performed on solutions of approximately 2.0 × 10^{-5} and 2.0 × 10^{-3} M, respectively. Spectra were recorded at regular intervals until the solution had equilibrated at a given potential. The plasma-desorption mass spectra were obtained as described before.[16]

The purity of the complexes was checked using analytical high performance liquid chromatography (HPLC). A Waters 990 photodiode array HPLC system with a NEC PAC 3 computer, a Waters Model 6000A pump, a 20 μL injector loop, and a μ Particil SCX radial PAK cartridge have been used for the measurements. The detection wavelength was 280 nm. Chromatography was performed by using acetonitrile/water (4/1 v/v) containing 0.08 M LiClO$_4$ with a flow rate of 3.5 mL/min.

Results

An outline for the synthesis of the mononuclear, homo- and heterodinuclear ruthenium and osmium complexes with 1-methyl-3-(pyrazin-2-yl)-1,2,4-triazole (L) is presented in Scheme 1. By this controlled reaction of Os(bpy)$_2$ and Ru(bpy)$_2$ moieties

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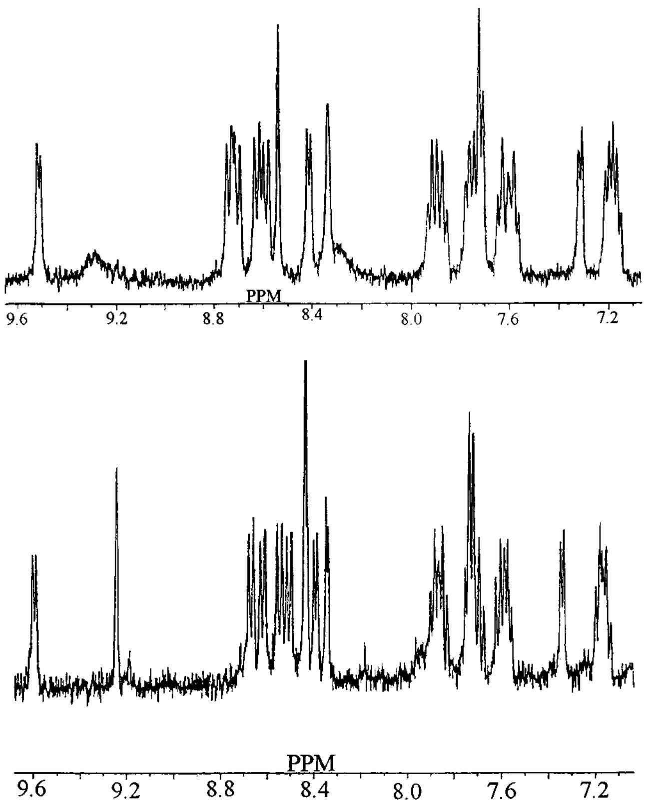

Figure 1. ^{1}H NMR spectra obtained for **OsCl** in $(CD_3)_2SO$ at (a) 323 and (b) 403 K.

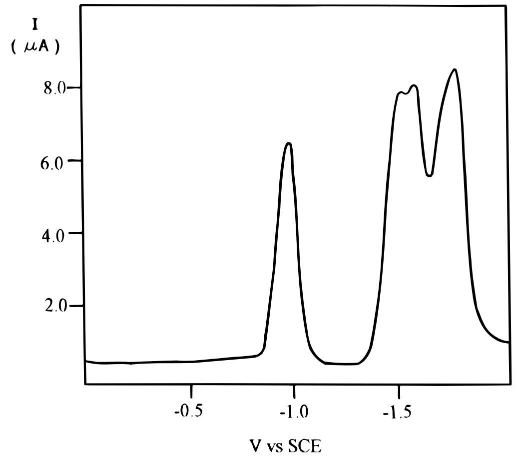

Figure 2. Differential pulse voltammogram for **RuRuCl** in acetonitrile containing 0.1 M TBAP.

with the two coordination sites of the pyrazyltriazole ligand seven complexes have been synthesized. The compounds have been fully characterized by elemental analysis and ^{1}H NMR spectroscopy. The ^{1}H NMR spectra obtained for OsCl are temperature dependent. Spectra obtained for this compound at 323 and 403 K are shown in Figure 1.

