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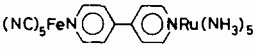
Syntheses and Properties of the Binuclear Complexes  and 

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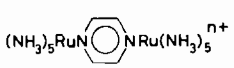
The binuclear complexes $(NC)_5FeLM(NH_3)_5$ (L = 4,4'-bipyridine, M = Ru, Rh) were prepared by the rapid reaction between $M(NH_3)_5L^{3+}$ and $Fe(CN)_5OH_2^{3-}$. The compound $Na[(NC)_5FeL'Ru(NH_3)_5]$ (L' = pyrazine) was prepared by the reaction between $Fe(CN)_5NH_3^{3-}$ and $Ru(NH_3)_5L^{2+}$. Oxidation of $Na[(NC)_5FeL'Ru(NH_3)_5]$ with cerium(IV) or peroxydisulfate yielded $(NC)_5FeL'Ru(NH_3)_5$. The reaction between $Fe(CN)_5NH_3^{3-}$ and $Rh(NH_3)_5L'^{3+}$ produced $(NC)_5FeL'Rh(NH_3)_5$. Cobalt analogs of the Fe–Ru complexes were prepared by reaction of $Co(CN)_5OH_2^{3-}$ with $Ru(NH_3)_5L^{2+}$ and $Ru(NH_3)_5L'^{2+}$. The compounds were characterized by solid state spectroscopic measurements (KBr pellets) in the visible, near infrared, and infrared regions. The wavelengths of the maxima of the metal to ligand charge transfer bands, cyanide stretching bands and ammonia deformation bands of the title compounds, and comparisons with the corresponding bands of their rhodium and cobalt analogs, are used to assign a valence-trapped formulation with localized iron(II) and ruthenium(III) oxidation states to the title compounds.

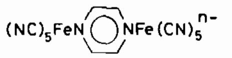
Introduction

Binuclear complexes with pyrazine (pz) as a bridging ligand and ruthenium in oxidation states 2 and/or 3, I, were first prepared and studied by Creutz and Taube [1]. Since then, a great deal of work has been devoted to this system, in particular to the mixed valence ion with n = 5 [2–8]. Taking advantage of the similarity between the $Ru(NH_3)_5^{2+}$ and $Fe(CN)_5^{3-}$ moieties [9], one of us [10] previously reported the preparation and some properties of the binuclear species II. The present paper reports the synthesis and some properties of the mixed binuclear complex III. In this compound, the sum of the oxidation states of the two metal ions is 5, and the question arises, just as in the case of ions I and II with n = 5, as to whether III contains trapped valences or features a delocalized system [11, 12]. In trying to answer this question, analogs of III where the $Fe(CN)_5$ moiety was replaced by $Co(CN)_5^{2-}$, the $Ru(NH_3)_5$ moiety was replaced by $Rh(NH_3)_5^{3+}$ and/or the bridging pyrazine was replaced by 4,4'-bipyridine (bp) were prepared and characterized. After this work was completed, a report of the preparation of III was published [13].



n = 4,5,6

I



n = 4,5,6

II

III

Experimental

Preparation of Complexes

$[Ru(NH_3)_5pzH]Br_4$

0.300 g of $[Ru(NH_3)_5Cl]Cl_2$ and 1.00 g of pyrazine in 25 ml of water were treated with several pieces of amalgamated zinc under an atmosphere of argon. After 30 min the solution was cooled to 0 °C and filtered. 1 ml of concentrated hydrobromic acid was added to the filtrate and the ruthenium(II) was oxidized to ruthenium(III) by adding bromine vapor to the solution. When the violet color changed to orange, 30 g of sodium bromide were added and the solution was kept at 0 °C for one hour. The orange product was filtered out and washed with ethanol and ether. The crude product was recrystallized by

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dissolution in 10 ml of 1 *M* hydrobromic acid, followed by addition of 5 g of sodium bromide. After cooling at 0° for one hour, the precipitate was collected by filtration and was washed with ethanol and ether. Yield: 0.180 g. The purity of the product was ascertained spectroscopically after reduction with ascorbic acid at pH 4 and 6. The observed maximum at 474 nm with molar absorbance 14,400 M^{-1} cm^{-1} is in excellent agreement with the previously reported value [1].

