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Binuclear Bridging Imidazolate Complexes of Cobalt and Ruthenium

Sir:

The imidazole ring of histidyl peptide residues is known to form part of the coordination environment of a large number of metalloenzymes.[1] More recently, the imidazolate anion (i), the conjugate base of imidazole (ii), has been proposed as a bridging ligand in a number of cases. For example, crystal-

Im, i

ImH, ii

lographic evidence supports the presence of imidazolate between copper and zinc in bovine superoxide dismutase.[3] Palmer et al.[4] have also postulated the involvement of bridging imidazolate between iron and copper in cytochrome *c* oxidase. Such a model implies the participation of the histidyl imidazolate in the electron-transfer process of oxygen reduction. The above facts and speculation have intensified the interest in studying imidazole and imidazolate as ligands in simple metal complexes.

Although there are a number of known imidazolate bridged transition metal complexes, almost all of these examples are insoluble polymeric species.[5] Solution identification of imidazolate bridging species is limited to only a few examples.[6] Recently, the synthesis and characterization of a series of soluble copper(II) complexes with bridging imidazolate[7] have been reported (e.g., $[Cu(pip)]_2$(imidazolate)$(NO_3)_3$ where pip = 2-[2-(2-pyridyl)ethyliminomethyl]pyridine). These latter complexes are of structural value; however, their lability precludes any detailed studies on the nature of imidazolate as a ligand and more specifically on the electron-mediating properties of the imidazolate anion.

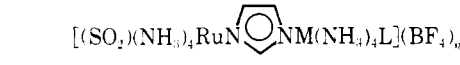
In contrast to these labile complexes, herein we report on the synthesis, characterization, and some of the properties of a class of binuclear complexes with imidazolate bridging groups in which the metal ions (ruthenium and cobalt) are relatively inert to substitution. These compounds allow for the first time the examination of the electron-mediating properties of the imidazolate anion when bridging between two metals of different oxidation states.

Table I. UV-Visible Spectra for Mononuclear and Binuclear Imidazole and Imidazolate Complexes

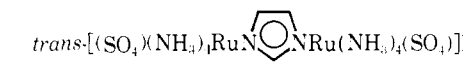
complex	λ_{max}, nm	ϵ, M^{-1} cm^{-1}
$[(NH_3)_5Ru(Im)Ru(NH_3)_4(SO_4)](BF_4)_3$	332	5.2×10^3
	420 (sh)	3.6×10^3
	460 (sh)	3.4×10^3
	296 (sh)	2.9×10^3
$[(NH_3)_5Co(Im)Ru(NH_3)_4(SO_4)](BF_4)_3$	339	4.3×10^3
	460 (sh)	4.5×10^2
	298 (sh)	2.2×10^3
$[(SO_4)(NH_3)_4Ru(Im)Ru(NH_3)_4(SO_4)]BF_4$	326	
	360 (sh)	
	500 (sh)	
$[(NH_3)_5Ru(ImH)](BF_4)_3$[a]	299	1.8×10^3
	430	1.9×10^2
$[(NH_3)_5Ru(Im)]^{2+}$ [a]	362	2.4×10^3
	550	6.2×10^2
$[(SO_4)(NH_3)_4Ru(ImH)](BF_4)$	312	3.0×10^3
	390 (sh)	4.8×10^2
$[(OH_2)(NH_3)_4Ru(ImH)]^{3+}$ [b]	297	2.8×10^3
	385	1.5×10^2
$[(SO_4)(NH_3)_4Ru(Im)]$	322	3.7×10^3
	440	1.7×10^2
$[(NH_3)_5Co(ImH)](ClO_4)_3$[c]	334	7.1×10^1
	472	6.2×10^1
$[(NH_3)_5Co(Im)]^{2+}$ [c]	344	1.1×10^2
	478	7.0×10^1

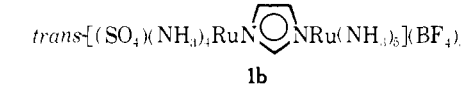
[a] Reference 10. [b] Generated by sulfate aquation from $[(SO_4)(NH_3)_4Ru(ImH)](BF_4)$. [c] Reference 9.