The electrochemical data of the compounds are listed in Table 1. Most redox proceses are reversible with peak-to-peak separations of about 90 mV. A typical differential pulse voltammogram obtained for the reduction of **RuRuCl** is presented in Figure 2. The absorption maxima in the visible part of the spectrum and the emission data are listed in Table 2. Some typical spectra are shown in Figures 3 and 4.

Table 2. UV/Vis Absorption and Emission Data for Compounds Prepared and Their Singly Oxidized Analogues[a]

compd	absorption[b] [λ_{max}/nm ($\epsilon/10^4$ M^{-1} cm^{-1})]				emission[c] (λ_{max}/nm) 77 K	300 K
OsCl	412 (1.21)	490 (1.33)	620 (0.40)	740 (sh)	n.o.	n.o.
Os	425 (1.20)	465 (1.38)	570 (0.39)	620 (sh)	708	755
Os$^+$	460 (0.4)	551 (0.35)				
Ru	437 (1.46)				577	633
Ru$^+$	415 (0.16)					
RuRuCl	440 (1.70)	530 (1.90)			705	730
RuRuCl$^+$	423 (0.95)	504 (1.9)				
OsOsCl	445 (1.76)	563 (2.55)	687 (1.08)	775 (1.87)	n.o.	n.o.
OsOsCl$^+$	423 (1.15)	522 (1.90)	749 (0.40)			
RuOsCl	443 (1.87)	560 (2.61)	745 (0.95)		n.o.	n.o
RuOsCl$^+$	418 (1.26)	509 (1.96)				
OsRuCl	455 (1.92)	545 (2.17)	680 (0.94)		786	n.o.
OsRuCl$^+$	425 (1.40)	520 (1.36)				

[a] n.o.: not observed. [b] In ethanol. [c] In CH_3CN at room temperature and methanol at 77 K.

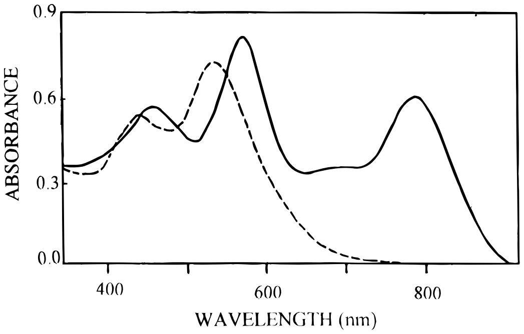

Figure 3. Absorption spectra of **RuRuCl** (a) and **OsOsCl** (b) in ethanol.

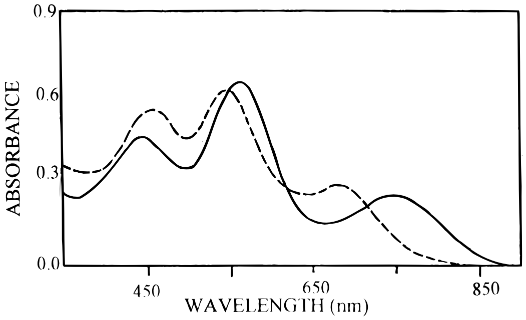

Figure 4. Absorption spectra of **RuOsCl** (a) and **OsRuCl** (b) in ethanol.

Spectroelectrochemical experiments have also been carried out. Upon one-electron oxidation of the dinuclear compounds **MM′Cl** stable mixed-valence species **MM′Cl$^+$** were obtained. The UV−vis spectral features observed for these singly oxidized compounds are listed in Table 2. A typical set of results obtained in the UV/vis region for **RuRuCl** is shown in Figure 5. Further oxidation of the compounds leads to a complete bleaching of the absorption features in the visible part of the spectrum. Intervalence charge transfer bands obtained upon the formation of the **MM′Cl$^+$** species are listed in Table 3. Since a slow decomposition of the fully oxidized species was observed, these spectra were not analyzed in detail. Near-infrared spectra for **OsOsCl$^+$** and the totally oxidized Os(III) compound are available as Supporting Information (Figure S1).

