Contribution from the Departamento de Quimica, Faculdade de Filosofia, Ciências e Letras de Ribeirão Preto,
Universidade de São Paulo, 14049 Ribeirão Preto, São Paulo, Brazil

Spectra, Reduction Potentials, and Coordinated Pyrazine Basicities in the Ruthenium(II) Complexes *trans*-Ru(NH₃)₄LL′ⁿ⁺ [1]

Maria Lúcia Bento and Elia Tfouni*

The syntheses and some properties of several disubstituted ruthenium(II) ammine complexes *trans*-Ru(NH₃)₄LL′ⁿ⁺ (L, L′ = pyridine (py), 4-picoline (4-pic), isonicotinamide (isn), 4-acetylpyridine (4-acpy), pyrazine (pz), or pyrazinium (pzH⁺)) are reported. The visible range spectra of these species each display, in general, two metal-to-ligand charge-transfer absorptions, the lower energy transition being the much more intense. The higher energy charge-transfer band generally appears when L ≠ L′, and it is not observed in the spectra of the complexes *trans*-Ru(NH₃)₄(py)₂²⁺, *trans*-Ru(NH₃)₄(4-pic)₂²⁺, and *trans*-Ru(NH₃)₄(py)(4-pic)²⁺, with ligands of relatively poor electron-withdrawing ability. The aqueous solution basicities of the coordinated pz in the new complexes have been determined, and when earlier data are included, the basicity order Ru(NH₃)₅pz²⁺ > *trans*-Ru(NH₃)₄(4-pic)(pz)²⁺ ≳ *trans*-Ru(NH₃)₄(py)(pz)²⁺ > *trans*-Ru(NH₃)₄(isn)(pz)²⁺ ≳ *trans*-Ru(NH₃)₄(4-acpy)(pz)²⁺ ≃ *trans*-Ru(NH₃)₄(pz)(pz)²⁺ > free pz > *trans*-Ru(NH₃)₄(pzH)(pz)³⁺ > Ru(NH₃)₅pz³⁺ is obtained. Formal reduction potentials (E_f) were obtained by cyclic voltammetry. For each series of *trans*-Ru(NH₃)₄LL′³⁺/²⁺, considering a fixed L ligand, the more positive E_f values are, in general, obtained with ligands L′ of higher π-acceptor and lower σ-donor abilities.

In an earlier paper,[2] some properties of trans-disubstituted tetraammineruthenium(II) complexes, *trans*-Ru(NH₃)₄LL′²⁺ (where L and L′ each are substituted pyridines) were reported. The visible range spectra of these complexes each display two metal-to-ligand charge-transfer (MLCT) absorptions, the lower energy transition being the much more intense. However, the higher energy charge transfer band generally appears when L ≠ L′. In order to examine the generality of these observations, several similar trans complexes were investigated. Formal reduction potentials of these complexes were obtained. We also examined the aqueous solution acid/base behavior of the pyrazine (pz) complexes and compared them with earlier data.

Experimental Section

Chemicals and Reagents. Ruthenium trichloride (RuCl₃·3H₂O) (Strem) was the starting material for ruthenium complex synthesis. Pyrazine (pz) (99.9%, Gold Label) (Aldrich) was used as supplied. Isonicotinamide (isn) (Aldrich) was recrystallized from hot water, with activated charcoal, before use. 4-Picoline (4-pic) (Aldrich) and 4-acetylpyridine (4-acpy) were distilled under reduced pressure before use. Sodium tetrafluoroborate (NaBF₄) was recrystallized from water. Ether, methanol, ethanol, and acetone were purified before use. Doubly distilled water was used throughout this work. All other chemicals were reagent grade and were used as supplied.

Synthesis. Ruthenium complexes were prepared by using previously described[2] procedures for trans complexes, *trans*-[Ru(NH₃)₄LL′](BF₄)₂, where L = L′ and L ≠ L′. *Trans*-[Ru(NH₃)₄(4-pic)₂](BF₄)₂ and *trans*-[Ru(NH₃)₄(4-acpy)₂](BF₄)₂, however, were synthesized by the method used for L ≠ L′,[2] since we were unsuccessful with the other method for these two complexes. The compounds were recrystallized, as described,[2] several times.

Analysis. Carbon, hydrogen, and nitrogen percentages were determined by microanalysis. Analytical data are listed in Table I.

Physical Measurements. The cyclic voltammograms of the complexes were taken with the same apparatus previously described[3] and under the same conditions.[3] Electronic spectra were recorded at room temperature in a Beckman UV-5270, a Perkin-Elmer-Coleman 575, or a Varian 634-S recording spectrophotometer using quartz cells. Solutions used to measure extinction coeficients were prepared gravimetrically with quantitative dilution. The pK_a values were determined by using the method described previously.[4,5] The reported pK_a is an average of three independent determinations.

