

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°, 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
VO_2^{2+}	$1.3{}^b$	-0.74	c

^a Acidic conditions. ^b Strongly basic conditions; $[\text{OH}^-] = 0.5 \text{ M}$. ^c 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 ^1H 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) ($2.6 \times 10^3 \text{ s}^{-1}$).⁷ The O-bound pyrazine-2-carboxylate complex $\text{Co}(\text{NH}_3)_5(\text{OCOpz})^{2+}$ also decays relatively slowly (90 s^{-1});¹⁵ however, the chelated ligand in $\text{Co}(\text{NH}_3)_4(\text{OCOpz})^{2+}$ decays rapidly ($> 3 \times 10^4 \text{ s}^{-1}$).¹⁶ It has been asserted that the aromatic nitrogen atom is a better lead-in group for the electron transfer than carboxylate.¹⁶ 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^- (H_2O) 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 π^* 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 V in H_2O . For the imidazole complex, only reduction of the metal ion was observed (-0.3 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.¹⁷ 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,⁸ 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 VO_2^{2+} and oxidant $\text{Co}(\text{NH}_3)_5(\text{Im})^{2+}$ in 0.5 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 π orbitals with the metal σ -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.¹⁶ 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; VO_2^{2+} , 20644-97-7; $\text{Co}(\text{II})$, 22541-53-3; OH^- , 3352-57-6; H_2O , 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.¹ Recently, tris(bipyridine) complexes of iron and ruthenium have been synthesized within the supercages of zeolite Y, and their properties have been studied.²⁻⁴ Both $\text{Fe}(\text{III})$ and $\text{Ru}(\text{III})$ 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 $\text{Co}(\text{II})$ 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.⁵⁻¹² For cobalt(II) the

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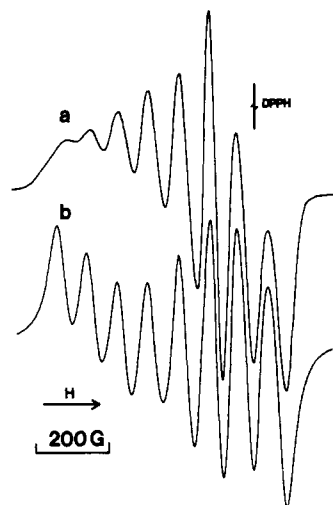


Figure 1. EPR spectra of tris(2,2'-bipyridine)cobalt(II) complex in zeolite Y: (a) experimental spectrum; (b) simulated spectrum.

${}^2E \rightleftharpoons {}^4T$, $\Delta S = 1$ transition has been determined as a function of temperature from both magnetic susceptibility and EPR measurements.⁶⁻¹¹ The $[\text{Co}^{\text{II}}(\text{terpy})_2]^{2+}$ complex (terpy = 2,2',2''-terpyridine) has been studied extensively, but to our knowledge a spin equilibrium for $[\text{Co}^{\text{II}}(\text{bpy})_3]^{2+}$ has not been previously reported. Moreover, there are no known examples of a spin equilibrium existing in a zeolite, although it has been shown that both the $S = 3/2$ and $S = 1/2$ states of a $[\text{Fe}^{\text{I}}(\text{NO})]^{2+}$ complex may be formed.¹³

Experimental Section

A CoK-Y zeolite was prepared from a Linde Na-Y zeolite (Lot. No. Y-52 3365-94) by exhaustive exchange (to 86%) of Na^+ with K^+ ions in a 1 M solution of KCl. The K-Y zeolite was subsequently exchanged with Co^{2+} ions in a 0.35 mM solution of cobalt nitrate at 70 °C for 24 h. A CoNa-Y zeolite was prepared from Na-Y by cobalt exchange. Cation analysis of the zeolites indicated that CoK-Y and CoNa-Y zeolites had 4.16×10^{19} and 3.92×10^{19} Co^{2+} ions/g, respectively. These values correspond to 1.25 and 1.12 Co^{2+} ions/unit cell.

The cobalt-bipyridine complex was prepared by allowing the cobalt zeolites to react with 2,2'-bipyridine (K & K Laboratories) in a manner similar to that described by DeWilde and co-workers.³ Mixtures of cobalt zeolites and 2,2'-bipyridine with different ratios of bpy to cobalt were outgassed at 25 °C for 12 h, followed by heating to 200 °C for 24 h in a closed system. The samples were subsequently evacuated at 200 °C for 24 h.