$[Ru(NH_3)_5bpH](ClO_4)_4$

0.300 g of $[Ru(NH_3)_5Cl]Cl_2$ in 30 ml was treated with several pieces of amalgamated zinc under argon. After 15 min, a solution of 0.600 g of 4,4'-bipyridine in 25 ml of water at 45 °C was added anaerobically. The resulting mixture was kept at 45 °C for 15 min, and then allowed to cool to 0 °C and filtered. The filtrate was treated with 2 ml of concentrated hydrobromic acid and then bromine vapor was added until the color changed from blue to orange. The solution was concentrated in a rotary evaporator to ~20 ml, and then 12 g of sodium bromide were added. Upon cooling to 0°, the bromide salt precipitated and was collected. The product was dissolved in the minimum amount of water at room temperature, and, then concentrated perchloric acid was added dropwise until a permanent turbidity was observed. Upon cooling to 0 °C, fine pale yellow crystals were formed. These were filtered and washed with ethanol and ether. Yield: 0.350 g. *Anal.* Calcd for $[Ru(NH_3)_5NC_{10}H_8NH](ClO_4)_4$: Ru, 13.64; C, 16.19; H, 3.26; N, 13.22. Found: Ru, 13.83; C, 15.83; H, 3.58; N, 12.49. A solution of the compound reduced by ascorbic acid at pH 6 exhibited a maximum at 482 nm with molar absorbance 12,100 M^{-1} cm^{-1}, in excellent agreement with the previously reported value [14].

$Na_3[Fe(CN)_5NH_3]\cdot 3H_2O$ [15] and $[Rh(NH_3)_5pz](ClO_4)_3$ [1] were prepared according to the cited literature methods.

$[Rh(NH_3)_5bpH](ClO_4)_4$

The preparation of this compound was similar to that of the pyrazine analog [1]. The crude product was purified by dissolution in the minimum amount of water at 60 °C, followed by addition of concentrated perchloric acid until a permanent turbidity was observed. Upon cooling to 0 °C, the desired solid precipitated out, and it was filtered and washed with ethanol and ether. *Anal.* Calcd for $[Rh(NH_3)_5NC_{10}H_8NH](ClO_4)_4$: C, 16.16; H, 3.25; N, 13.19. Found: C, 15.01; H, 3.15; N, 13.28.

$(NC)_5FebpM(NH_3)_5\cdot xH_2O$ (M = Ru or Rh)

These complexes precipitated out quantitatively by mixing at 10 °C equal volumes of 1.0 × 10^{-4} *M* $Fe(CN)_5OH_2^{3-}$ (prepared by aquation [15] of $Fe(CN)_5NH_3^{3-}$) and $M(NH_3)_5bp^{3+}$ (M = Ru or Rh). The resulting precipitate was washed with water, ethanol and ether. *Anal.* Calcd for $(NC)_5FeNC_{10}H_8NRu(NH_3)_5\cdot 2H_2O$: Fe, 9.89; Ru, 17.91; C, 31.92; H, 4.82; N, 29.78. Found: Fe, 9.20; Ru, 18.52; C, 31.07; H, 4.72; N, 29.97. Calcd for $(NC)_5FeNC_{10}H_8NRh(NH_3)_5\cdot 6H_2O$: Fe, 7.52; C, 28.22; H, 5.52; N, 26.33. Found: Fe, 7.79; C, 28.14; H, 5.21; N, 26.49. An alternate preparation of $(NC)_5FebpRu(NH_3)_5$ was achieved by oxidation with 0.01 *M* Ce(IV) in 0.1 *M* H_2SO_4 of ~10^{-4} *M* $(NC)_5FebpRu(NH_3)_5^-$ prepared by mixing equimolar amounts of $Fe(CN)_5NH_3^{3-}$ and $Ru(NH_3)_5bp^{2+}$. The compounds prepared by these two methods had identical spectroscopic properties.