Results and Discussion

Spectra of Ruthenium(II) Complexes. The electronic spectral data for the series of *trans*-Ru(NH₃)₄LL′²⁺ complexes, along with those of related compounds, are summarized in Table II. Figure 1 shows the spectra of some of these complexes.

The strong absorption bands in the UV region are similar in intensity and position to bands observed in the spectra of the free ligands and can be assigned as intraligand π–π* (IL) in character,[4] as is the case for other *trans*-Ru(NH₃)₄LL′²⁺.[2] The electronic spectra of these complexes are dominated in the visible region by one very intense absorption band (MLCT-1, ε > 10⁴ M⁻¹ cm⁻¹), assigned as a MLCT transition in analogy with the assignments for other *trans*-Ru(NH₃)₄LL′ⁿ⁺ complexes.[2]

This transition is highly sensitive to the substituents on the aromatic heterocycles as evidenced by the red shift upon protonation of the pyrazine complexes. In addition to the MLCT-1 band, there is a less intense band, previously assigned as MLCT-2 (ε ∼ 10³ M⁻¹ cm⁻¹) apparent at higher energy (Figure 1). This is in contrast with the electronic spectra of Ru(NH₃)₅L²⁺ complexes, which show one CT band,[4] and of *cis*-Ru(NH₃)₄LL′²⁺, which display two CT bands of similarly high intensities (ε ∼ 10⁴ M⁻¹ cm⁻¹).[3,10] Excepting *trans*-Ru(NH₃)₄(4-pic)(py)²⁺, where the second band was not observed, the heterodisubstituted (L ≠ L′) complexes display both MLCT-1 and MLCT-2 bands. However, in *trans*-Ru(NH₃)₄(4-acpy)(isn)²⁺ (Figure 1) and *trans*-Ru(NH₃)₄(4-acpy)(pz)²⁺, MLCT-2 is very weak. On the other hand, the homodisubstituted complexes (L = L′) *trans*-Ru(NH₃)₄(py)₂²⁺ and *trans*-Ru(NH₃)₄(4-pic)₂²⁺ (Figure 1) display only one MLCT band, while the others display two. This second band is also assigned for *trans*-Ru(NH₃)₄(4-acpy)₂²⁺ (Figure 1) as a MLCT, as for the other trans complexes.[2] Assignment of MLCT-2 was made by using the same arguments used for MLCT-1 assignment: λₘₐₓ is solvent- and substituent-dependent, and extinction coefficients assume values up to 1800 M⁻¹ cm⁻¹, much higher than expected for LF (ligand-field) transitions. Notably, similar bands have not been reported for analogous Ru(NH₃)₅(py-X)²⁺ complexes,[4,9] indicating that these bands are characteristic of the bis(heterocycle) complexes. The lowest energy LF transition expected for ruthenium(II) ammine complexes with LF strength comparable to pyridine was predicted to be nearby 400 nm, but these are obscured by MLCT bands.[9] This assignment was based on inference from complexes lacking back-bonding, such as Ru(NH₃)₆²⁺. However, even considering orbital energy splitting due to the lowering of symmetry and taking into account increased LF transition energy due to back-bonding, the observed features of this band fit a CT pattern better. At best, LF transitions may merely be contributing to the total absorption in that region.

As pointed out previously,[2] the origin of the MLCT-2 band is

(1) Taken in part from: Bento, M. L. Master's Dissertation, Instituto de Quimica de Araraquara da UNESP, Araraquara, SP, 1985.
(2) Tfouni, E.; Ford, P. C. *Inorg. Chem.* **1980,** *19,* 72.
(3) Pavanin, L. A.; Giesbrecht, E.; Tfouni, E. *Inorg. Chem.* **1985,** *24,* 4444.
(4) Ford, P. C.; Rudd, De F. P.; Gaunder, R.; Taube, H. *J. Am. Chem. Soc.* **1968,** *90,* 1187.
(5) Clarke, R. E.; Ford, P. C. *Inorg. Chem.* **1970,** *9,* 495.
(6) Ford, P. C.; Sutton, C. *Inorg. Chem.* **1969,** *8,* 1544.
(7) (a) Isied, S. S. Ph.D. Thesis, Stanford University, Stanford, CA, 1973. (b) Isied, S. S.; Taube, H. *Inorg. Chem.* **1976,** *15,* 3070.
(8) Gaunder, R. G.; Taube, H. *Inorg. Chem.* **1970,** *9,* 2627.
(9) (a) Malouf, G.; Ford, P. C. *J. Am. Chem. Soc.* **1977,** *99,* 7213. (b) Malouf, G. Ph.D. Thesis, Univeristy of California, Santa Barbara, CA, 1977.

