Inorganica Chimica Acta, 65 (1982) L29–L30 L29

An EPR Study of Ruthenium(III) Aquo Complexes in Water and in Zeolite-Y

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Received February 4, 1982

Ruthenium, both in reduced and ionic states, is effective for the activation of CO when incorporated into zeolites [1–3]. Normally the ruthenium is exchanged into zeolites as the $[Ru^{III}(NH_3)_6]^{3+}$ complex, which is a satisfactory route to the formation of small metallic particles (<13 Å) in the zeolite cavities [2]. Attempts to produce ruthenium ions coordinated only to the zeolite lattices are complicated by oxidation and reduction reactions, depending on the atmosphere, which result in complex ions such as $[Ru(O_{zeol})_3(NH_3)_x(NO)]$ [4]. The difficulties introduced by the ammine ligands may be circumvented by exchanging into the zeolite $[Ru^{III}(H_2O)_6]^{3+}$ or related hydroxy complexes. These complexes have characteristic EPR spectra which may be used to identify the ionic species within the zeolite.

Coughlan *et al.* [5] previously reported the preparation of $[Ru(H_2O)_6]^{3+}$ and its exchange into several zeolites, but the mode of preparation of the complex and the diffuse reflectance spectra of the zeolites make it questionable as to whether this proposed complex was actually introduced into the zeolite. Most significant is the fact that the exchange was carried out at a pH of 6.5 where $[Ru^{III}(H_2O)_6]^{3+}$ is unstable and polymerized hydroxy species are known to occur [6].

In the present study $[Ru^{III}(H_2O)_6]^{3+}$ was prepared in 2 *M* HBF_4 using the method of Kallen and Earley [7]. The presence of fluoride ions proved to be deleterious to the zeolite crystallinity; therefore, a modification of the method suggested by Buckley and Mercer [8] was used to substitute toluene sulfonate ions for tetrafluoroborate ions via an anion exchange resin.

Optical spectra in the region 250–700 nm of solutions with either counter ion exhibited absorption maxima at 295 nm and at 390 nm. The former is due to the $[Ru^{III}(H_2O)_5(OH)]^{2+}$ complex (λ_{max} = 290 nm [6]) and the latter to the $[Ru^{III}(H_2O)_6]^{3+}$ complex (λ_{max} = 225, 392 nm [7]). Based on the reported extinction coefficients [6, 7] ($\epsilon^{290} = 1650$ and $\epsilon^{392} = 30$) it is evident that $[Ru^{III}(H_2O)_6]^{3+}$ was the dominant complex in solution. As the pH was increased by adding NaOH, the band at 390 nm decreased and the band at 295 nm increased in intensity, which is consistent with the equilibrium reaction

$$[Ru^{III}(H_2O)_6]^{3+} \rightleftarrows [Ru^{III}(H_2O)_5OH]^{2+} + H^+ \qquad (1)$$

Using CF_3SO_3H, Harzion and Navon [6] have recently established that pK = 2.4 ± 0.2 for this reaction. At pH values greater than 2 we observed that λ_{max} shifted to longer wavelengths, until at a pH of 4.3 λ_{max} was at 325 nm. This may be indicative of a $[Ru^{III}(H_2O)_5(OH)_2]^+$ complex.

The EPR spectra of a frozen toluene sulfonic acid solution at various pH values are given in Fig. 1. The spectrum of the complex in 2 *M* toluensulfonic acid solution is characterized by $g_\perp = 2.399$ and a broad minimum at $g_\parallel = 1.615$ (The errors in g values are estimated to be ±0.005). As the pH increased the spectrum of a new species became evident, and at a pH of 2.8 the dominant species had $g_\perp = 2.373$ and $g_\parallel = 1.722$. The concentration of paramagnetic species, as determined by double integration of the EPR signals, was approximately one-half of the total ruthenium concentration in freshly prepared samples.

Ion exchange of the ruthenium complex was carried out at pH = 3.8 using 1 g of zeolite, in 1 l of 6×10^{-4} *M* ruthenium for 24 h. The temperature was 25 °C. After exchange the zeolite was washed with deionized distilled water and allowed to dry in air at room temperature. X-ray diffraction spectra of the resulting material confirm that the crystallinity of the zeolite was maintained, provided toluene sulfonate was the anion.

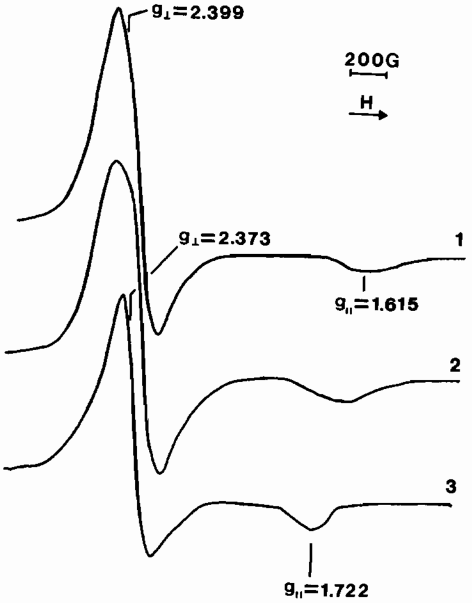

Fig. 1. EPR spectra of ruthenium(III) complexes at 77 K (1) in 2 *M* toluenesulfonic acid; (2) at pH = 0.57; (3) at pH = 2.8.

