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## A Proton Magnetic Resonance Cation Solvation Study of Uranyl Perchlorate, Uranyl Nitrate, and Uranyl Perchlorate-Hydrochloric Acid Solutions in Water-Dimethyl Sulfoxide-Acetone Mixtures

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A competitive solvation and complex formation study has been completed for solutions of  $\text{UO}_2(\text{ClO}_4)_2$ ,  $\text{UO}_2(\text{NO}_3)_2$ , and  $\text{UO}_2(\text{ClO}_4)_2\text{-HCl}$  in water-dimethyl sulfoxide-acetone mixtures using a low-temperature proton magnetic resonance (pmr) technique. At temperatures in the  $-80$  to  $-100^\circ$  range, the ligand and proton exchange rates are slow enough to permit the direct observation of pmr signals for water and DMSO molecules in the  $\text{UO}_2^{2+}$  ion solvation shell. Signal areas gave a quantitative measure of the contribution of water and DMSO to the  $\text{UO}_2^{2+}$  ion solvation number. The difference between the sum of these contributions and the maximum value of 4 for this ion was used to estimate the amount of anion complexed. In all systems, DMSO is preferentially bound by the  $\text{UO}_2^{2+}$  at the expense of water. Solvation by DMSO is an energetically more favorable process than cation-anion complex formation.

### Introduction

The behavior of ions in mixed aqueous solvents has been studied primarily by electrochemical techniques,<sup>1,2</sup> and in several cases by ion-exchange<sup>3-7</sup> and Raman spectroscopic<sup>8-10</sup> methods. Recent works<sup>11-25</sup> have demonstrated the utility of proton magnetic resonance (pmr) spectroscopy for the observation of separate pmr signals for solvent molecules in a cation solvation shell and in bulk medium. Area measurements then provide a reliable solvation number value. With this method, hydration numbers have been determined for diamagnetic  $\text{Al}^{3+}$ ,  $\text{Ga}^{3+}$ ,  $\text{In}^{3+}$ ,  $\text{Be}^{2+}$ , and  $\text{Mg}^{2+}$ ,<sup>11-14</sup>  $\text{Sc}^{3+}$ ,  $\text{Y}^{3+}$ , and  $\text{Th}^{4+}$ ,<sup>15,16</sup>  $\text{Sn}^{4+}$ ,  $\text{UO}_2^{2+}$ , and  $\text{Zn}^{2+}$ ,<sup>17-19</sup>  $\text{La}^{3+}$  and  $\text{ZrO}^{2+}$ ,<sup>20</sup> and paramagnetic  $\text{Co}^{2+}$ .<sup>21</sup> Competitive

solvation of  $\text{Al}^{3+}$  in aqueous mixtures of a variety of organic bases has been studied<sup>22-24</sup> and inner-shell complex formation has been observed in solutions of several diamagnetic cations, including  $\text{UO}_2^{2+}$ .<sup>15-19,25</sup>

Since mixed solvents provide a convenient means of varying physical properties, such as the dielectric constant and viscosity, their use as investigative media is extensive. The ion-exchange studies of King and co-workers provided detailed analyses of the ionic species present in solutions of  $\text{Cr}^{3+}$  in aqueous mixtures of methanol,<sup>3,4</sup> ethanol,<sup>5</sup> pyridine *N*-oxide,<sup>6</sup> and DMSO.<sup>7</sup> While not as specific as ion-exchange methods, the pmr measurements of this report can yield a rapid, direct determination of the average contribution of each solvent component to the total cation solvation number. The  $\text{UO}_2^{2+}$  ion and the water-DMSO combination were chosen to complement a previous complex formation study<sup>19</sup> and to compare these systems to those involving  $\text{Al}^{3+}$  and  $\text{Cr}^{3+}$ .<sup>7</sup>

### Experimental Methods

Reagent grade uranyl salts (Alfa), ultrapure hydrochloric acid solution (Brinkmann), and spectroquality solvents were used as received without further purification. Samples were prepared by adding known quantities of DMSO, acetone-*d*<sub>6</sub>, and, in the  $\text{Cl}^-$  ion solutions, aqueous HCl to an aqueous uranyl salt stock solution, the composition of which had been determined by passage through a Dowex 50W-X8 ion-exchange column, followed by titration of the resultant solution. All samples were prepared in duplicate and their spectra were recorded immediately thereafter.

Chemical shifts and signal areas were determined with a Varian A-60 spectrometer, equipped with a variable-temperature device for measurements from  $-150$  to  $+200^\circ$ . The experiments involve cooling the sample in the spectrometer probe until the ligand and proton exchange rates have been reduced sufficiently to allow the observation of resonance signals for solvent molecules in the cation solvation shell. In this study, this observation was possible between  $-80$  and  $-100^\circ$ , a range made accessible by dilution of the samples with acetone. The use of acetone-*d*<sub>6</sub> avoided signal overlap in the methyl group spectral region.