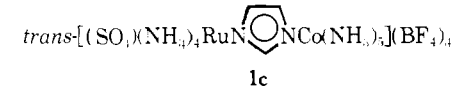
A brief description of the synthesis of these species is as follows. Addition of solutions of $[(O_3S)(NH_3)_4Ru^{II}(OH_2)]$[8] to concentrated solutions of $[(NH_3)_5Co(Im)]^{2+}$ [9] (ImH = imidazole and Im = imidazolate anion), $[(NH_3)_5Ru(Im)]^{2+}$,[10] or $[(SO_4)(NH_3)_4Ru(Im)]$[11] under an argon atmosphere in 0.1 M LiOH resulted in a very rapid reaction (~1 s). Acidification with 48% HBF_4 led to the precipitation of



where for M = Ru^{III}, L = NH_3 (n = 4) or SO_4^{2-} (n = 2), and for M = Co^{III} L = NH_3 (n = 4). Oxidation of each of the above compounds with hydrogen peroxide[12] in aqueous 20% HBF_4, followed by addition of ethanol, resulted in the precipitation of **1a, 1b,** and **1c** salts. Compounds **1a, 1b,** and **1c**


1a


1b


1c

were purified by gel chromatography. Elemental analyses of the complexes corresponded to the above formulations.[13]

The UV-visible spectra of the binuclear ions are sufficiently different from the corresponding mononuclear species to differentiate them. Table I lists the UV-visible characteristics, λ_{max} and extinction coefficients for the binuclear and the corresponding mononuclear complexes for comparison. Dilute aqueous solutions of compounds **1b** and **1c** showed no sign of decomposition for periods of hours.

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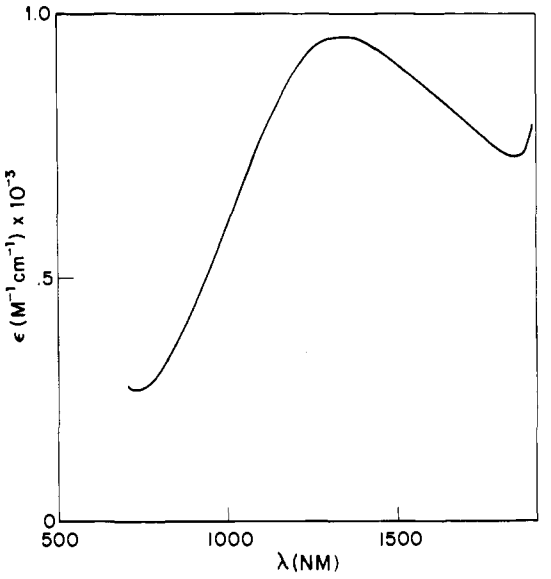


Figure 1. Near-infrared spectrum for $[L(NH_3)_4Ru\text{-}Im\text{-}Ru(NH_3)_5]^{5+}$ mixed valence ion in D_2O (L = D_2O).

When compound **1b** is reduced with 1 equiv of $[(NH_3)_5Ru(ImH)]^{2+}$ or Eu^{2+} in D_2O, a new band in the near-infrared region of the spectrum is observed (λ_{max} 1375 nm (ϵ 1.0×10^3 M^{-1} cm^{-1})[25] (Figure 1). This band appears to be similar to the bands observed in a number of previously known mixed valence $-Ru^{II}\text{-}L\text{-}Ru^{III}-$ complexes.[17] This band is therefore assigned to the electronic intervalence transition within this binuclear complex. This band completely disappears in the ruthenium(II,II) and ruthenium(III,III) forms. The symmetrical complex $[(SO_4)(NH_3)_4Ru\text{-}Im\text{-}Ru(NH_3)_4(SO_4)]BF_4$ (**1a**), when reduced by 1 equiv, shows a similar band at λ_{max} 1300 nm. However, in this mixed valence species of **1a,** one cannot ascertain whether in aqueous solution the environments of both Ru centers are identical,[24] because of the short residence time of oxygen ligands in the coordination sphere of ruthenium(II).[12]