Irradiation of **OsRuCl** and **RuRuCl** in acetone leads to photochemically induced ligand labilization as shown in Figure 6 for **RuRuCl**. The spectroscopic changes observed upon radiation of **OsRuCl** are available as Supporting Information (Figure S2). HPLC analysis of the reaction shows the formation of **Os** and **Ru**, respectively. **Ru**, **Os**, **OsCl**, **OsOsCl**, and **RuOsCl** were all photostable under the conditions used for at least 4 h.

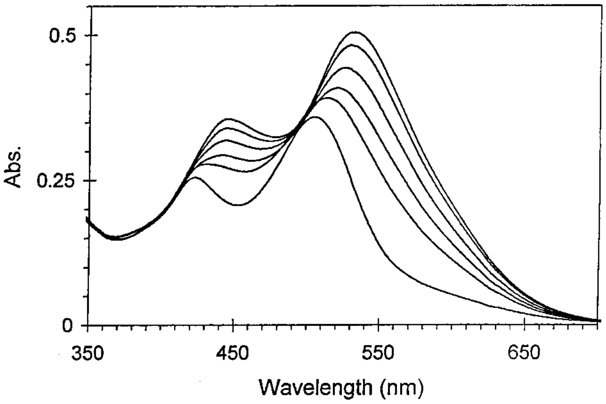

Figure 5. Spectroelectrochemistry for **RuRuCl** in the UV/vis region. Potentials applied from top to bottom: 0, 0.90, 0.93, 0.95, 0.97, and 1 V vs SCE. Solvent: acetonitrile.

Table 3. Intervalence Transition Parameters for Mixed-Valence Species

	E_{obs} (cm^{-1})	$E_{calc}{}^{a}$ (cm^{-1})	ϵ ($M^{-1}\ cm^{-1}$)	$\Delta\nu_{1/2}{}^{obs}$ (cm^{-1})	$\Delta\nu_{1/2}{}^{calc\ b}$ (cm^{-1})	α^2
RuRuCl$^+$	10400		480	4300	4000	1.8×10^{-3}
OsOsCl$^+$	7812	10500	360	2900	3200	1.2×10^{-3}
	5470		1200	1240	2250	1.7×10^{-3}
	4000		1050	460	1300	1.1×10^{-3}
RuOsCl$^+$	6000	13600	720	1070	2550	1.2×10^{-3}
OsRuCl$^+$	7690	7900	850	3100	3200	3.0×10^{-3}

[a] Values calculated with respect to **RuRuCl**; see text. [b] Values calculated according to: Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391.

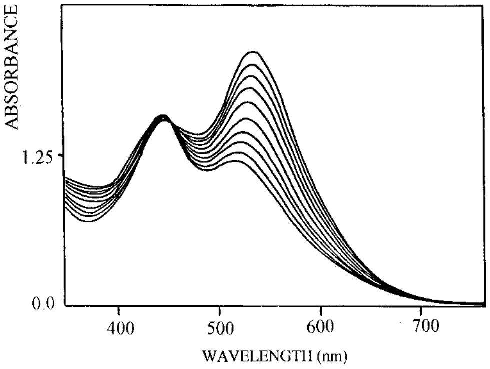

Figure 6. UV−vis absorption spectra of **RuRuCl** upon irradiation in acetone. The time between scans is 30 min.

Discussion

Synthesis and Characterization. By a systematic variation of the reaction components and the use of chromatographic techniques, all compounds reported in this study could be prepared without much difficulty. We were however unable to isolate **RuCl**. Even in the absence of water, a reaction condition that normally favors the formation of species with a [Ru(N_5)Cl] coordination mode,[17] only **Ru** was obtained. The osmium analog **OsCl** was obtained in small yield. Taking into account the decreased reactivity of osmium polypyridyl complexes, this is not unexpected. The homonuclear dimers were synthesized by reacting the ligand with an excess of *cis*-[M(bpy)$_2$Cl$_2$]. **RuOsCl** was prepared from the mononuclear ruthenium complex with an equimolar amount of *cis*-[Os(bpy)$_2$Cl$_2$]. **OsRuCl** was obtained in the same way but starting with mononuclear osmium complex and *cis*-[Ru(bpy)$_2$Cl$_2$]·2H$_2$O.