(10) Pavanin, L. A.; Giesbrecht, E.; Tfouni, E., work in progress.

Table I. Elemental Analyses of *trans*-[Ru(NH₃)₄LL'](BF₄)₂ Complexes

	% N		% C		% H	
complex	calcd	found	calcd	found	calcd	found
trans-[Ru(NH₃)₄(pz)(py)](BF₄)₂	19.53	19.80	21.53	22.00	4.22	4.15
trans-[Ru(NH₃)₄(4-pic)(py)](BF₄)₂	16.32	16.51	25.66	25.82	4.70	4.68
trans-[Ru(NH₃)₄(isn)(4-pic)](BF₄)₂	17.57	17.65	25.83	25.45	4.52	4.77
trans-[Ru(NH₃)₄(4-pic)(pz)](BF₄)₂	19.00	19.72	23.28	22.97	4.49	4.71
trans-[Ru(NH₃)₄(4-acpy)(4-pic)](BF₄)₂	15.09	15.75	28.03	28.57	4.71	4.47
trans-[Ru(NH₃)₄(4-acpy)(py)](BF₄)₂·H₂O	14.98	14.84	25.69	25.28	4.67	3.89
trans-[Ru(NH₃)₄(4-acpy)(isn)](BF₄)₂	16.73	16.10	26.64	27.04	4.30	4.10
trans-[Ru(NH₃)₄(isn)(pz)](BF₄)₂·H₂O	19.90	20.53	21.33	21.35	4.30	4.45
trans-[Ru(NH₃)₄(isn)(py)](BF₄)₂·2H₂O	16.90	16.88	22.78	23.11	4.69	4.28
trans-[Ru(NH₃)₄(4-acpy)(pz)[(BF₄)₂	18.02	18.13	24.29	23.37	4.26	4.40
trans-[Ru(NH₃)₄(4-pic)(4-pic)](BF₄)₂	15.88	14.95	27.24	27.77	4.95	4.92
trans-[Ru(NH₃)₄(4-acpy)(4-acpy)](BF₄)₂	14.36	14.79	28.74	29.64	4.48	4.53
trans-[Ru(NH₃)₄(py)(py)](BF₄)₂	16.77	16.84	23.97	23.73	4.43	4.30

Table II. Electronic Spectral Data of *trans*-Ru(NH₃)₄LL'ⁿ⁺ and Related Complexes in Aqueous Solutions[a]

	λ_{max}, nm (log ϵ)[b]		
complex	MLCT-1	MLCT-2	IL (intraligand bands)
trans-Ru(NH₃)₄(4-pic)₂²⁺	417 (4.26)		244 (3.84)
trans-Ru(NH₃)₄(4-pic)(py)²⁺	420 (4.21)		245 (3.91)
trans-Ru(NH₃)₄(4-pic)(isn)²⁺	474 (4.21)	355 (3.51)	260 (3.59); 246 (3.83)
trans-Ru(NH₃)₄(4-pic)(pz)²⁺	477 (4.23)	344 (3.44)	258 (3.81); 252 (3.91); 245 (3.83)
trans-Ru(NH₃)₄(4-pic)(pzH)³⁺ [c,d]	558 (4.26)	307 (3.17)	
trans-Ru(NH₃)₄(4-pic)(4-acpy)²⁺	513 (4.17)	358 (3.54)	271 (3.56); 249 (3.66); 243 (3.72); 222 (3.92)
trans-Ru(NH₃)₄(py)₂²⁺	422 (4.24)		244 (3.96)
	423 (4.22)[e]		245 (3.93)[e]
trans-Ru(NH₃)₄(py)(isn)²⁺	470 (4.21)	363 (3.45)	260 (3.57); 246 (3.88); 214 (2.93)
	470[f]		
trans-Ru(NH₃)₄(py)(pz)²⁺	475 (4.28)	352 (3.42)	259 (3.88); 253 (3.96); 251 (4.00)
	474 (4.27)[g]	348 (3.40)[g]	251 (3.99)[g]
trans-Ru(NH₃)₄(py)(pzH)³⁺ [g,h]	559 (4.31)	~310 (3.18)	272 (3.89); 237 (3.74)
trans-Ru(NH₃)₄(py)(4-acpy)²⁺	507 (4.11)	369 (3.52)	272 (3.53); 246 (3.80); 219 (3.90)
	508 (4.21)[g]	366 (3.48)[g]	271 (3.56); 247 (3.78); 221 (3.91)[g]
trans-Ru(NH₃)₄(isn)(pz)²⁺	490 (4.34)	380 (3.19)	258 (4.01); 220 (4.05)
trans-Ru(NH₃)₄(isn)(pzH)³⁺ [d,i]	565 (4.34)	365 (3.09)	
trans-Ru(NH₃)₄(isn)(4-acpy)²⁺	514 (4.28)	378 (3.25)	262 (3.80); 214 (4.17)
trans-Ru(NH₃)₄(pz)₂²⁺	486 (4.34)	375 (3.04)	256 (4.13)
trans-Ru(NH₃)₄(pz)(pzH)³⁺ [g,j]	572 (4.32)	375 (3.11)	273 (3.92); 258 (sh) (3.85)
trans-Ru(NH₃)₄(pzH)₂⁴⁺ [g,k]	626 (4.46)	~440 (2.93)	282 (3.95); 258 (sh) (3.81)
trans-Ru(NH₃)₄(pz)(4-acpy)²⁺	502 (4.30)	368 (3.11)	274 (3.65); 257 (4.14); 219 (4.24)
trans-Ru(NH₃)₄(pzH)(4-acpy)³⁺ [d,l]	576 (4.37)	380 (4.07)	
trans-Ru(NH₃)₄(4-acpy)₂²⁺	532 (4.32)	383 (3.27)	270 (3.80); 221 (4.18)
cis-Ru(NH₃)₄(isn)₂²⁺ [m]	478 (4.13)	413 (4.01)	257 (3.88)
cis-Ru(NH₃)₄(isn)(pz)²⁺ [m]	476 (4.14)	405 (3.98)	257 (4.05)
Ru(NH₃)₅(py)₂²⁺ [n]	407 (3.89)		244 (3.66)
Ru(NH₃)₅(4-pic)²⁺ [n]	397 (3.89)		244 (3.66)
Ru(NH₃)₅(isn)²⁺ [o]	479 (4.06)		260 (3.66)
Ru(NH₃)₅(4-acpy)²⁺ [p]	523 (3.97)		271 (3.53); 223 (3.76)
Ru(NH₃)₅(pz)²⁺ [n]	472 (4.03)		253 (3.78)
Ru(NH₃)₅(pzH)³⁺ [n]	529 (4.08)		272 (3.81)