### Results

The spectra of Figures 1 and 2 are typical of those obtained with the solutions of this study. In Figure 1,

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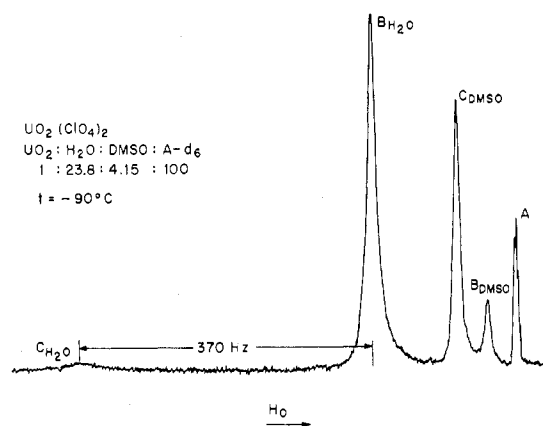


Figure 1.—The pmr spectrum of a  $\text{UO}_2(\text{ClO}_4)_2$  solution in a water–dimethyl sulfoxide–acetone- $d_6$  mixture. The signals arising from bulk water ( $B_{\text{H}_2\text{O}}$ ), coordinated water ( $C_{\text{H}_2\text{O}}$ ), bulk dimethyl sulfoxide ( $B_{\text{DMSO}}$ ), coordinated dimethyl sulfoxide ( $C_{\text{DMSO}}$ ), and acetone- $d_6$  proton impurities (A) are labeled. The mole ratios of all species also are shown.

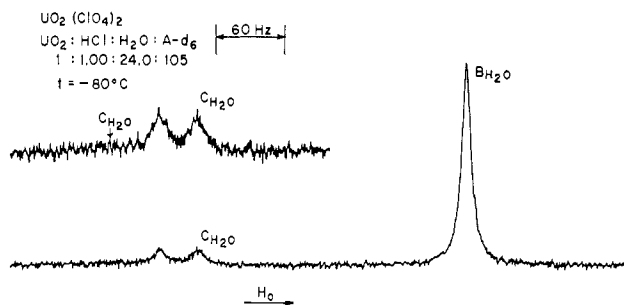


Figure 2.—The water pmr spectrum of a  $\text{UO}_2(\text{ClO}_4)_2$  solution in a water–acetone- $d_6$  mixture containing a 1:1 mole ratio of HCl to cation. The signals arising from bulk water ( $B_{\text{H}_2\text{O}}$ ) and coordinated water ( $C_{\text{H}_2\text{O}}$ ) are labeled, the latter shown at two amplitudes. The mole ratios of all species also are shown.

pmr signals are apparent for bound and bulk water, bound and bulk DMSO, and the acetone- $d_6$  proton impurities. The bulk DMSO signal is shifted 35–40 Hz upfield from the bound signal. Although a  $\text{UO}_2(\text{ClO}_4)_2$  solution is responsible for the spectrum of Figure 1, exactly analogous patterns were obtained with  $\text{UO}_2(\text{NO}_3)_2$  solutions. The multiple pattern at low field in Figure 2 is due to bound water in a  $\text{UO}_2(\text{ClO}_4)_2$  solution containing a 1:1 mole ratio of  $\text{Cl}^-$  to  $\text{UO}_2^{2+}$  and no DMSO. In the presence of DMSO and at higher  $\text{Cl}^-$  concentrations, the pattern remains unchanged but the signal intensity decreases sharply.

From area measurements with spectra such as these, the  $\text{UO}_2^{2+}$  solvation numbers of Tables I–III were obtained. In all cases the integrations of the DMSO signals were made with a precision of about 5%, but the broadness of the bound water signal and the large area difference between the bound and bulk water peaks limited the determination of the solvation number contribution of this component to a precision of 10%. The water concentrations were chosen to maintain a high ratio of this solvent to DMSO and to ensure solubility in the  $\text{Cl}^-$  and  $\text{NO}_3^-$  systems. In those cases in Tables I and III where a water contribution is not listed, the coordinated water signal either could not be detected,