We have shown before[8−10,17,18] that ^{1}H NMR can be helpful in the elucidation of the coordination modes of triazole-based ligands. The ^{1}H NMR spectra and in particular the resonances observed for the ligand L were therefore carefully analyzed. Resonances observed for the bpy ligands are as expected and do not yield any additional information.

The proton NMR spectra of **Ru** and **Os** are very similar (see Experimental Section), indicating similar structures for both compounds. Comparison with NMR and X-ray structural analyses on related compounds[8−10] suggests binding of L *via* N4′ of the triazole group and N1 of the pyrazine ring. With this in mind, coordination of the second metal center in the mixed-metal dinuclear compounds has to be *via* either N2′ of the triazole ring or N4 of the pyrazine moiety. This issue can be addressed by considering the ^{1}H NMR spectra obtained for **OsCl**. For this compound evidence for the presence of the coordinated chloride anion is obtained from the H6-bpy proton resonance at 9.73 ppm. A resonance at such low field is indicative of the presence of nonaromatic ligands and is caused by the absence of through-space interaction of this H6 proton with an adjacent aromatic ring.[17] The spectra obtained for this compound were shown to be temperature dependent (see Figure 1), and spectra were therefore recorded between 203 and 403 K. At 323 K the H3 and H5 pyrazine-based resonances are broadened considerably and are ill-defined. However, upon heating, sharp resonances at 9.24, 8.45, and 8.34 ppm are observed that can be assigned to the pyrazine protons H3, H5, and H6, respectively. The doublet observed for the H5 proton at 8.45 ppm overlaps with the signal obtained for H6 of a bipyridyl ring. Upon lowering of the temperature, sharpening of the resonances is again observed at about 250 K. The triazole- and bpy-based resonances in the spectrum are hardly affected by a change in temperature. The observed broadening of the pyrazine protons, in particular H3, suggests the presence of hindered rotation around the Os−pyrazine bond and therefore coordination of the monodentate bound metal center *via* the N4 atom of the pyrazine ring. The NMR spectra observed for the dimers are complex but show similar features. Most importantly we can rule out a coordination of the N2′ triazole atom since in this case we would expect a significant shift of the neighboring methyl group to higher field because changes in electron density but most importantly because of interaction of the methyl group with the bpy ligands. In ruthenium complexes containing similar triazole ligands upfield shifts of between 0.5 and 1.0 ppm were observed as a result of these combined effects.[18] We therefore conclude that the coordination in all dinuclear compounds is the same and consistent with that observed for **OsCl**. This assumption is furthermore substantiated by the electrochemical properties of the compounds (*vide infra*).

Electrochemistry. The metal-based redox potentials for the RuCl and OsCl units are indicative of the coordination mode of the pyrazyltriazole ligand. The value observed for the **OsCl** complex of 0.45 V is similar to that reported by Meyer and co-workers for [(bpy)$_2$Os(pyr)Cl]$^+$ (0.51 V) (pyr = pyrazine).[19] The coordination of an azole type ligand rather than pyrazine would lead to a lower redox potential. For example, the value obtained for the [(bpy)$_2$Os(imidazole)Cl]$^+$ of 0.23 V[20] is substantially lower than that observed for **OsCl**. In addition, the redox potential reported by Meyer and co-workers of 0.88

