

What does and what does not constitute a mercury-nitrogen bonding interaction has been exhaustively reviewed in a succession of papers by Canty et al.,<sup>7,8,14</sup> but the kind of orbital overlap that might lead to an increase in coordination number at Hg in HgA<sub>2</sub> derivatives while maintaining linearity of the A-Hg-A configuration has not been satisfactorily addressed in circumstances where A is not electron withdrawing. The structure of **5** reasserts this problem. On the basis of an interpretation<sup>8</sup> in which an Hg-N contact of 2.96 (2) Å is *definitely bonding* and Hg-As = 3.40 (5) Å in [(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>HgAsPh<sub>2</sub>]<sub>2</sub>CH<sub>2</sub> should be viewed as a *significant interaction*, the ((dimethylamino)methyl)phenyl groups in **5** are clearly functioning as unsymmetrical chelating ligands (type B), i.e., with coordinate bonding from N to Hg. However, like the CH<sub>3</sub>C vector, the NHgN linkage is strictly linear, these two intersecting one another at 71° (Figure 1). Thus, any interpretation based<sup>7</sup> on electron donation of LP (lone pair) density on N into empty mercury 6p<sub>x,y</sub> orbitals must necessarily involve only one of the latter. A similar conclusion can also be applied to several of the structures described by Canty and co-workers,<sup>7,14</sup> in which rather distant donor atoms face each other at or very close to 180° across a linear HgA<sub>2</sub> or HgAB unit in which bonds to A and B are short. Where A and/or B are strongly electron-withdrawing substituents 4- or 6-coordinate structures may result from addition of neutral ligands, attached by bonding that is largely ionic, in arrangements explicable in terms of simple electrostatics.<sup>15</sup> In these circumstances d-s mixing has also been invoked to account for distorted digonal coordination; such a situation, however, is held to be unlikely in diorganomercurials, for which feeble acceptor properties have been related to low charge on the metal and predominance of sp hybridization.<sup>16</sup> It should also be noted in this context that recently a more complex view of valence-orbital energy relationships for heavy atoms (e.g., 5d elements) has begun to emerge on the basis of relativistic effects.<sup>17</sup> In this note we simply wish to point out that interpretation of the structure adopted by compound **5** (and others like it<sup>7,14</sup>) seems to require either (a) d-s mixing in circumstances where this has hitherto been regarded as unlikely or (b) donation into a single acceptor orbital (6p<sub>x</sub> or 6p<sub>y</sub>) of electron density simultaneously from two donor LP hybrids, necessitating an orbital description based on three-center delocalized bonding and coincidentally predicating a long Hg-N distance, as is observed.

The long mercury-nitrogen bond in **5** may be placed in context by reference to structural data for other metal derivatives incorporating the chelate arrangement (B). The description of transition-metal 2-((dimethylamino)methyl)phenyl derivatives<sup>5,6</sup> has recently been extended to include crystallographic characterization for two chromium species;<sup>18</sup> while the structure of one of these is particularly interesting, it has no direct bearing on the present discussion. However, diphenyl(2-((dimethylamino)methyl)phenyl)tin(IV) bromide has also been investigated<sup>19</sup> by X-ray methods, revealing a

pentacoordinate geometry that arises through intramolecular chelation. The resulting Sn-N bond (trans to Br) is unusually long, a result which indicates that chelating interaction involving the dimethylamino residue in 2-Me<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub> metal compounds can in certain circumstances be weak. This conclusion is substantiated by a temperature dependence observed in the NMR spectra of a range of (2-((dimethylamino)methyl)phenyl)silanes, interpreted<sup>20</sup> in terms of dissociation of a pentacoordinate structure via reversible detachment of N from Si.

The spectroscopic data for **1-5**, particularly the NMR results given in Table I, provide disappointingly little further insight in terms of structure. The lack of any conspicuous changes over the series **3-5** suggests that a common geometry exists in solution for the three molecules, and this may correspond to the chelated arrangement characterized by the X-ray study of the mercury compound (**5**). One unusual feature encountered for the latter is the resolution of spin coupling to <sup>199</sup>Hg of both methylene C and H nuclei in appropriate spectra, both rather large at <sup>3</sup>J = 63 and <sup>4</sup>J = 18 Hz, respectively.

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**Registry No.** **1**, 87101-91-5; **2**, 87101-92-6; **3**, 85380-67-2; **4**, 87101-93-7; **5**, 81352-61-6; *o*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>, 609-72-3; C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>NMe<sub>2</sub>, 103-83-3.