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The EPR spectra of a RuY zeolite containing 3.6 ruthenium ions per unit cell are depicted in Fig. 2. After degassing the sample under vacuum at 25 °C for 16 h the spectrum of curve 1 was observed. The g values are compared in Table I with those obtained for the ruthenium complex in aqueous solution. When the zeolite was heated to progressively higher temperatures, the spectrum decreased in amplitude, and after 300 °C none of the original spectrum remained.

Harzion and Navon [6] have previously noted that $[Ru^{III}(H_2O)_2]^{3+}$ has a low-spin d^5 electronic configuration as indicated by its magnetic moment and its optical spectrum The g values of the spectra in Fig. 1 are consistent with this electronic configuration We therefore assign the species having $g_\perp = 2.399$ and $g_\parallel = 1.615$ to $[Ru^{III}(H_2O)_6]^{3+}$ and the species having $g_\perp = 2.373$ and $g_\parallel = 1.722$ to its conjugate base, $[Ru^{III}(H_2O)_5OH]^{2+}$ Under the pH conditions of the exchange reaction $[Ru^{III}(H_2O)_5OH]^{2+}$ is the major component of the solution, and it is expected this monomeric species would enter the zeolite. Indeed the g values of the aquo complex in the zeolite are similar to those observed for $[Ru^{III}(H_2O)_5OH]^{2+}$ in solution. It is interesting to note that more than 50% of these complexes remained even after most of the water had been removed from the zeolite by heating the sample under vacuum at 100 °C.

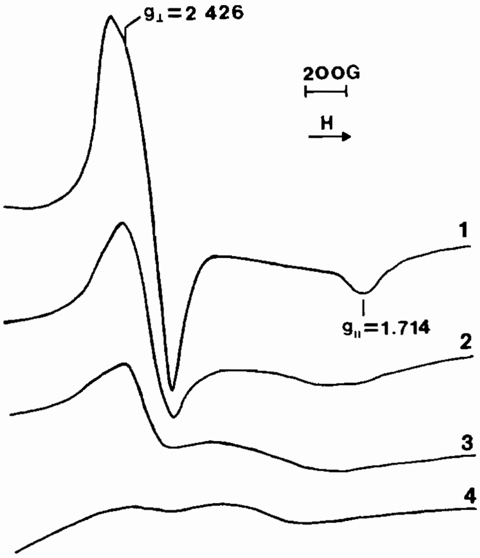

Fig. 2. EPR spectra of ruthenium(III) complex in $Ru_{3.6}Y$ zeolite. (1) after degassing 16 h at 25 °C, (2) after degassing 1 h at 100 °C; (3) after degassing 2 h at 200 °C; (4) after degassing 3 h at 300 °C.

TABLE I EPR Parameters for Tuthenium(III) Complexes

Complex	$g_\perp$	$g_\parallel$	δ (cm^{-1})
$[Ru^{III}(H_2O)_6]^{3+}$	2.399	1.615	350
$[Ru^{III}(H_2O)_5OH]^{2+}$	2.373	1.722	419
$[Ru^{III}(H_2O)_5OH]Y$	2.426	1.714	388

The theory of low-spin d^5 complexes having a t_2^5 groung state has been described by Wertz and Bolton [9], where $g_\parallel = g_e(\cos^2\omega - \sin^2\omega) - 2\sin^2\omega$ and $g_\perp = g_e\cos^2\omega - 2\sqrt{2}\ \sin\omega\cos\omega$, $\tan 2\omega = \dfrac{\sqrt{2}\eta}{1 + 1/2\eta}$ and $\eta = \lambda/\delta$. Here, λ is the spin–orbit coupling constant and δ is the extent of tetragonal distortion Using $\lambda = -250$ cm^{-1}, the calculated values of δ for the three systems of interest are listed in Table I. As expected, the extent of tetragonal distortion increases as H_2O is replaced by OH^- in the complex

In conclusion, this note describes the EPR spectrum of $[Ru^{III}(H_2O)_6]^{3+}$ and $[Ru^{III}(H_2O)_5OH]^{2+}$ complexes Moreover, $[Ru^{III}(H_2O)_5OH]^{2+}$ may be exchanged into a zeolite, which provides a means of introducing ionic ruthenium into a zeolite without the complications imposed by more reactive ligands.

Acknowledgement

The authors wish to acknowledge the support of this work by the Division of Basic Energy Sciences, Department of Energy.

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