From the position of the near-infrared band, one can calculate an approximate rate constant for the intramolecular electron transfer within the binuclear $-Ru^{II}\text{-}Im\text{-}Ru^{III}-$ complex using Hush's theory.[15] Assuming that the differences due to asymmetry of the complex are small, a rate constant of the order of 10^9 s^{-1} is calculated for the intramolecular electron-transfer process in these mixed valence complexes.

The stability of the mixed valence complex of ruthenium(II, III) derived from **1b** toward dissociation was followed by monitoring the decrease in absorbance at 1350 nm.[16] At pH 5 a half-life of ~1 h was calculated for its decomposition. It was also observed that this decomposition process was accelerated by acids (e.g., DCl). In neutral and weakly basic solutions (0.5 M $NaHCO_3$) the mixed valence complex is stable for longer periods of time (ca. hours).

Cyclic voltammetry and differential pulse polarography of **1b** in 0.5 M $NaHCO_3$ using a pyrolytic graphite (or platinum button) electrode (Figure 2) showed two separate waves with E_f = −0.02 and −0.37 V vs. NHE. In the cyclic voltammetry experiment the first wave proved to be more reversible (60-mV separation) than the second wave (130-mV separation). These two waves correspond to the reduction of the two ruthenium(III) centers of the binuclear complex. Compound **1a** in 0.5 M $NaHCO_3$ also showed similar electrochemical behavior, E_f = −0.27 and −0.42 V vs. NHE. However, the two waves for **1a** are closer together than those for **1b.** This is an indication that part of the difference in potential between the semireduced and fully reduced species of **1b** (Figure 2) can be attributed to the different electronic environments of the ruthenium(II) centers.

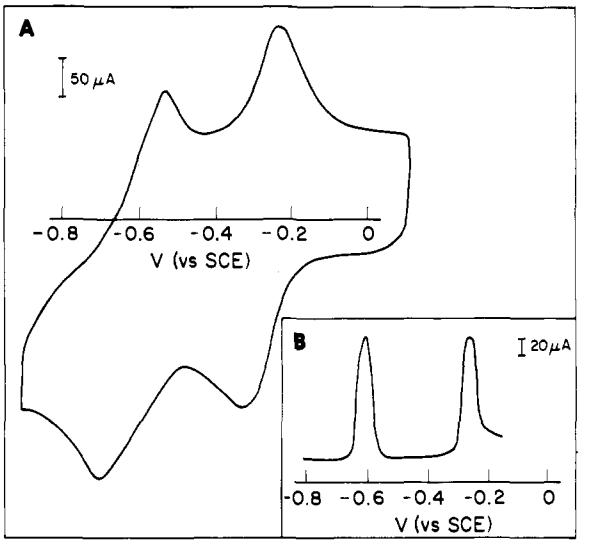
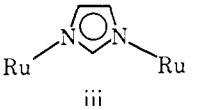


Figure 2. Cyclic voltammetry (A) (rate = 500 mV/s) and differential pulse polarography (B) (rate = 2 mV/s, pulse amplitude = 25 mV) for $[(NH_3)_5Ru\text{-}Im\text{-}Ru(NH_3)_4(SO_4)](BF_4)_3$ in 0.5 M $NaHCO_3$ on a pyrolytic graphite electrode (potentials vs. SCE).