**Supplementary Material Available:** Listings of thermal parameters, least-squares planes, and observed and calculated structure factors for compound **5** (9 pages). Ordering information is given on any current masthead page.

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### A Pulse Radiolysis Study of (Imidazole)pentaamminecobalt(III) Perchlorate in Water: Ligand to Metal Electron Transfer

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The inner-sphere electron-transfer mechanism involves the prior formation of a binuclear complex in which the metal centers of the oxidant and reductant are bridged by a ligand through which electron transfer occurs.<sup>1</sup> Ligand radicals have been suggested as intermediates in the metal ion reduction of many cobalt(III) ammine complexes.<sup>2</sup> Generally, detection of these putative intermediates has been frustrated by their short lifetimes, although limited evidence has been obtained by stopped-flow spectroscopy.<sup>3</sup> Recently, however, the radical binuclear intermediate, generated by the reaction of (pyrazine-2-carboxylato)pentaamminecobalt(III) with chromous ion, has been observed by ESR spectroscopy.<sup>4</sup> The prospect

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of coordinated ligand radical intermediates in metal to metal redox reactions implies that information on the rate of electron transfer from a coordinated ligand radical to a metal center could be useful for our understanding of the overall redox process.

The fast kinetic technique of pulse radiolysis is particularly useful in investigating problems of intramolecular electron transfer. The hydrated electron,  $e_{aq}^-$ , generated in the radiolysis of aqueous solutions, frequently reacts with simple pentaamminecobalt(III) complexes without any transient being detected,<sup>5</sup> yielding Co(II) quantitatively.<sup>6</sup> The implication is that attack occurs by direct tunneling into the orbitals of the metal ion or that intramolecular electron transfer is extremely rapid. However, (nitrobenzoato)- and (dinitrobenzoato)pentaamminecobalt(III) complexes recently have been shown to react with reducing radicals intermolecularly to form ligand radical intermediates with the added electron localized on the nitrobenzoato ligands, which subsequently decay by a measurable intramolecular electron-transfer path.<sup>7</sup>

As part of our investigation of redox processes, we have chosen to study, specifically by the pulse radiolytic technique, pentaamminecobalt(III) complexes of ligands that have the potential to act as bridging groups in inner-sphere electron-transfer reactions. The biologically important imidazole (ImH) can perform such a role. It bridges Cu(II) and Zn(II) in bovine erythrocyte superoxide dismutase; synthetic  $\mu$ -imidazolate complexes are also known.<sup>8</sup> We wish to report now the reaction of coordinated imidazole in  $\text{Co}(\text{NH}_3)_5(\text{ImH})^{3+}$  with both the reductant  $e_{aq}^-$  and the oxidizing radical OH.

## Experimental Section

The complex  $[\text{Co}(\text{NH}_3)_5(\text{ImH})](\text{ClO}_4)_3$ <sup>9</sup> in triply distilled water ( $[\text{Co}] = 10^{-3}$  M) was reacted with  $e_{aq}^-$  (by using a  $\text{N}_2$ -purged solution containing 0.1 M *tert*-butyl alcohol) or with the OH radical (by using a  $\text{N}_2\text{O}$ -saturated solution). The 1-MeV pulse radiolysis facility, optical system, and process of kinetic analysis have been described previously.<sup>10</sup> Radiolysis of aqueous solutions with a pulse of fast electrons generates  $e_{aq}^-$ , OH, and H radicals; the OH radical is a powerful oxidant ( $E^\circ \sim 2$  V) and  $e_{aq}^-$  is a powerful reductant ( $E^\circ = -2.8$  V).<sup>5</sup> The former is effectively quenched by radical scavengers such as *tert*-butyl alcohol added to the solution. The  $\cdot\text{CH}_2\text{C}(\text{CH}_3)_2\text{OH}$  radical produced is a weak reducing agent that does not react rapidly with cobalt(III) ammine complexes, leaving the aquated electron and H<sup>+</sup> as reacting species;<sup>11</sup> of these,  $e_{aq}^-$  reacts much more rapidly than H<sup>+</sup>.  $\text{N}_2\text{O}$  effectively scavenges  $e_{aq}^-$  with the formation of an equivalent amount of OH radical.