TABLE I  
CATION SOLVATION NUMBERS FOR URANYL PERCHLORATE  
SOLUTIONS IN WATER–DIMETHYL SULFOXIDE–  
ACETONE- $d_6$  MIXTURES

| Mole ratios                                      |                                | Solvation numbers    |      |                      |
|--|--------------------------------|----------------------|------|----------------------|
| $\text{UO}_2(\text{ClO}_4)_2$ :<br>DMSO:A- $d_6$ | $\text{H}_2\text{O}$ :<br>DMSO | $\text{H}_2\text{O}$ | DMSO | Total                |
| 1:23.7:0.38:105                                  | 62:1                           | 3.6                  | 0.4  | 4.0                  |
| 1:23.3:1.13:70                                   | 20:1                           | 2.8                  | 1.1  | 3.9                  |
| 1:23.3:1.13:120                                  | 20:1                           | 2.9                  | 1.1  | 4.0                  |
| 1:24.0:1.70:100                                  | 14:1                           | 2.6                  | 1.6  | 4.2                  |
| 1:24.0:1.70:134                                  | 14:1                           | 2.4                  | 1.7  | 4.1                  |
| 1:22.0:2.56:105                                  | 8.6:1                          | 1.8                  | 2.3  | 4.1                  |
| 1:22.0:2.56:150                                  | 8.6:1                          | 1.7                  | 2.4  | 4.1                  |
| 1:19.7:4.18:50                                   | 4.7:1                          | ...                  | 3.8  | (4.0) <sup>a,b</sup> |
| 1:23.8:4.15:100                                  | 5.7:1                          | ...                  | 3.3  | (4.0) <sup>a,c</sup> |
| 1:19.5:8.13:50                                   | 2.4:1                          | ...                  | 3.9  | 3.9 <sup>a</sup>     |
| 1:19.5:8.50:50                                   | 2.3:1                          | ...                  | 4.0  | 4.0 <sup>a</sup>     |
| 1:12.5:12.5:50                                   | 1.0:1                          | ...                  | 4.2  | 4.2 <sup>a</sup>     |

<sup>a</sup> The bound water signal was observable but too small to be measured accurately. <sup>b</sup> The water contribution was assumed to be 0.2. <sup>c</sup> The water contribution was assumed to be 0.7.

TABLE II  
CATION SOLVATION NUMBERS FOR URANYL NITRATE  
SOLUTIONS IN WATER–DIMETHYL SULFOXIDE–  
ACETONE- $d_6$  MIXTURES

| Mole ratios                                     |                                | Solvation numbers    |      |       | Moles<br>of<br>$\text{NO}_3^-$<br>complex |
|---|--------------------------------|----------------------|------|-------|---|
| $\text{UO}_2(\text{NO}_3)_2$ :<br>DMSO:A- $d_6$ | $\text{H}_2\text{O}$ :<br>DMSO | $\text{H}_2\text{O}$ | DMSO | Total |   |
| 1:25.0:0.30:80                                  | 83:1                           | 2.3                  | 0.3  | 2.6   | 0.70                                      |
| 1:25.0:0.18:100                                 | 140:1                          | 1.8                  | 0.2  | 2.0   | 1.0                                       |
| 1:25.0:0.51:95                                  | 49:1                           | 1.8                  | 0.5  | 2.3   | 0.85                                      |
| 1:25.0:0.83:80                                  | 30:1                           | 1.6                  | 0.7  | 2.3   | 0.85                                      |
| 1:25.0:0.93:95                                  | 27:1                           | 1.5                  | 0.8  | 2.3   | 0.85                                      |
| 1:25.0:0.88:190                                 | 23:1                           | 1.4                  | 0.7  | 2.1   | 0.95                                      |
| 1:25.0:1.71:85                                  | 14:1                           | 1.7                  | 1.4  | 3.1   | 0.45                                      |
| 1:25.0:1.75:105                                 | 14:1                           | 1.3                  | 1.4  | 2.7   | 0.65                                      |
| 1:25.0:2.00:100                                 | 12:1                           | 1.2                  | 1.7  | 2.9   | 0.55                                      |
| 1:25.0:2.24:140                                 | 11:1                           | 1.4                  | 1.4  | 2.8   | 0.60                                      |
| 1:25.0:2.33:200                                 | 11:1                           | 0.9                  | 1.8  | 2.7   | 0.65                                      |

or as indicated in the footnotes, its intensity was too low to be integrated accurately. Since the individual numbers remained unchanged when several of the solutions of Tables I and II were acidified, hydrolysis is not extensive. This confirms the results of a prior pmr hydration study of the  $\text{UO}_2^{2+}$  ion.<sup>17,19</sup> In view of the numerous demonstrations of the inert nature of acetone as a solvating agent in these aqueous solutions,<sup>13,14,22,23</sup> the data of Tables I–III represent the total number of solvent molecules in the  $\text{UO}_2^{2+}$  ion solvation shell.