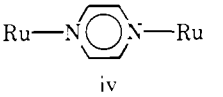
In the $-Ru^{II}\text{-}Im\text{-}Co^{III}-$ complex a relatively large activation barrier to electron transfer is present.[17] The net rate of electron transfer can be measured by reducing the $-Ru^{III}\text{-}Im\text{-}Co^{III}-$ complex with Eu^{2+} (reduction occurs preferentially at the ruthenium site), to generate the intermediate $-Ru^{II}\text{-}Im\text{-}Co^{III}-$ species. The decrease in absorbance in the cobalt(III) d-d band was followed using a stopped-flow spectrophotometer. First-order behavior corresponding to the *intra*molecular electron-transfer process within the $-Ru^{II}\text{-}Im\text{-}Co^{III}-$ intermediate was observed (k = 6 ± 1 s^{-1}, T = 22 °C, I = 0.02, and pH 3).[18,19]

Examination of the product of the intramolecular process resulting from mixing a 1:1 solution of $-Ru^{III}\text{-}Im\text{-}Co^{III}-$ (**1c**) and Eu^{2+} showed that all the cobalt is in the Co^{2+} oxidation state as determined by Co^{2+} analysis.[20] The ruthenium(III) retained the imidazolate ligand and most of the sulfate ligand, as determined from the UV spectrum of the product after electron transfer[21] (Table I).

The above spectral, electrochemical, and kinetic results for the imidazolate complexes allow us to draw some conclusions concerning the electron-transfer properties of the imidazolate anion, especially when bridging between two metal ions. This can be done by comparing imidazolate to other similar bridging ligands already studied.[17,23] A bridging ligand which has been extensively studied[23] and is similar to imidazolate is pyrazine. Both are aromatic and their size is roughly comparable (a five-membered ring vs. a six-membered ring). Our experiments show that, although both ligands are able to mediate electrons, imidazolate is less efficient than pyrazine. This difference can be explained by examining the electronic structure of both complexes and by examining molecular models or crystal structures of related binuclear imidazolate and pyrazine species.[26] The angular structure of the imidazolate complex (iii), when compared with the linear structure of the pyrazine complex (iv), can result in a decrease in the overlap between



iii



iv

the metal d-π orbitals and the imidazolate π^* orbitals. The difference in energy between the π^* orbitals of the imidazolate ion and pyrazine and the difference in geometry between the two binuclear species, iii and iv, can account for a weaker in-

teraction between the two ruthenium centers in the imidazolate case. This is valid if the electron mediation is accomplished with the π-bond system of the ligand. Imidazolate ion, however, can possibly make use of its σ-bond system in a manner similar to halides and hydroxide ligands. The relatively fast net rate of electron transfer for $-Ru^{II}-Im-Co^{III}-$ ($k = 6 \pm 1\ s^{-1}$) may be a result of such a mechanism. Note that the rate is faster than the rate of electron transfer in similar binuclear complexes with other bridging N-heterocyclic ligands that have been studied.[17] The σ-bond system of imidazolate anion can interact more effectively with a d-σ acceptor orbital as in cobalt(III) than can many pyridine-type heterocycles. The possible use of the π- as well as the σ-bond system of imidazolate anion renders it a versatile ligand which can interact with σ- and π-donor and -acceptor metal ion orbitals.