Product analyses were performed on solutions pulsed repetitively ( $50$  s<sup>-1</sup>), as previously described.<sup>10</sup> Chromatographic separation on Dowex 50W-X2 (H<sup>+</sup>) resin allowed the recovery of free ligand, cobalt(II), ammonium ion, and unreacted complex.<sup>10</sup> A solution of  $\text{Co}(\text{NH}_3)_5(\text{ImH})(\text{ClO}_4)_3$  (1.84 mmol, 500 mL) purged with  $\text{N}_2\text{O}$  was irradiated with a train of pulses ( $50$  s<sup>-1</sup>) while cycling through the 1-cm cell at 15 mL min<sup>-1</sup> and collected. Elution separated 0.29 mmol

Table I. Rate Constants for the Reaction of  $e_{aq}^-$  and OH Radicals with Imidazole and (Imidazole)pentaamminecobalt(III) Ion and Decay Kinetics of the Intermediates Produced

reaction	$k(\text{formation}),$ M <sup>-1</sup> s <sup>-1</sup>	$k(\text{decay})$	ref
$\text{ImH}_2^+ + e_{aq}^-$	$4.3 \times 10^9$	$2.1 \times 10^9$ M <sup>-1</sup> s <sup>-1</sup>	12
$\text{MeImH}^+ + e_{aq}^-$	$1.9 \times 10^{10}$	$2.3 \times 10^9$ M <sup>-1</sup> s <sup>-1</sup>	12
$(\text{NH}_3)_5\text{CoImH}^{3+} + e_{aq}^-$	$6.8 \times 10^{10}$	$2.5 \times 10^3$ s <sup>-1</sup>	a
$\text{ImH}_2^+ + \text{OH}$	$5.5 \times 10^9$	$5.5 \times 10^9$ M <sup>-1</sup> s <sup>-1</sup>	12
$\text{MeImH}^+ + \text{OH}$	$5.0 \times 10^9$		12
$(\text{NH}_3)_5\text{CoImH}^{3+} + \text{OH}$	$4.6 \times 10^9$	$3.2 \times 10^3$ s <sup>-1</sup>	a

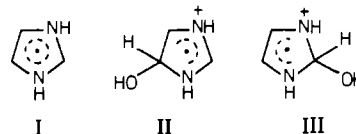
<sup>a</sup> This work.

of Co(II) and 0.62 mmol of unreacted Co(III). For reaction with  $e_{aq}^-$ , a solution of  $\text{Co}(\text{NH}_3)_5(\text{ImH})^{3+}$  (1.90 mmol, 400 mL) in 0.1 M *tert*-butyl alcohol was irradiated ( $50$  s<sup>-1</sup> pulses, flow rate 20 mL min<sup>-1</sup>) and yielded 0.16 mmol Co(III) and 0.58 mmol of unreacted Co(III). The  $G$  value for the combined OH, H, and  $e_{aq}^-$  reactions was 4.7, by dosimetry. Products were analyzed by one or more of the techniques of vis/UV spectroscopy, atomic absorption spectroscopy, <sup>1</sup>H NMR spectroscopy (Varian HA 100 spectrometer), and mass spectrometry.

Redox reactions of freshly prepared and nitrogen-purged solutions of vanadium(IV) ( $\text{VO}^{2+}$ ) and  $\text{Co}(\text{NH}_3)_5(\text{ImH})^{3+}$  were followed by using a Cary 118 spectrophotometer and a manual stopped-flow mixer. A constant ionic strength (1.0 M, adjusted with NaCl) and strongly basic conditions (0.5 M NaOH) were employed.

## Results and Discussion

Reaction of the complex with  $e_{aq}^-$  yielded a transient with an absorption maximum at 290 nm ( $\epsilon_{\text{max}} = 6 \times 10^3$  M<sup>-1</sup> cm<sup>-1</sup>). This compares with the previously reported transient spectrum of free  $\text{ImH}_2^+$  and  $e_{aq}^-$  ( $\lambda_{\text{max}}$  300 nm,  $\epsilon_{\text{max}} 5.6 \times 10^3$  M<sup>-1</sup> cm<sup>-1</sup>),<sup>12</sup> attributed to radical I although the absorption shoulder



at 360 nm reported for free imidazole was not detected in this study of the coordinated ligand. The similarity in the transient spectra from reaction of free  $\text{ImH}_2^+$  and coordinated ImH is consistent with the added electron being localized on the ImH ligand in the  $\text{Co}(\text{NH}_3)_5(\text{ImH})^{2+}$  transient. This region of the complex spectrum shows minimal absorbance, and it is not surprising therefore that the spectrum of the coordinated radical is perceived. The rate constant for the formation was determined by monitoring the decay kinetics of  $e_{aq}^-$  at 580 nm in the presence of different concentrations of complex and is in the usual range of  $(2-8) \times 10^{10}$  M<sup>-1</sup> s<sup>-1</sup> reported previously for reactions with cobalt(III) ammine complexes.<sup>5</sup>