$(NC)_5CobpRu(NH_3)_5\cdot 2H_2O$

Five ml of a solution 1 × 10^{-2} *M* in $Co(CN)_5OH_2^{2-}$ (prepared by aquation [16] of $Co(CN)_5Cl^{3-}$) was mixed with 10 ml of a solution 5 × 10^{-3} *M* in $Ru(NH_3)_5bp^{2+}$ (prepared by reduction of the corresponding Ru(III) complex with ascorbic acid). The mixture was kept at 50 °C for 8 hours under an atmosphere of argon. After cooling to 0 °C, the precipitate that had formed was filtered out and washed with ethanol and ether. Yield: 16 mg. *Anal.* Calcd for $(NC)_5CoNC_{10}H_8NRu(NH_3)_5\cdot H_2O$: Co, 10.72; Ru, 18.40; C, 32.79; H, 4.59; N, 30.59. Found: Co, 10.39; Ru, 18.93; C, 30.97; H, 4.36; N, 27.63.

$Na[(NC)_5FepzRu(NH_3)_5]$

12 mg (0.037 mmol) of $Na_3[Fe(CN)_5NH_3]\cdot 3H_2O$ was added under argon to 10 ml of a solution at 25 °C containing an equimolar amount of $Ru(NH_3)_5pz^{2+}$. After cooling to 0 °C, the precipitate that formed was filtered out and washed with ethanol and ether. Yield: 14 mg. In an alternate preparation, equal volumes of 2 × 10^{-2} *M* $Na_3[Fe(CN)_5NH_3]$ and 2 × 10^{-2} $[Ru(NH_3)_5pz](PF_6)_2$ at 40 °C were combined, and the resulting mixture was allowed to cool slowly to 0 °C. *Anal.* Calcd for $Na[(NC)_5FeNC_4H_4NRu(NH_3)_5]\cdot 2H_2O$: Ru, 19.8; Fe, 10.9; C, 21.1; H, 4.5; N, 32.9. Found: Ru, 19.4; Fe, 10.8; C, 21.0; H, 4.5; N, 32.5.

$(NC)_5FepzRu(NH_3)_5$

A solution (15 ml, 0 °C) 10^{-3} *M* in $(NC)_5FepzRu(NH_3)_5^-$ was treated with one equivalent of $K_2S_2O_8$ under argon. After one hour, the resulting solid was filtered out, and washed with ethanol and ether. Yield: 4.2 mg. Similar results were obtained when the oxidation was carried out with one quivalent of 0.01 *M* Ce(IV) in 0.1 *M* H_2SO_4. *Anal.* Calcd for $[(NC)_5FeNC_4H_4NRu(NH_3)_5]\cdot H_2O$: C, 23.0; H, 4.5; N, 35.7. Found: C, 23.0; H, 4.4; N, 34.3.

$(NC)_5FepzRh(NH_3)_5$

20 mmol of $Na_3[Fe(CN)_5NH_3]\cdot 3H_2O$ were added to 10 ml of 2.0 × 10^{-3} *M* $Rh(NH_3)_5pz^{3+}$ under argon

at room temperature. After 30 min, the solution was allowed to cool to 0 °C and kept at that temperature for one hour. The resulting solid was filtered out and then washed with ethanol and ether. Yield: 10 mg.

$(NC)_5CopzRu(NH_3)_5$

A solution (20 ml) 5 × 10^{-3} *M* in $Co(CN)_5OH_2^{2-}$ and 5 × 10^{-3} *M* in $Ru(NH_3)_5pz^{2+}$ was kept at 56 °C for 8 hours under an atmosphere of argon. After cooling to 0° for 2 hours, the precipitate formed was filtered out and washed with ethanol and ether. Yield: 17 mg.