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V for the $[Ru(bpy)_2(pyz)Cl]^+$ moiety and of 0.89 V in the corresponding dinuclear compound[21] is in line with the value observed for the $(bpy)_2RuCl$ center in this investigation. The only value reported in the literature for a $[(bpy)_2Ru(triazole)Cl]^+$ moiety is substantially lower at 0.66 V.[17] This again indicates that the monodentate unit is coordinated through the pyrazine rather than the triazole ring. In general, comparison of analogous osmium and ruthenium complexes shows a difference in the metal-based redox potential of 400 mV. This is explained by the higher energy of the 5d orbitals compared to the 4d orbitals of ruthenium leading to a lower redox potential for the osmium centers.[22] The dinuclear complexes reported exhibit two metal-based oxidation potentials. The difference in potentials varies from 180 mV for **OsRuCl** and 500 mV for **RuRuCl** and **OsOsCl** to 880 mV for **RuOsCl** (Table 1). These potential differences may be caused by a number of effects.[23-29] First, the different chemical environment of the two metal centers due to the different coordination modes will greatly influence the oxidation potential. In particular, the presence of the chloride group yields a significant lowering in oxidation potential. Also electrostatic effects play a role; oxidation of the first metal unit will cause an increase in charge of the complex, and this will result in a higher oxidation potential for the second metal unit. Finally, delocalization of charge of the mixed-valence species will shift the second oxidation potential to higher values than for localized systems. By comparison of the difference between the first and second oxidation potential of **OsOsCl** ($\Delta E = 500$ mV) with that observed between **Os** and **OsCl** (410 mV), the combined influence of electrostatic and delocalization effects of 90 mV in the dimer has been inferred. Similarly, the second, ruthenium-based oxidation potential in **RuOsCl** and **RuRuCl** is 90 mV higher than observed for **Ru**.

While in **RuOsCl** the low oxidation potential has been assigned to the $OsCl(bpy)_2$ site and the higher oxidation potential to the bidentate-bound $Ru(bpy)_2$ group, an unambiguous assignment of the first oxidation potential for **OsRuCl** cannot be given, since both redox couples are expected at around 0.9 V.

The first reduction potential of **Ru** is observed at −1.27 V and has been assigned to a reduction of the pyrazyltriazole ligand.[10,26] The second and third reductions are assigned to bpy-based reductions. The currents measured for all redox processes are indicative of one-electron redox reactions. The first reduction of **RuRuCl** at −0.97 V is at considerably less negative potential than the first reduction of **Ru**. This is explained by a decrease in the electron density on the bridging ligand because of the presence of a second electron accepting ruthenium moiety. As expected, the pyrazine-based reduction is still a one-electron reduction, but the bpy-based reductions are now two-electron reductions (see Figure 2). Similarly, we propose that in the **Os**, **OsRuCl**, **RuOsCl,** and **OsOsCl** complexes the first reduction is pyrazine-based. The first reduction of **OsCl** is observed at considerably more negative potentials (−1.44 V) and has been tentatively assigned as a bpy reduction.

Electronic Spectroscopy. The spectra obtained for the mononuclear compounds show the expected features. A series of bands in the UV can be assigned to bpy-based $\pi \rightarrow \pi^*$ transitions. L-based transitions of this type could not be identified. For **Ru** ^{1}MLCT bands are observed in the visible part of the spectrum at about 440 nm. For **Os** and **OsCl** such bands are observed at 465 and 490 nm, respectively. The lower energy of these transitions is explained by a destabilization of the metal-based ground state in the Os complexes. The osmium complexes show additional bands in the 500−800 nm region. These are assigned to formally spin forbidden ^{3}MLCT transitions, which in osmium-based systems become partially allowed because of the large spin−orbit coupling observed for this second-row metal ion.[22]

The absorption observed for **RuRuCl** at 530 nm is in agreement with values observed for systems such as $[Ru(bpy)_2Cl(pyz)Ru(bpy)_2Cl]^{2+}$ and can be assigned to the monodentate coordinated RuCl unit. Work by Meyer and co-workers has shown that, upon assembly of the $[Ru(bpy)_2(pyz)Cl]^+$ unit in the dinuclear complex $[Ru(bpy)_2Cl(pyz)Ru(bpy)_2Cl]^{2+}$, a shift to lower energy is observed for the lowest MLCT transition from 478 to 513 nm.[19,21] For $[Ru(NH_3)_5(pyz)Ru(bpy)_2Cl]^{3+}$ a similar shift from 455 to around 500 nm was observed for the $Ru(NH_3)_5$ moiety upon incorporation into the dinuclear compound.[19] With this in mind it is unlikely that the band observed at 440 nm in **RuRuCl** can be assigned to the Ru → L transition in the Ru moiety in this complex. We therefore propose that in **RuRuCl** the lowest energy MLCT band for the bidentate coordinated Ru center is hidden under the strong band at 530 nm. This analysis is confirmed by the spectra observed for the mixed-valence compounds discussed below. Because of their complexity the osmium spectra were not analyzed in detail. However, it is noted that the absorption spectrum of **OsOsCl** is not simply the sum of the spectra **Os** and **OsCl**. The interaction between the metal centers, as inferred from the electrochemical experiments, also affects the energies of the excited-state energy levels. It is worth noting that in the 400−500 nm region the osmium and ruthenium compounds show quite similar features (Figures 3 and 4). All dinuclear complexes show a band between 440 and 455 nm and a second one between 530 and 563 nm. This complicates a complete assignment of the absorption spectra of the compounds.