[a] In dilute aqueous solution except where noted; BF₄⁻ salts in each case. [b] ϵ is the molar extinction coefficient. [c] In 0.33 N aqueous HCl (μ = 1 M, (H⁺, Na⁺, Cl⁻)). [d] Measured only in the visible–near-UV region. [e] Reference 6. [f] Reference 7; measured in solution with excess isonicotinamide, without isolating the complex. [g] Reference 2. [h] In 1.0 N aqueous HCl (μ = 2 M (H⁺, Na⁺, Cl⁻)). [i] In 0.33 N aqueous HCl (μ = 1 M (H⁺, Na⁺, Cl⁻)). [j] In 2 N aqueous HCl. [k] In 10 N aqueous HCl. [l] In 0.16 N aqueous HCl (μ = 1 M (H⁺, Na⁺, Cl⁻)). [m] Reference 3. [n] Reference 4. [o] Reference 8. [p] Reference 9.

not obvious. Earlier workers[11] observed only one visible CT band[11] (MLCT-1) in some symmetrically substituted *trans*-Ru-(NH₃)₄L₂²⁺ complexes but two CT bands of similar intensities for *cis*-Ru(NH₃)₄L₂²⁺. Zwickel and Creutz attempted to explain these differences in terms of a qualitative molecular orbital (MO) utilizing one metal d_π orbital and two π^* orbitals, one from each ligand L. This model, successful in several features but lacking further evidence at the time, assumed that the ligands L were in mutually perpendicular planes in the cis complexes and were coplanar in the trans complexes. According to this model, two CT bands are predicted for the cis complexes, while for the trans the second, higher energy, band predicted is parity forbidden.