Analytical Methods

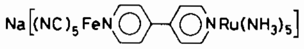
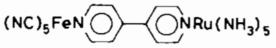
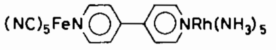
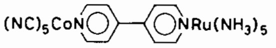
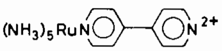
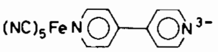
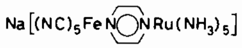
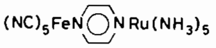
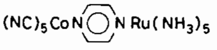
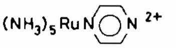
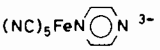
Iron [17] and cobalt [18] analyses were carried out by standard spectrophotometric methods following decomposition of the complexes by fuming with concentrated perchloric acid, a procedure which removes ruthenium as RuO_4. Ruthenium analyses [19] were carried out spectrophotometrically following decomposition of the complexes by boiling in peroxydisulfate solution (in 2 *M* KOH) and removal of iron or cobalt as the hydroxides. Carbon, hydrogen and nitrogen analyses were performed by Galbraith Laboratories.

Visible spectra were measured with a Cary 17 or Cary 118 spectrophotometer. Measurements of absorption spectra in the near infrared region were carried out with a Cary 17 spectrophotometer. Infrared spectra were obtained with a Perkin-Elmer 567 spectrophotometer. All measurements were carried out with KBr pellets.

Results and Discussion

At the outset it is important to mention that the binuclear complexes containing 4,4′-bipyridine underwent a rapid decomposition reaction in the solid state. The changes in the spectroscopic properties were readily apparent within one hour from the time of preparation and were very considerable within 24 hours. The changes were observed in the pure solids as well as in KBr pellets. Therefore, in what follows, unless specified to the contrary, the spectroscopic measurements reported were carried out with *freshly* prepared samples, within 10 minutes from the preparation. No changes in the spectroscopic properties of the binuclear complexes containing pyrazine were detected within 24 hours. Nevertheless, unless specified otherwise, the spectroscopic measurements for the pyrazine complexes were also carried with freshly prepared samples. In this context, it is noteworthy that difficulties with solid state decomposition of salts of complex I have been recorded [20].

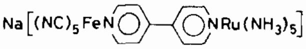
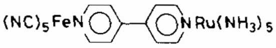
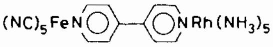
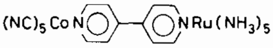
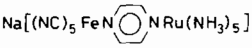
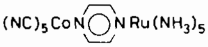
TABLE I. Metal to Ligand Charge Transfer Bands of Iron and Ruthenium Complexes of Nitrogen Heterocycles.[a]

Complex	λ_{max}, nm
	497[b]
	505
	515
	532
	482
	432
	535
	567
	570
	524
	474
	457

[a] Binuclear complexes as KBr pellets. Mononuclear complexes in aqueous solution. [b] In aqueous solution.

The absorption maxima in the visible spectra of the binuclear complexes prepared in the present work are presented in Table I. Included in Table I for comparison are the corresponding values for the parent mononuclear complexes. The bands in the visible and near ultraviolet spectra of complexes of pentaammineruthenium(II) [21] and pentacyanoferrate(II) [9] with nitrogen heterocycles have been assigned to metal to ligand charge transfer (MLCT). The binuclear complexes prepared in the present work also display metal to ligand charge transfer bands, but the bands exhibit a bathochromic shift when compared to the bands of the appropriate parent complexes. Before making these comparisons, however, it is important to point out that there are two classes of compounds listed in Table I. The Ru(II)–Fe(II), Ru(II)–Co(III) and Rh(III)–Fe(II) complexes have well defined oxidation states, whereas the Ru–Fe complexes, where the sum of the oxidation states of the metals is 5, could feature trapped valences, such as Ru(III)–Fe(II) or Ru(II)–Fe(III), or a delocalized situation. In trying to distinguish between the alternative formulations for the latter complexes, it is useful to consider first the shifts in the MLCT bands that occur in systems with well defined oxidation states. Thus, the 432 nm band of $Fe(CN)_5bp^{3-}$ is shifted to 515 nm upon coordination of the exposed pyridine nitrogen to $Rh(NH_3)_5^{3+}$. A similar shift, to 505 nm, is observed upon coordination to $Co(NH_3)_5^{3+}$ [22]. The 482 nm band of $Ru(NH_3)_5bp^{2+}$ is shifted to 532 nm upon coordination of the remote nitrogen to $Co(CN)_5^{2-}$. Using the values ~510 and ~530 nm as representing Fe(II) and Ru(II) MLCT bands shifted by coordination of the exposed pyridine nitrogen to a non-π bonding, electropositive center, and assuming a trapped valence formulation, the observed 505 nm value for the MLCT band of $(NC)_5FebpRu(NH_3)_5$ can be taken to indicate the presence of Ru(III) and Fe(II) oxidation states. A similar argument can be used to assign the valences of Ru and Fe in $(NC)_5FepzRu(NH_3)_5$. The 457 nm band of $Fe(CN)_5pz^{3-}$ is shifted to 570 nm by coordination of the exposed pyrazine nitrogen to $Rh(NH_3)_5^{3+}$. The 474 nm band of $Ru(NH_3)_5pz^{2+}$ is shifted to 524 nm by coordination of the remote nitrogen to $Co(CN)_5^{2-}$. Therefore, using the trapped valence formulation, the observed band at 567 nm can be taken to indicate the presence of Ru(III) and Fe(II). Although these comparisons provide a clear distinction between the two trapped valence formulations, the possibility of a delocalized structure still remains at this point. However, the delocalized description can be ruled out by comparing the position of the MLCT in I and in its 4,4′-bipyridine analog with the corresponding binuclear complexes containing Ru(II) and Fe(II). If the delocalized description is applicable, the MLCT bands of the mixed valence complexes would be expected [1] to occur at higher energy than those of the compounds containing Ru(II) and Fe(II). The opposite trend is observed experimentally and we infer that the mixed valence complexes are best formulated as containing the localized oxidation states Ru(III) and Fe(II).