Reaction of the complex with the OH radical produced a transient with an absorption maximum at 280 nm, analogous to the maximum for reaction with free ImH (295 nm).<sup>12</sup> The rate constant for its formation, determined by competition kinetics with KSCN,<sup>10</sup> is similar to that reported for free  $\text{ImH}_2^+$  and  $\text{MeImH}^+$  (Table I).<sup>12,13</sup> Pulse radiolysis and ESR studies of free  $\text{ImH}_2^+$  suggest that OH radicals add at both C<sub>2</sub> and C<sub>5</sub> positions, producing radicals II and III in acid.<sup>13,14</sup>

Decomposition of the radical intermediate complexes produced by  $e_{aq}^-$  and OH reacting with  $\text{Co}(\text{NH}_3)_5(\text{ImH})^{3+}$  yielded cobalt(II) quantitatively (determined by atomic absorption analysis); other products were ammonia (detected by <sup>1</sup>H NMR spectroscopy as  $\text{NH}_4^+$ ) and free organic ligand. Following the reaction with  $e_{aq}^-$ , mass spectrometry and <sup>1</sup>H NMR spec-

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**Table II.** Rate Constants for Reduction of the (Imidazole)pentaamminecobalt(III) Ion with Various Metal Ions

reductant	$k(25^\circ\text{C}), \text{M}^{-1} \text{s}^{-1}$	$E^\circ, \text{V}$	ref
$\text{V}_{\text{aq}}^{2+}$	$2 \times 10^{-2}{}^a$	-0.25	17
$\text{Ru}(\text{NH}_3)_6^{2+}$	$3.7 \times 10^{-2}{}^a$	+0.051	17, 18
$\text{Cr}_{\text{aq}}^{2+}$	$3.5 \times 10^{-4}{}^a$	-0.41	17
$\text{VO}_2^{2+}$	$1.3{}^b$	-0.74	c

<sup>a</sup> Acidic conditions. <sup>b</sup> Strongly basic conditions;  $[\text{OH}^-] = 0.5 \text{ M}$ . <sup>c</sup> This work.

troscopy showed that the only organic molecule recovered was imidazole. The reaction with the OH radical yielded the expected decay products of II and III, detected by  $^1\text{H}$  NMR spectroscopy and mass spectrometry. These observations are consistent with transient complexes of the radicals I-III decaying by an intramolecular redox process, yielding cobalt(II).

The uncoordinated radicals decay rapidly by second-order kinetics (Table I). The analogous complexed radicals decay by a first-order pathway, which is independent of dose or complex concentration. The rate of this intramolecular electron transfer ( $\sim 3 \times 10^3 \text{ s}^{-1}$ ) is analogous to that reported for the intramolecular redox step in (*p*-nitrobenzoato)pentaamminecobalt(III) ( $2.6 \times 10^3 \text{ s}^{-1}$ ).<sup>7</sup> The O-bound pyrazine-2-carboxylate complex  $\text{Co}(\text{NH}_3)_5(\text{OCOpz})^{2+}$  also decays relatively slowly ( $90 \text{ s}^{-1}$ );<sup>15</sup> however, the chelated ligand in  $\text{Co}(\text{NH}_3)_4(\text{OCOpz})^{2+}$  decays rapidly ( $> 3 \times 10^4 \text{ s}^{-1}$ ).<sup>16</sup> It has been asserted that the aromatic nitrogen atom is a better lead-in group for the electron transfer than carboxylate.<sup>16</sup> This was supported by dramatically different absorption spectra for the chelated complexed radical and the free ligand radical in that case, whereas the O-bound radical was spectroscopically similar to the free radical. Since the latter observation has also been noted here for the N-bound imidazole radicals, the result for chelated pyrazine-2-carboxylate is unusual. The unidentate N-bound ligand has not been studied, however, so the effect of chelation in that system cannot be determined unequivocally. Nevertheless, the decay rates for the chelated pyrazine-2-carboxylate and the imidazole complexes differ by only approximately 1 order of magnitude, and the strictly limited data available at present do not warrant extensive comment at this stage.