EPR spectra were recorded on a Varian E6S spectrometer for X-band (9.1 GHz) measurements. The g values were determined relative to a diphenyl picrylhydrazyl (DPPH) standard ($g = 2.0036$). Spin concentrations were calculated by numerical double integration of the derivative spectra and comparison with a phosphorus-doped

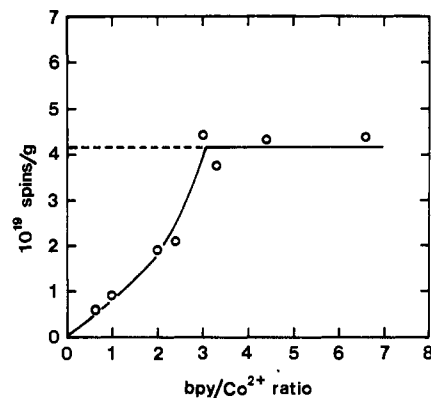


Figure 2. Variation of $[\text{Co}(\text{bpy})_3]^{2+}$ complex concentration as a function of the molar ratio of bpy to Co^{2+} ion in a CoK-Y zeolite.

silicon standard having a known spin concentration. Maximum uncertainty in the spin concentration is estimated to be $\pm 10\%$. Simulated EPR spectra were calculated by using the computer program SIM 13.¹⁴

Results and Discussion

After reaction of the CoK-Y zeolite with bpy, the EPR spectrum depicted in Figure 1a was recorded with the sample at 77 K. The set of eight lines is characteristic of the ${}^{59}\text{Co}$ ($I = 7/2$) hyperfine interaction. Identical spectra were observed following the reaction of the CoNa-Y zeolite with bpy. Since the spectra were not clearly separated into perpendicular and parallel components, it was not possible to determine directly the anisotropic g and A values. By computer simulation it was possible to obtain a reasonable facsimile (Figure 1b) of the experimental spectrum. The spectrum was simulated with $|A_{\parallel}^{\text{Co}}| = 58$ G, $|A_{\perp}^{\text{Co}}| = 84$ G, $g_{\parallel} = 2.12$, and $g_{\perp} = 2.150$. The shape of the spectrum was not very sensitive to variation in the parallel components; thus, relatively large errors accompany these values. Nevertheless, comparable values for the perpendicular and parallel components reflect a high degree of symmetry, consistent with a molecule having D_3 symmetry. In addition, the large deviation of g_{\parallel} from 2.0 suggests compressed octahedral symmetry.¹⁵

The variation of the bpy/ Co^{2+} ratio did not change the spectral shape but simply altered the intensity. The spin concentration was determined as a function of the amount of bipyridine added to the CoK-Y zeolite, and the results are depicted in Figure 2. The dashed line in the figure represents the Co^{2+} concentration in the zeolite, determined by atomic absorption. The important feature of this curve is the saturation that occurred at a bpy/ Co^{2+} ratio of 3. After this point, no additional complexes were formed. These observations indicate that the EPR spectrum of Figure 1 results from a low-spin $[\text{Co}^{\text{II}}(\text{bpy})_3]^{2+}$ complex. Thermodynamic considerations confirm that the tris complex is the most stable among the mono-, bis-, and tris(bipyridine)cobalt(II) complexes.¹⁶

Additional evidence for the formation of $[\text{Co}^{\text{II}}(\text{bpy})_3]^{2+}$ complexes in zeolites comes from a comparison of the EPR spectrum of Figure 1 with that found in a frozen dimethyl sulfoxide solution, which was prepared under vacuum from CoCl_2 and bipyridine (molar ratio 1/10 and 1/30).¹⁷ The major component of the latter spectrum, recorded with the sample at 77 K, was a broad, single line having a g value of 4.35. This g value is consistent with a high-spin d^7 ion in the weak-field limit. In addition, an eight-line spectrum, nearly identical with that depicted in Figure 1, was observed. This

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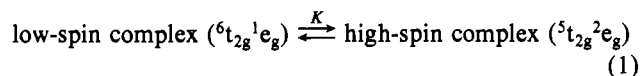
Table I. Concentrations and Equilibrium Constants of Low-Spin and High-Spin $[\text{Co}(\text{bpy})_3]^{2+}$ Complexes in a K-Y Zeolite

temp, K	concn, 10^{19} molecules/g		equil const
	low-spin complex	high-spin complex	
77	4.40 (4.16) ^a	0	
82	2.65	1.75	0.66
96	2.23	2.17	0.97
107	1.81	2.59	1.43
121	1.49	2.91	1.95
139	1.43	2.97	2.08

^a The value in parentheses indicates the concentration of cobalt as determined by atomic absorption.

spectrum is attributed to the low-spin $[\text{Co}^{\text{II}}(\text{bpy})_3]^{2+}$ complex. When the temperature of the sample was increased to 100 K, the spectrum of the high-spin complex decreased in intensity by a factor of 50, whereas the intensity of the low-spin complex decreased by a factor of 3.