TABLE II. Selected Infrared Bands of Ruthenium and Iron Complexes.[a]

Complex	CN stretch, cm^{-1}	$\delta(NH_3)$, sym, cm^{-1}
	2050	1290
	2040	1335
	2050	1330
	2120	1290
	2040, 2100[b]	1290
	2050, 2100[b]	1340
	2050, 2100[b]	1350
	2130, 2200[b]	1290

[a] In KBr pellets. [b] Weak shoulder.

The infrared spectra measurements confirm the above assignment of oxidation states. Thus, the cyanide stretching frequencies of iron(II) cyanide complexes fall in the vicinity of 2045 cm^{-1}, whereas for iron(III) the value is ~2135 cm^{-1} [23]. For a delocalized formulation involving a cyanide bound to an iron in an oxidation state intermediate between II and III, the cyanide stretching frequency would be intermediate between 2045 and 2135 cm^{-1} [24, 25]. As can be seen in Table II, all the iron complexes exhibit the cyanide stretching frequency at 2045 ± 5 cm^{-1}, showing clearly that the mixed oxidation state complexes have the iron in the trapped valence II. Similarly, the symmetric ammonia deformation frequency serves to assign the oxidation state of the ruthenium in these compounds. Values in the ranges 1260–1290 cm^{-1} and 1330–1360 cm^{-1} are characteristic of pentaammine complexes of Ru(II) and Ru(III) [1, 26], respectively, whereas an intermediate value would be expected for a fractional oxidation state between II and III [27]. The cobalt–ruthenium complexes, where the oxidation state of Ru is definitely II, exhibit the symmetric ammonia deformation at 1290 cm^{-1}. The complex $(NH_3)_5RupzFe(CN)_5$ and its 4,4′-bipyridine analog exhibit the symmetric ammonia deformation band at 1340 and 1335 cm^{-1}, respectively. These values clearly show that the mixed valence compounds contain Ru in the oxidation state (III).

The assignments of the oxidation states of iron and ruthenium based on the cyanide stretching frequency and the symmetric ammonia deformation frequency are consistent with each other as well as with the assignments based on the MLCT bands. Therefore, the mixed oxidation state complexes $(NC)_5FepzRu(NH_3)_5$ and $(NC)_5FebpRu(NH_3)_5$ must be formulated as trapped valence species containing Ru(III) and Fe(II).