Mixed-Valence Compounds. In this section the spectral features of the $\mathbf{MM'Cl^+}$ mixed-valence compounds in the UV/vis region are discussed. In the UV part of the spectra oxidation of the first metal center leads in all compounds to the formation of a new double peak between 300 and 320 nm. The appearance of this peak is typical for the formation of trivalent Ru and Os species.[30] The disappearance of the band at 437 nm of the mononuclear **Ru** upon oxidation of the complex is in agreement with its assignment as a MLCT band. A new weak band at 680 nm has been assigned to a LMCT (ligand-to-metal charge transfer) band originating from the Ru(III) species.[7,31] In a similar way the visible absorptions observed for **Os** disappear upon oxidation.

The electrochemical data suggest that, upon formation of the mixed-valence species $\mathbf{RuRuCl^+}$, the RuCl moiety is oxidized first and therefore any features associated with this center should be absent in the spectrum obtained for the singly oxidized species (Figure 5). The remaining band at 504 nm (Table 2) has consequently been assigned as a ^{1}MLCT transition located

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on the Ru center remaining. It has been shown before that upon oxidation of one of the metal centers in pyrazine dimers only a relatively small change is observed in the absorption spectrum of the remaining Ru(II) moiety even if interaction between the centers is present.[19] The values observed in the mixed-valence compound for the bidentate bound Ru center, therefore, support our earlier assumption that in **RuRuCl** species the lowest ^{1}MLCT absorption of this Ru unit is located under the 530 nm band.

Using similar arguments the bands at 563, 455, 687, and 775 nm that disappear upon the formation of the mixed-valence **OsOsCl**$^+$ species have been assigned to ^{1}MLCT and ^{3}MLCT bands from the monodentate bound OsCl site. The remaining absorptions at 526 and 428 nm are assigned to transitions originating from the bidentate bound metal center.

A single electron oxidation of **RuOsCl** leads to the disappearance of the absorptions at 745, 560, and 443 nm, which on the basis of the electrochemical data are assigned to the OsCl moiety. The new features at 504 and 423 nm are assigned to the ruthenium site. The energy of these absorptions is very similar to those observed for **RuRuCl**$^+$, suggesting that the bidentate coordinated Ru moieties in both compounds have very similar properties.

As already stated above the location of the first oxidation in **OsRuCl** is difficult to establish since both sites have similar redox potentials. Upon formation of **OsRuCl**$^+$ bands at 683, 545, and 459 nm disappear while new bands are observed at 523 and 425 nm. The band at 680 nm is most likely associated with the osmium center, while the new band at 523 nm is similar to that observed for the RuCl center in **RuRuCl**. We therefore propose that the first redox process is osmium-based.

Intervalence Transitions. In this section the spectroscopic features of the singly oxidized compounds in the near infrared region are investigated. **RuRuCl**$^+$ shows a weak absorption band at 10 400 cm^{-1} that disappears upon further oxidation. By comparison with other similar compounds[19,21] and since the band disappears upon further oxidation, this absorption has been assigned to an intervalence transition (IT). Information about the electron delocalization between the metal centers (α^2) can be obtained from the spectral features observed for the IT band using eq 1,[22,32,33] where ϵ is the extinction coefficient of the IT

$$\alpha^2 = \frac{(4.2 \times 10^{-4})\epsilon(\Delta\nu_{1/2}{}^{\mathrm{obs}})}{d^2 E_{\mathrm{obs}}} \qquad (1)$$

band (M^{-1} cm^{-1}), $\Delta\nu_{1/2}{}^{\mathrm{obs}}$ is observed bandwidth (cm^{-1}), d is the distance estimated between the metal centers (6.8 Å), and E_{obs} is energy of the IT band. The values obtained from this equation for the various compounds are given in Table 3 and are similar to those reported for other pyrazine-bridged dimers.[21]