According to this model, the cis and trans bands would lie at the same energy. Tfouni an Ford,[2] noticing the presence of a second, relatively weaker, absorption band in some trans-heter-odisubstituted complexes and its fading in the symmetrically disubstituted ones, modified the model, including two different π^* orbitals, one from each different L ligand in the hetero complexes. However, recent studies[3] with *cis*-Ru(NH₃)₄(isn)L²⁺ showed that for cis complexes, the model would require two d_π metal orbitals and two π^* ligand orbitals, since the spatial orientation of the L ligands, in the cis complexes, is not in mutually perpendicular planes as previously[11] assumed. As a result, although two CT bands would still be expected to occur (in fact, more transitions are allowed), the calculated energy for the higher energy band in the trans complexes, using the Zwickel and Creutz model,[11] as it is, is no longer valid, since it is based partly on the energies of the cis CT bands. However, since there are no contrary indications but rather further support, the ligands L in trans complexes are still assumed to be coplanar. The modified qualitative MO model still holds for trans complexes, and it uses linear combinations of one d_π metal orbital plus one π^* orbital,
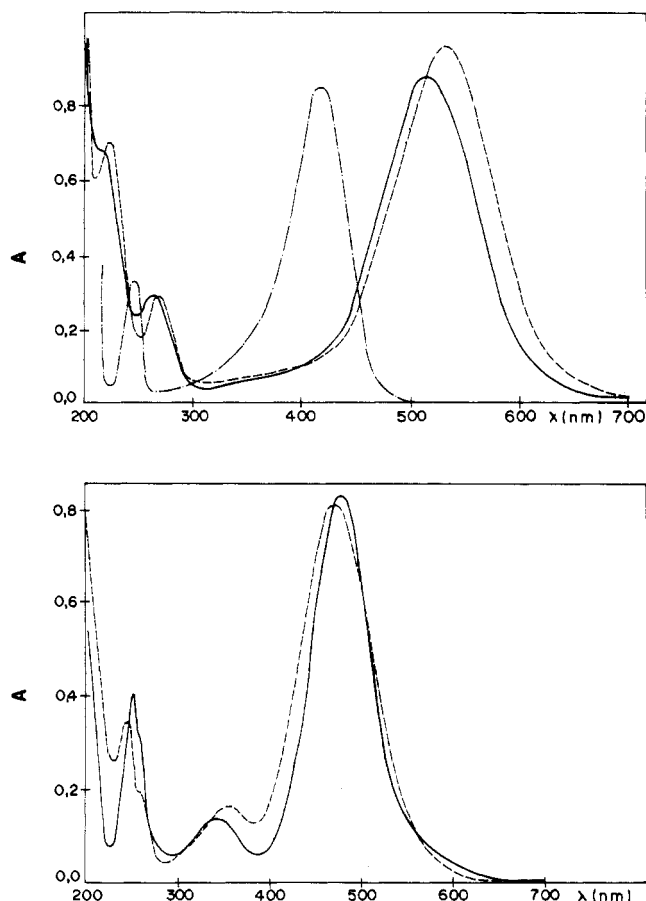
(11) Zwickel, A.; Creutz, C. *Inorg. Chem.* **1971**, *10*, 2395.

Figure 1. Electronic spectra in dilute aqueous solutions. Upper: (—) *trans*-Ru(NH$_3$)$_4$(4-acpy)(isn)$^{2+}$; (- -) *trans*-Ru(NH$_3$)$_4$(4-acpy)$_2$$^{2+}$; (—·—) *trans*-Ru(NH$_3$)$_4$(4-pic)$^{2+}$. Lower: (—) *trans*-Ru(NH$_3$)$_4$(4-pic)(isn)$^{2+}$; (- -) *trans*-Ru(NH$_3$)$_4$(4-pic)(pz)$^{2+}$.

π_L* and $\pi_{L'}$* from each ligand, to form three delocalized molecular orbitals, ψ_1, ψ_2, and ψ_3 (ψ_1 filled and ψ_2 and ψ_3 empty in the ground state). Accordingly, two transitions are possible, one (from the ground state to a state with ψ_1 and ψ_2 both half-filled), lower in energy, is allowed and the other (from the ground state to a state with ψ_1 and ψ_3 both half-filled), higher in energy, is symmetry forbidden. Thus, in homodisubstituted complexes this band is forbidden, having very low intensity, and in heterodisubstituted complexes this forbiddance is relaxed and the band intensity is enhanced.

With exceptions noted, this model is in agreement with the spectra of the trans-disubstituted complexes. In the symmetrically disubstituted complexes, the MLCT-2 band is very weak or absent, while in the unsymmetrical ones it is enhanced. In the spectra of (4-pic)(py) and (4-pic)(4-pic) complexes, the MLCT-2 bands may be enveloped by the MLCT-1 or IL bands, since π* orbitals lie high in energy in these ligands of relatively poor electron-withdrawing ability.