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(13) Calcd for $[Ru_2C_3H_{27}N_{10}S_2O_8](BF_4 \cdot 2H_2O$ (**1a**): C, 5.00; H, 4.34; N, 19.44. Found: C, 4.84; H, 4.94; N, 18.43. Calcd for $[Ru_2C_3H_{30}N_{11}SO_4](BF_4)_3$ (**1b**): C, 4.65; H, 3.88; N, 19.78. Found: C, 4.80; H, 3.84; N, 17.95. Calcd for $[CoRuC_3H_{30}N_9SO_4](BF_4)_3$ (**1c**): C, 4.89; H, 4.10; N, 20.91; Co, 8.00; Ru, 13.72. Found, C, 5.40; H, 4.43; N, 20.18; Co, 7.6; Ru, 13.0. We have no reasonable explanation for the low nitrogen content in the above compounds.
(14) The residence times of all the ligands in the metal coordination spheres of the complexes in question are much longer than the electron-transfer time scale. The only exception to this is $Ru^{II}SO_4$ where the rate of loss of sulfate for a closely related system has been determined ($t_{1/2} = 0.3$ s).[12] This fact presents slight complications as to which species, the $Ru^{II}SO_4$ or the $Ru^{II}OH_2$, one is dealing with.
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(24) Note that the rate of loss of sulfate is not known for the mixed valence species and therefore the ligand trans to imidazolate can be SO_4^{2-}, OH_2, or OH^-. We are currently attempting the synthesis of the symmetrical decaammine-imidazolate complexes for a detailed study of the solvent dependence of the intervalence band for $Ru^{II}-Im-Ru^{III}$ and the magnetic exchange properties of the fully oxidized $Ru^{III}-Im-Ru^{III}$ complex.
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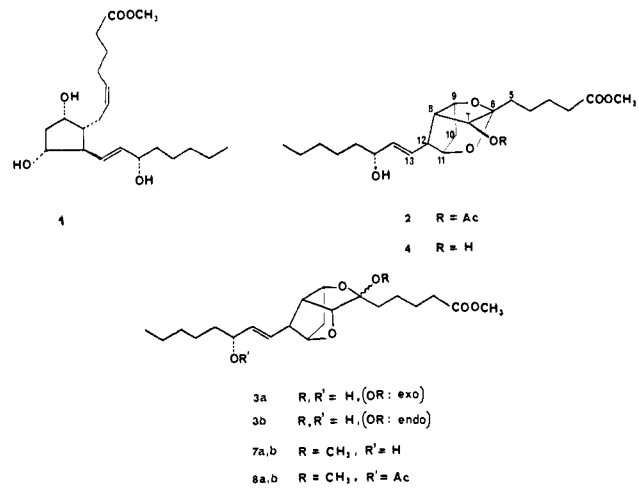
A Novel Functionalization of Prostaglandin Skeleton. Addition of Thallium Triacetate to $PGF_{2\alpha}$ Methyl Ester

Sir:

According to synthetic strategies published to this date, the preparation of the highly potent antiaggregatory PGI_2 and analogues starts with the electrophilic activation of the 5,6 double bond of $PGF_{2\alpha}$ (or equivalents) accompanied by the formation of the five-membered ring through participation of the 9-positioned OH (or SH) function. The cyclization was shown to proceed with various electrophilic agents, viz., I^+, Br^+, $PhSe^+$, and Hg^{2+}.[1] The well-known electrophilic properties of Tl^{3+} and the ease with which C-Tl bonds are broken[2] have prompted us to test the applicability of Tl^{3+} as an electrophilic agent in these processes. We have found that the reaction of $PGF_{2\alpha}$ methyl ester (**1**) with thallium triacetate



proceeds with the participation of both C-9 and C-11 hydroxyl functions and leads to the formation of two novel dioxatricyclo systems, **2** and **3**, hiterto unknown in prostaglandin chemistry. These products may be readily converted into other derivatives with the prostaglandin skeleton functionalized in position 7.

Treatment of **1** with 3 molar equiv of thallium triacetate in acetic acid (90 mL/g of **1**) at 25 °C for 24 h produced a 1:2.5 mixture of **2** and **3**. Chromatographic separation gave the pure substances (R_f 0.54 for **2** and R_f 0.28 for **3**, 2:1 ethyl acetate–hexane) as oils in 70–75% yields (overall from **1**). Spectral data disclosed that the highly acid-sensitive **2** is isomerically pure, while the more polar product is a chromatographically nonseparable mixture of two isomers, **3a** and **3b** (~1:3).

The structure and stereochemistry of these novel systems as shown were unambiguously proved by means of the IR and mass spectral[2,3,4] data and careful analysis of the ^1H and ^{13}C spectra,[5,6] aided by the evaluation of characteristics chemical-shift changes upon derivatization of **2** and **3a,b.** Chemical transformations provided corroboration for the correctness of

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