For the compounds containing osmium centers the analysis in the near-infrared region is complicated by the overlap of solvents peaks, Os(III)-based dπ−dπ transitions, and intervalence bands. **Os$^{\mathrm{II}}$Os$^{\mathrm{III}}$Cl**$^+$ exhibits bands at 7812, 5470, and 4000 cm^{-1}. Upon further oxidation of the species bands at 6290, 5305, and 4274 cm^{-1} are observed, while the three bands observed for the mixed-valence species have disappeared. We assign the bands observed for the totally oxidized species to transitions between different spin−orbit states localized at the Os(III) centers.[21] The bands observed for the mixed-valence species are tentatively assigned to the three IT bands expected for a dinuclear osmium compound. The parameters obtained for these transitions are given in Table 3.

A band observed at 6000 cm^{-1} in the spectrum of **RuOsCl**$^+$ has been assigned to an intervalence transition since the band disappears upon formation of the fully oxidized species. In the totally oxidized species a band at 6349 cm^{-1} has been assigned to a transition between different spin−orbit states located on the osmium(III) center. **OsRuCl**$^+$ shows an IT band at 7690 cm^{-1}. For this compound bands at 5947 and 4814 cm^{-1} also appear in the spectrum upon initial oxidation, which are assigned as Os(III) spin−orbit state transitions. This also indicates that the first redox process is osmium-based.

Some additional remarks can be made about the intervalence bands. As shown previously, the location of the IT bands is partly dependent on the coordination environment of the two metal centers.[21,34] By comparing the differences in the metal-based redox potentials for the various compounds, we can make some predictions about the location of intervalence transitions. The difference in these redox potentials ($\Delta E_{1/2}$) for **RuRuCl** is 490 mV and for **OsRuCl** is 180 mV. The difference in $\Delta E_{1/2}$ for the compounds ($\Delta\Delta E_{1/2}$ = 310 mV or 2500 cm^{-1}) suggests by comparison with **RuRuCl**$^+$ (10 400 cm^{-1}) an energy of 7900 cm^{-1} for the intervalence transition in **OsRuCl**$^+$, close to the observed one at 7690 cm^{-1} (Table 3).

Applying the same approach to **RuOsCl**, we calculate an energy of 13 600 cm^{-1} for the IT transition for **RuOsCl**$^+$. This is at quite high energy, and this band is therefore most likely buried under the other bands in the visible region. The band observed at 6000 cm^{-1} is therefore most likely one of the other two IT bands expected. The calculated IT band energy of 10 500 cm^{-1} for the **OsOsCl**$^+$ species is higher that the value observed (Table 3). This suggests that the transition observed at 7812 cm^{-1} is not the highest energy IT transition. If that is the case, one of the two bands observed at lower energy is not related to IT transitions. The spectroelectrochemical data observed for the mixed-valence compounds are clearly indicative of a weak interaction via the pyrazine ring. In comparison with other compounds this most likely occurs *via* a superexchange mechanism[35] involving pyrazine-based excited-state levels.

Emission Spectroscopy. The complexes **OsCl**, **OsOsCl**, and **RuOsCl** do not exhibit emission at room temperature or at 77 K. This is in line with the observed low oxidation potential of the OsCl unit, yielding a small energy gap between excited and ground state. Consequently the emission is expected to be weak[36,37] and in addition most likely outside the range of our equipment (limit of 900 nm). Emission is, however, observed for **RuRuCl** and **OsRuCl**. **RuRuCl** exhibits a weak emission at 705 nm at 77 K and 730 nm at room temperature (Table 2) in agreement with the energy expected for the emission of a RuN$_5$Cl moiety.[20]