However, as previously noted,[2,11] this model is very simplistic, needing improvements such as more accurate electronic descriptions and energy calculations. As mentioned above, it also can be argued that the MLCT-2 band is rather LF in character, but at present, lacking further evidence, it is best described as MLCT.

pK_a of Coordinated Pyrazine. The marked changes in the absorption spectra of the ruthenium(II) pyrazine complex upon protonation of the remote pyrazine nitrogen (Figure 1) allow evaluation of complex pK_a[4,5] (–log K for eq 1), using similar experimental procedures and data treatment as previously reported.[2]
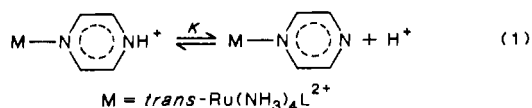
$$M-N\underset{}{\bigcirc}NH^+ \overset{K}{\rightleftharpoons} M-N\underset{}{\bigcirc}N + H^+ \quad (1)$$

$$M = \textit{trans}\text{-Ru(NH}_3)_4L^{2+}$$

Table III. pK_a Values[a] for Pyrazinium Species

pyrazinium species	pK_a
[Ru(NH$_3$)$_5$(pzH)]$^{3+}$	2.5[b]
trans-[Ru(NH$_3$)$_4$(4-pic)(pzH)]$^{3+}$	2.1[c]
trans-[Ru(NH$_3$)$_4$(pzH)(py)]$^{3+}$	2.0[d]
trans-[Ru(NH$_3$)$_4$(isn)(pzH)]$^{3+}$	1.6[c]
trans-[Ru(NH$_3$)$_4$(4-acpy)(pzH)]$^{3+}$	1.5[c]
trans-[Ru(NH$_3$)$_4$(pz)(pzH)]$^{3+}$	1.5[d]
pzH$^+$ free	0.65[b]
trans-[Ru(NH$_3$)$_4$(pzH)$_2$]$^{4+}$	–0.6[d] (–1.4)[e]
[Ru(NH$_3$)$_5$(pzH)]$^{4+}$	–0.8[b] (–2.5)[e]

[a] pK_a equals the –log [HX] where [Mpz] = [MpzH$^+$]. [b] Reference 4, HX = HClO$_4$. [c] This work, HX = HCl. [d] Reference 2, HX = HCl. [e] Corrected pK_a value using H_o value rather than –log [HX].

Table IV. Formal Reduction Potentials of Ruthenium Complexes

redox couples	E_f,[a] V	medium	ref
Ru(NH$_3$)$_5$(py)$^{3+/2+}$	0.289	b	3
	0.298	c	14
	0.305	d	13
	0.350	d	15
	0.420	e	8
Ru(NH$_3$)$_5$(isn)$^{3+/2+}$	0.375	c	1
	0.440	e	8
Ru(NH$_3$)$_5$(4-acpy)$^{3+/2+}$	0.392	c	14
Ru(NH$_3$)$_5$(pz)$^{3+/2+}$	0.490	f	13
trans-Ru(NH$_3$)$_4$(4-pic)$_2$$^{3+/2+}$	0.419	b	g
trans-Ru(NH$_3$)$_4$(4-pic)(py)$^{3+/2+}$	0.447	b	g
trans-Ru(NH$_3$)$_4$(4-pic)(isn)$^{3+/2+}$	0.502	b	g
cis-Ru(NH$_3$)$_4$(4-pic)(isn)$^{3+/2+}$	0.539	b	3
trans-Ru(NH$_3$)$_4$(4-pic)(pz)$^{3+/2+}$	0.613	b	g
trans-Ru(NH$_3$)$_4$(4-pic)(4-acpy)$^{3+/2+}$	0.524	b	g
trans-Ru(NH$_3$)$_4$(py)$_2$$^{3+/2+}$	0.474	b	g
	0.494	c	14
cis-Ru(NH$_3$)$_4$(py)$_2$$^{3+/2+}$	0.505	c	14
trans-Ru(NH$_3$)$_4$(py)(isn)$^{3+/2+}$	0.553	b	g
cis-Ru(NH$_3$)$_4$(py)(isn)$^{3+/2+}$	0.576	b	3
trans-Ru(NH$_3$)$_4$(py)(pz)$^{3+/2+}$	0.649	b	g
trans-Ru(NH$_3$)$_4$(py)(4-acpy)$^{3+/2+}$	0.551	b	g
trans-Ru(NH$_3$)$_4$(isn)(pz)$^{3+/2+}$	0.699	b	g
cis-Ru(NH$_3$)$_4$(isn)(pz)$^{3+/2+}$	0.754	b	3
trans-Ru(NH$_3$)$_4$(isn)(4-acpy)$^{3+/2+}$	0.609	b	g
cis-Ru(NH$_3$)$_4$(isn)(4-acpy)$^{3+/2+}$	0.656	b	3
trans-Ru(NH$_3$)$_4$(pz)$_2$$^{3+/2+}$	0.780	f	13
cis-Ru(NH$_3$)$_4$(pz)$_2$$^{3+/2+}$	0.860	f	13
trans-Ru(NH$_3$)$_4$(pz)(4-acpy)$^{3+/2+}$	0.739	b	g
trans-Ru(NH$_3$)$_4$(4-acpy)$_2$$^{3+/2+}$	0.602	b	g