When the temperature of the zeolite sample was increased above 77 K, the EPR spectrum was reversibly reduced in intensity and the line width increased. The spectrum eventually disappeared at 298 K. If the concentration of the low-spin complex had remained unchanged, the second integral of the spectrum would have been proportional to the reciprocal of the sample temperature. The observation that the integral measured at 298 K was far less than 1/3.87 of that at 77 K indicates a decrease in concentration of the low-spin complex, due to a spin equilibrium of the type



A $[\text{Co}^{\text{II}}(\text{bpy})_3]^{2+}$ complex was found to be in a high-spin state at room temperature, with a magnetic moment of $4.85 \mu_B$.¹⁸ A short relaxation time at $T > 80$ K is probably responsible for the absence of its EPR spectrum in zeolites. Such was the case for $[\text{Co}^{\text{II}}(\text{NH}_3)_6]^{2+}$, $[\text{Co}^{\text{II}}(\text{en})_3]^{2+}$, and $[\text{Co}^{\text{II}}(\text{en})_2]^{2+}$ complexes in zeolites,^{19,20} as well as for $[\text{Co}^{\text{II}}(\text{bpy})_3]^{2+}$ in Me_2SO at $T > 100$ K.

The concentrations of the low-spin and high-spin complexes with a gross $\text{bpy}/\text{Co}^{2+}$ ratio of 4.4 are tabulated in Table I, after taking into account the normal temperature dependence of the signal intensity. From these values the equilibrium constant, K , was calculated, with the assumption that all of the complex at 77 K was in the low-spin state (see Figure 2). From a plot of $\ln K$ vs. $1/T$, $\Delta H^\circ = 0.5 \pm 0.2$ kcal/mol and $\Delta S^\circ = 5 \pm 1$ eu were determined. K vs. $1/T$, $\Delta H^\circ = -0.5 \pm 0.2$ kcal/mol and $\Delta S^\circ = 5 \pm 1$ eu were determined. Enthalpy values of 0.8–1.4 kcal/mol have been obtained from the spin equilibrium of cobalt-terpyridine complexes.^{9,11} These thermodynamic parameters suggest that the spin equilibrium of $[\text{Co}^{\text{II}}(\text{bpy})_3]^{2+}$ in a zeolite is analogous to that of several cobalt complexes, in which a low-spin state is the one of lower energy, and the transition from a low-spin level to a high-spin level accompanies increases both in spin multiplicity and in molecular dimension.⁷ Relative to $[\text{Co}^{\text{II}}(\text{bpy})_3]^{2+}$ in more conventional solvents such as Me_2SO , the geometric limitations imposed by the zeolite may stabilize the low-spin state since the cavity and the complex have approximately the same dimensions (11–13 Å).

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Intermolecular Energy Transfer between Lanthanide Complexes. 9. Terbium(III) Donor and Europium(III) Acceptor Complexes of Amino Polycarboxylic Acids

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The commercial availability of separated lanthanide elements became possible through the use of ion-exchange chromatography, and the best methods employed amino polycarboxylic acids as complexing agents.¹ As a result, a great deal of work has focused on the study of lanthanide complexes with a wide variety of amino polycarboxylate ligands, and in many cases the association constants have been determined for all members of the series.^{2,3} In addition, several lanthanide amino polycarboxylate complexes have been used as aqueous NMR shift reagents capable of functioning in alkaline solutions.^{4,5} It is known that a ternary amino polycarboxylate hydroxo compound is formed above pH 10⁶ and that formation of the hydroxy species interferes with the shift reagent functions of the complexes.⁴

Recently, we reported a series of investigations in which circularly polarized luminescence spectroscopy was employed to study the complexation between chiral amino polycarboxylate ligands and lanthanide ions.⁷ At that time, it was noted that a wide variety of spectral changes could be observed when the solution pH was raised from 10 to 13 and that these modifications appeared to be associated with formation of the hydroxo species. In the present work, we have further investigated the complexation phenomena through an examination of the intermolecular transfer among lanthanide amino polycarboxylate complexes. With this spectroscopic technique, one may determine the conditions under which the formation of polynuclear species might take place. Such interactions were noted in several instances.

Experimental Section

Amino polycarboxylate ligands were generally obtained from Eastman or Aldrich and were used as received. The ligands examined were ethylenediaminetetraacetic acid (EDTA), 1,2-propanediaminetetraacetic acid (PDTA), (2-hydroxyethyl)ethylenediaminetetraacetic acid (HEDTA), *trans*-1,2-cyclohexanediaminetetraacetic acid (CDTA), ethylenebis(oxyethylenenitrilo)tetraacetic acid (EGTA), and diethylenetriaminepentaacetic acid (DTPA). In addition, 1,3-propanediaminetetraacetic acid (trimethylenedinitrilotetraacetic acid, TMDTA) was furnished by Professor G. R. Choppin (Florida State University).

Stock solutions of Tb(III) and Eu(III) were prepared by dissolving the 99.9% oxides (Research Chemicals) in a stoichiometric amount of 70% HClO_4 , neutralizing to pH 3.5 with NaOH, and then diluting to the desired volume. Stock solutions of Tb(III) and the amino polycarboxylate ligands were combined in such volumes as to yield an initial Tb(III) concentration of 15 mM and a final ligand:metal ratio of 1:1. In the energy-transfer experiments, microliter amounts of a stock Eu(III) solution were added to 3.0 mL of the Tb/amino polycarboxylate solution and extra ligand was also added to keep the

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