While the emission in **RuRuCl** is based on the RuCl center, for **OsRuCl** the situation is less clear. The spectroelectrochemical data suggest that, in **OsRuCl**, the Os(bpy)$_2$ moiety has a lower oxidation potential than the Ru(bpy)$_2$Cl moiety (*vide supra*), and one would consequently infer the emission to be Os(bpy)$_2$-based. Furthermore the emission energy observed is much lower than found for **RuRuCl**. This makes a RuCl-based emission unlikely. The fact that the emission band of **OsRuCl**

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is at considerably lower energy than observed for the mononuclear **Os** compound is explained by a stabilization of the emitting π^* level in the dinuclear compound.[7,38,39]

All dinuclear compounds could in principle show a dual emission. This is however not observed, and this reflects effective quenching of the higher energy emitting state. For example, excitation of **RuRuCl** at various wavelengths between 550 and 400 nm at 77 K showed only a RuCl-based emission at 705 nm, indicating that the emission occurs only from the low energy RuCl unit. Quenching of the higher energy emission can occur either by an energy-transfer or a electron-transfer mechanism.[40-42] Support from the presence of an energy-transfer mechanism is obtained from the fact that the excitation spectrum of **RuRuCl** attained at 705 nm is quite similar (λ_{max} at 511 and 446 nm) to the absorption bands assigned to the **RuRuCl** complex (530 and 440 nm). Similar arguments are also valid for **OsOsCl** and **RuOsCl**.

Photochemical Properties. As expected **Os**, **OsCl**, and **OsOsCl** are stable upon irradiation in acetone for at least 4 h. This photostability can be explained by the large ligand-field splitting of the Os(II) ion, which prevents population of the photoreactive ^{3}MC state.[37] Also **Ru** and **RuOsCl** are photostable upon irradiation in the same solvent. The stability of the mononuclear **Ru** complex is most likely caused by the relatively low-lying π^* orbitals of pyrazyltriazole ligand, yielding a relatively large ^{3}MLCT$-^3$MC gap. Such an effect has been noted previously for other $[Ru(bpy)_2(LL)]^{2+}$ complexes (LL = 2,2′-bipyrazine, 2,2′-bipyrimidine).[43] In addition, for **RuOsCl** efficient energy-transfer processes take place from the ruthenium center to the OsCl moiety, which further prevent population of the ^{3}MC state located on the ruthenium(II). Irradiation of **RuRuCl** and **OsRuCl** in acetone leads to a well-defined clean photochemically induced ligand exchange reaction (Figure 6). The spectral changes observed, together with an HPLC analysis of the reaction, indicate the formation of the mononuclear **Ru** and **Os** compound, respectively. The photolability of the ruthenium site in **OsRuCl** is interesting since, on the basis of the electrochemical and emission results, we concluded that in this compound the emitting site is most likely osmium-based. In this case we would not expect a photolabilization of the ruthenium site. An explanation for the behavior observed may be that the energies of the Os- and Ru-based ^{3}MLCT states are comparable. In that case equilibrium between the Ru- and Os-based ^{3}MLCT states can be established[44] and the ^{3}MC state of the Ru site can be thermally populated leading to the observed photolability.

Conclusions

The results obtained here suggest that pyrazyltriazoles have several attractive features as bridging ligands, and in view of the continuing interest in the pyrazine-based bridging systems this new ligand offers a valuable alternative approach. In the ligand a strong π-acceptor, pyrazine, is bound to a strong σ-donor, the triazole ring. This yields compounds that are substantially different from those reported by Brewer,[45] Balzani,[46] and others,[7] where pyrazine groupings are bound to pyridine type moieties. In addition the presence of the triazole ring might lead to solvent-dependent behavior as recently observed by Meyer and co-workers.[47] In view of this we are at present investigating pyrazine−triazole-based ligands with triazole rings containing an N−H bond rather than N−CH_3. This will allow the study of the interaction between the two units in the dimer as a function of the protonation of the triazole ring and introduce a strong σ-donor in the bridge.

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Supporting Information Available: Figures showing spectroelectrochemical data for the compound **OsOsCl** (Figure S1) and UV−vis absorption spectra of **OsRuCl** obtained upon radiation in acetone (Figure S2) (2 pages). Ordering information is given on any current masthead page.

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