[a] Vs the NHE; all new values reported are ±0.010 V as obtained from reversible waves from cyclic voltammetry. [b] At 25 °C, complex is ~1 × 10^{-3} M in an aqueous solution of 1 × 10^{-3} M CF$_3$CO$_2$H/0.1 M CF$_3$CO$_2$Na$^+$; by cyclic voltammetry. [c] At 25 °C, complex is ~1 × 10^{-3} M in an aqueous solution of 0.10 M *p*-toluenesulfonic acid/0.10 M potassium *p*-toluenesulfonate. [d] Aqueous solution of 0.10 M CF$_3$CO$_2$H/0.1 M CF$_3$CO$_2$Na$^+$; by cyclic voltammetry. [e] Measured from the potential of an equimolar Ru(II)/Ru(III) solution at a platinum electrode vs a silver wire in 1.00 M KCl/0.001 M HCl. [f] 1 M NaCl. [g] This work.

The band maxima of the protonated species are red shifted and are listed in Table II. The pK_a's so determined are listed in Table III.

Inclusion of earlier data[2] with those obtained in this work for trans 4-pic, isn, and 4-acpy complexes results in the acidity order Ru(NH$_3$)$_5$pzH^{3+} < *trans*-Ru(NH$_3$)$_4$(4-pic)pzH^{3+} ≲ *trans*-Ru(NH$_3$)$_4$(py)pzH^{3+} < *trans*-Ru(NH$_3$)$_4$(isn)pzH^{3+} ≲ *trans*-Ru(NH$_3$)$_4$(4-acpy)pzH^{3+} ≃ *trans*-Ru(NH$_3$)$_4$(pz)pzH^{3+} < uncoordinated pzH$^+$ < *trans*-Ru(NH$_3$)$_4$(pzH)pzH^{4+} < Ru(NH$_3$)$_5$pzH^{4+}.

Previous studies with Ru(NH$_3$)$_5$(pz)$^{n+4}$ and *trans*-Ru(NH$_3$)$_4$L(pz)$^{2+2}$ complexes showed that the decreased acidity of the Ru(II)-coordinated pzH$^+$ relative to the free ligand could be attributed to π back-bonding delocalizing electron density from the Ru(II) center into the π* orbitals of the nitrogen heterocycle and, furthermore, that the effect of the trans ligand L, in *trans*-Ru(NH$_3$)$_4$L(pz)$^{n+}$ on the acidity of Ru(II)-coordinated pzH$^+$ follows the order of increasing ligand acidity, consistent with both

decreasing σ-donor and increasing π-acceptor strengths of the trans L group.[2] Although some pK_a values are too close (those for 4-pic and py and those for isn, 4-acpy, and pz) to be used to make a very definite distinction in the σ and π acidity of the trans ligands, the approximate ligand acidity order is NH₃ < 4-pic ≲ py < isn ≲ 4-acpy ≃ pz < pzH⁺ in these complexes.

Reduction Potentials. Formal reduction potentials of *trans*-Ru(NH₃)₄(L)L′ $^{3+/2+}$ determined by cyclic voltammetry are listed in Table IV. The CV values of each complex fitted most of the criteria for a reversible couple.[12] A CV of the reversible Ru-(NH₃)₅py$^{3+/2+}$ couple was run under the same conditions and its values were used for comparison. Peak to peak separations increased (from 57 to 72 mV) with increasing scan rate (in different ranges, from 10 to 500 mV), which might be due to cell resistance. Some differences in the values of formal reduction potentials appeared in the literature (Table IV), and in some cases the differences are attributed to different experimental conditions.[3,13]

Previous observations showed that π-unsaturated ligands, such as pyridines (py-X), lead to substantially more positive reduction potentials for the Ru(NH₃)₅$^{3+/2+}$ couples than when L is H₂O or NH₃ and that electron-withdrawing substituents (X) increase E_f; that is, the π-accepting abilities of the ligands increase E_f values.[14] It was also observed[13] that the substitution of a second ammonia by another ligand to give a Ru(NH₃)₄L₂$^{3+/2+}$ complex yields more positive E_f values than for the corresponding Ru-(NH₃)₅L$^{3+/2+}$ complex. Again, when an ammonia of Ru-(NH₃)₅(L)$^{3+/2+}$ is substituted by another ligand L′ to yield Ru-(NH₃)₄(L′)(L)$^{3+/2+}$, more positive E_f values are also obtained.