It seems reasonable that the nitrobenzoate ligand can trap  $e^-$  ( $\text{H}_2\text{O}$ ) through the electron-deficient nitro group in preference to the metal ion. It is more surprising that the coordinated imidazole traps the hydrated electron before the metal ion does. Presumably, the electron is trapped by the unfilled delocalized  $\pi^*$  antibonding orbitals of the heterocycle, but there is no strong evidence, that we could find, for imidazole being a good electron sink. For free imidazole, the reduction potential is more negative than  $-1.5 \text{ V}$  in  $\text{H}_2\text{O}$ . For the imidazole complex, only reduction of the metal ion was observed ( $-0.3 \text{ V}$ ). The very low activation energies associated with these high-energy radical processes presumably allow even the high-energy minima to be relatively efficient traps initially.

An outer-sphere mechanism has been suggested for the redox reaction of (imidazole)pentaamminecobalt(III) with metal(II) reductants.<sup>17</sup> However, these experiments were conducted in acidic solutions, which limit the possibility of a bridging inner-sphere pathway by protonating the imidazole. Since bridging modes for binding imidazole between metal ions has been established,<sup>8</sup> we sought a redox system that was

accessible in basic solution and subsequently selected the  $\text{VO}_2^{2+}/\text{VO}_2^+$  couple. Reaction of fresh nitrogen-purged solutions of  $\text{VO}_2^{2+}$  and oxidant  $\text{Co}(\text{NH}_3)_5(\text{Im})^{2+}$  in  $0.5 \text{ M}$  NaOH solution was appreciably faster ( $10^2$ - $10^4$  times) than reduction reactions performed in acid solution with  $\text{Co}(\text{NH}_3)_5(\text{ImH})^{3+}$  as the oxidant (Table II). An inner-sphere mechanism may be implied, but the reductant is also more potent than the other outer-sphere reductants. Also the rate is still not sufficiently fast to allow detection of transients by stopped-flow spectroscopy or electron spin resonance techniques.

Determination of the rate at which an electron is transferred intramolecularly from a coordinated and potentially bridging ligand into the metal center is of importance particularly in extending our understanding of inorganic and biological redox processes. The rate of electron transfer from the coordinated imidazole radical to the cobalt(III) center is relatively slow, and this may be a consequence of a limited overlap of ligand  $\pi$  orbitals with the metal  $\sigma$ -acceptor orbitals. An alternative recent suggestion has invoked an unfavorable equilibrium step between the cobalt(III)-radical ligand complex and the (presumably low spin) cobalt(II)-ligand complex preceding dissociation (and spin rearrangement), so that the measured rate is a composite term, disguising a rapid electron transfer.<sup>16</sup> The reasons for the apparently slow rates are not clearly resolved and are being pursued. Subsequent to this study, we are extending our investigations to pentaamminecobalt(III) complexes of a range of potentially bridging ligands.

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**Registry No.**  $\text{Co}(\text{NH}_3)_5(\text{ImH})^{2+}$  (isomer 1), 87050-20-2;  $\text{Co}(\text{NH}_3)_5(\text{ImH})^{2+}$  (isomer 2), 87050-21-3;  $[\text{Co}(\text{NH}_3)_5(\text{ImH})](\text{ClO}_4)_3$ , 15279-15-9;  $\text{VO}_2^{2+}$ , 20644-97-7;  $\text{Co}(\text{II})$ , 22541-53-3; OH, 3352-57-6;  $\text{H}_2\text{O}$ , 7732-18-5; ammonium, 14798-03-9.

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### Electron Paramagnetic Resonance Study of Tris(2,2'-bipyridine)cobalt(II) Complexes in Zeolite Y: Evidence for a Spin Equilibrium

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Evidence for the formation of transition-metal complexes within the cavities of zeolites has been provided by a number of investigations.<sup>1</sup> Recently, tris(bipyridine) complexes of iron and ruthenium have been synthesized within the supercages of zeolite Y, and their properties have been studied.<sup>2-4</sup> Both Fe(III) and Ru(III) in the respective complexes were found to be in the low-spin state at 77 K. An extension of this study to 2,2'-bipyridine (bpy) complexes of Co(II) in zeolite Y reveals that for  $[\text{Co}^{\text{II}}(\text{bpy})_3]^{2+}$  an equilibrium occurs between two spin states.

A dynamic spin equilibrium has been observed for certain iron, cobalt, and nickel compounds.<sup>5-12</sup> For cobalt(II) the

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