One of the characteristic properties of the mixed valence ion I where n = 5 is the presence of an intervalence band in the near infrared region. We spent a lot of time and effort investigating the near infrared spectra of the mixed valence complexes prepared in this work. Freshly prepared, dilute samples of $(NC)_5FebpRu(NH_3)_5$ did not exhibit an absorption in the NIR region, but after the sample aged for an hour, a weak, broad band was observed at ~1370 nm. The band increased in intensity for the next few hours, and was approximately constant after about a day. Two other changes were also observed after a day. The 505 nm band shifted to 490 nm and a weak shoulder developed at 2130 cm^{-1}. A very significant observation was made with $(NC)_5FebpRh(NH_3)_5$. Here again, freshly prepared samples (dilute or concentrated) showed no absorption in the NIR region, but after a few hours a weak band at 1370 nm was observed. Simultaneously, the visible band shifted to 498 nm and a weak shoulder developed at 2130 cm^{-1}. Since the oxidation state $Rh(NH_3)_5^{2+}$ is not easily accessible, an intervalence absorption for the Rh–Fe–bipyridine complex is unlikely, and we conclude that the 1370 nm NIR band is related to some (unknown) decomposition process that takes place in the solid state and produces an absorbing iron compound, perhaps similar to $Fe_2(CN)_{11}^{6-}$ prepared previously by Ludi and coworkers [24]. Additional, albeit indirect, evidence for this conclusion is found in the observation that the spectrum of $(NC)_5CobpRu(NH_3)_5$ in the visible, infrared and NIR regions did not change with time, even after several months. Moreover, the fact that the NIR band of the Ru–Fe–bipyridine complex appears in the same region as that of the corresponding rhodium complex, and only after aging, is taken to mean that the NIR band does *not* represent an intrinsic property of the Ru–Fe binuclear complex but that of an iron decomposition product [24].

For $(NC)_5FepzRu(NH_3)_5$, an NIR band at 1370 nm was detected in freshly prepared samples and was found not to change with time. For $(NC)_5FepzRh(NH_3)_5$, freshly prepared samples did not exhibit an NIR absorption, but after aging for two months [28], the band at 1370 nm was observed. Since the NIR band of the Ru–Fe–pyrazine system appears in freshly prepared samples, it might be inferred that the band represents an intrinsic property of the complex. However, we are inclined to believe that the band is associated with a small amount of an iron decomposition product. First, the corresponding rhodium complex, where an intervalence absorption band is precluded, also exhibits the band (albeit after aging). Second, the position of the NIR band is independent of the nature of the pyridine ligand. Thus, the Fe–Ru binuclear complexes of pyrazine (freshly prepared), 4,4′-bipyridine and 1,2-bis-4-pyridylethylene (after aging) all exhibit an NIR band at 1370 ± 20 nm. It is noteworthy that the corresponding binuclear complexes $(NH_3)_5RuLRu(NH_3)_5^{5+}$ where L is pyrazine or 4,4′-bipyridine display the intervalence NIR band at 1570 and 930 nm, respectively [1, 29]. Third, samples of the Fe–Ru–pyrazine complex have been reported [13, 30] to exhibit maxima at 523 nm and 1330 nm. However, it is apparent that these results are associated with extensive decomposition [31]. A structure Fe(II)-pzRu(III) is unlikely to exhibit the MLCT band at the same wavelength as the Fe(II)pzRu(II) structure [32]. Therefore, the presence of the NIR band in freshly prepared samples as well as in decomposed products casts doubt upon the authenticity of the NIR band as an intrinsic property of the pure complex.

In conclusion, the binuclear complexes $(NC)_5FeLRu(NH_3)_5$, where L is 4,4′-bipyridine or pyrazine, are valence-trapped structures containing the localized oxidation states Ru(III) and Fe(II). The NIR band at 1350 ± 20 nm exhibited by aged samples of the 4,4′-bipyridine complex, fresh samples of the pyrazine complex, and aged samples of the corresponding rhodium complexes is assigned to a small amount of an iron decomposition product.

Acknowledgments

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28 Measurements were made only in freshly prepared samples and in 2-month old samples. Therefore, the length of time necessary for the NIR band to develop has not been established.

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30 Occasionally, our sample also exhibited a visible absorption at 530 nm.

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32 In fact, Santos and Toma [13] commented that "it is remarkable that the visible absorption band of the Ru(II)–pz–Fe(II) complex is not shifted in the oxidation process".