This is expected since another π-acceptor ligand, with weaker σ-donor strength, is being added, favoring the stabilization of Ru(II) relative to Ru(III). For each series of *trans*-Ru-(NH₃)₄LL′ $^{3+/2+}$, considering a fixed L ligand, the more positive E_f values are in general, obtained with ligands L′ of higher π-acceptor and lower σ-donor abilities, and this order is the same as that observed in Ru(NH₃)₅L′ $^{3+/2+}$,[14] i.e., pz > 4-acpy > isn > py > 4-pic. For *trans*-Ru(NH₃)₄(py)L′ $^{3+/2+}$ and *trans*-Ru-(NH₃)₄(4-acpy)L′ $^{3+/2+}$, the E_f values, when L′ is 4-acpy or isn, are too close and could also be considered within the experimental error. However, the remaining values are sufficiently distinct to allow that ordering. The difference between E_f values of *cis*-Ru(NH₃)₄(isn)L$^{3+/2+}$ and Ru(NH₃)₅L$^{3+/2+}$, for each L, is almost the same,[3] which suggested that the two unsaturated ligands interact with a different d_π metal orbital each, and thus, the two ligands are unlikely to be coplanar in the cis isomers.[3] Similar patterns for the E_f values of *trans*-Ru(NH₃)₄LL′ $^{3+/2+}$ and Ru-(NH₃)₅L′ $^{3+/2+}$ were not obtained. Furthermore, considering the E_f values of the *cis*- and *trans*-Ru(NH₃)₄(isn)L$^{3+/2+}$ couples, it can be observed that the cis isomers have higher values (although close) than the trans analogues. This would suggest heterocycle ligand coplanarity in the trans isonicotinamide complexes, implying that only one d_π metal orbital is involved in bonding with the heterocyclic ligands, a feature consistent with the spectral data.

(12) (a) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706. (b) *Ibid.* **1965**, *37*, 178.
(13) Lim, H. S.; Barclay, D. J.; Anson, F. C. *Inorg. Chem.* **1972**, 11, 1460.
(14) Matsubara, T.; Ford. P. C. *Inorg. Chem.* **1976**, *15*, 1107.
(15) Meyer, T. J.; Taube, H. *Inorg. Chem.* **1968**, *7*, 2369.

Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, Texas 77843

Discrete Trinuclear Complexes of Niobium and Tantalum Related to the Local Structure in Nb₃Cl₈

F. Albert Cotton,* Michael P. Diebold, Xuejun Feng, and Wieslaw J. Roth

The preparations of three discrete trinuclear cluster compounds of group V metals are described: Nb₃Cl₇(PMe₂Ph)₆, (PEt₃H)[Nb₃Cl₁₀(PEt₃)₃], and (PEt₃H)[Ta₃Cl₁₀(PEt₃)₃]. The structures have been established in detail by X-ray crystallography and in each case there is an M₃(μ₃-Cl)(μ₂-Cl)₃ core surrounded by the remaining nine ligands. The relationship of this core structure to the subunit in Nb₃Cl₈ is discussed. The M–M distances (Å) in these three compounds are 2.832 (4), 2.976 (6), and 2.932 (3), respectively. The large difference between the first two has been correlated with the difference in the number of electrons available for Nb–Nb bonding, namely eight and six, by means of Fenske–Hall molecular orbital calculations. It is shown that in both cases there are six strongly bonding electrons and that the additional two electrons in the eight-electron case occupy another singly degenerate orbital of bonding character. The crystallographic data for the three compounds are as follows. Nb₃Cl₇(PMe₂Ph)₆: $P2_1/n$, a = 12.339 (2) Å, b = 27.275 (8) Å, c = 19.187 (9) Å, β = 92.76 (2)°, Z = 4. (PEt₃H)[Nb₃Cl₁₀(PEt₃)₃]: $P2_1/n$, a = 12.615 (1) Å, b = 18.731 (3) Å, c = 23.662 (4) Å, β = 98.59 (1)°, Z = 4. (PEt₃H)[Ta₃Cl₁₀(PEt₃)₃]: $P2_1/n$, a = 11.864 (3) Å, b = 20.664 (2) Å, c = 18.779 (2) Å, β = 97.61°, Z = 4.

Introduction

Infinite chains, infinite sheets, or three-dimensional arrays, which are the distinctive features of the solid state of matter, are sometimes resolvable into well-defined subunits linked by bridging atoms that are shared between them. The character of a subunit naturally plays a predominant role in determining the character of the material in which it inheres, although the strong linking together of the subunits means that the whole is not simply the sum of its parts. In attempting to understand the properties and behavior of the entire solid, it is essential to understand the subunit,

and this task is, in turn, facilitated by having access to individual subunits in molecular form. To accomplish this it is necessary to make provision for satisfying the coordination requirements of the subunit by ligands that are independent of, and different from, those present in the solid state. If this can be done in a conservative way, the molecular species should be good models, although not actually replicas, of the subunits in the solid.

This report describes a successful exercise of the type just described. It may be observed first of all that there are in principle