### Discussion

In a previous pmr study of  $\text{UO}_2(\text{ClO}_4)_2$  in water–acetone mixtures,<sup>17,19</sup> a cation hydration number of 4 was obtained. Since the  $\text{ClO}_4^-$  anion does not form inner-shell complexes in these systems, this value was taken as a maximum for  $\text{UO}_2^{2+}$ . On the other hand, strong evidence for complex formation was obtained in  $\text{NO}_3^-$ ,  $\text{Cl}^-$ , and  $\text{Br}^-$  solutions. The data of Tables I–III for water–DMSO mixtures are consistent with these previous observations. For example, in Table I, the sum of the water and DMSO contributions to the  $\text{UO}_2^{2+}$  ion solvation number is essentially 4 in each solution, and the value does not depend on acetone concentration.

TABLE III  
CATION SOLVATION NUMBERS FOR URANYL PERCHLORATE-HYDROCHLORIC ACID SOLUTIONS IN WATER-DIMETHYL  
SULFOXIDE-ACETONE-*d*<sub>6</sub> MIXTURES

| Mole ratios  |                       | Solvation numbers |      |       | Moles of<br>Cl <sup>-</sup> Complex |
|--|-----------------------|-------------------|------|-------|-------------------------------------|
| UO <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> :HCl:H <sub>2</sub> O:DMSO:A- <i>d</i> <sub>6</sub> | H <sub>2</sub> O:DMSO | H <sub>2</sub> O  | DMSO | Total |                                     |
| 1:1.00:24.0:0:105  | ...                   | 3.3               | ...  | 3.3   | 0.7                                 |
| 1:1.00:24.1:1.12:105   | 21:1                  | 2.2               | 1.1  | 3.3   | 0.7                                 |
| 1:1.00:24.1:3.13:95  | 7.7:1                 | 0.8               | 2.6  | 3.4   | 0.6                                 |
| 1:1.00:24.1:6.00:100   | 4.0:1                 | (0) <sup>a</sup>  | 3.2  | 3.2   | 0.8                                 |
| 1:1.50:17.3:0:100  | ...                   | 2.8               | ...  | 2.8   | 1.2                                 |
| 1:1.50:17.3:2.56:100   | 6.7:1                 | 0.9               | 2.5  | 3.4   | 0.6                                 |
| 1:1.50:17.3:5.63:100   | 3.1:1                 | ...               | 3.6  | 3.6   | 0.4                                 |
| 1:1.50:30.0:5.44:100   | 5.5:1                 | ...               | 3.5  | 3.5   | 0.5                                 |
| 1:2.10:25.3:0.92:110   | 27:1                  | 1.1               | 0.9  | 2.0   | 2.0                                 |
| 1:2.10:25.3:1.93:125   | 13:1                  | ...               | 1.9  | 1.9   | 2.1                                 |
| 1:2.10:25.3:3.86:105   | 6.5:1                 | ...               | 2.7  | 2.7   | 1.3                                 |
| 1:2.10:25.3:3.78:210   | 6.7:1                 | ...               | 2.7  | 2.7   | 1.3                                 |
| 1:2.10:25.3:6.78:95  | 3.7:1                 | ...               | 3.4  | 3.4   | 0.6                                 |
| 1:3.15:22.5:1.03:100   | 22:1                  | 0.7               | 1.0  | 1.7   | 2.3                                 |
| 1:3.15:22.5:3.31:100   | 6.8:1                 | ...               | 2.3  | 2.3   | 1.7                                 |
| 1:3.15:22.5:6.64:100   | 3.4:1                 | ...               | 3.2  | 3.2   | 0.8                                 |
| 1:4.30:25.6:0.94:105   | 27:1                  | ...               | 0.9  | 0.9   | 3.1                                 |
| 1:4.30:25.6:2.51:100   | 10:1                  | ...               | 1.8  | 1.8   | 2.2                                 |
| 1:4.30:25.6:5.61:100   | 4.6:1                 | ...               | 2.9  | 2.9   | 1.1                                 |
| 1:4.30:25.6:6.15:110   | 4.2:1                 | ...               | 3.6  | 3.6   | 0.4                                 |

<sup>a</sup> A bound water signal was observed but it was too small to be accurately integrated.

The lack of dependence on dielectric constant is a reliable indication that complex formation is not occurring to any appreciable extent.

The UO<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> solution spectra revealed several interesting features of these solutions. At lower DMSO concentrations, only one DMSO signal is observed and the resonance position corresponds to the solvation shell peak. At higher DMSO concentrations, as seen in Figure 1, a bulk DMSO signal gradually appears. The fact that DMSO is practically completely coordinated even when water is present in a 20:1 molar excess or greater conclusively demonstrates the preference of UO<sub>2</sub><sup>2+</sup> for this base. This result is consistent with calorimetric data which indicate that solvation of ions by DMSO is energetically more favorable than solvation by water.<sup>26</sup> It contrasts, however, with the random solvation of Al<sup>3+</sup> by water and DMSO in comparable solutions<sup>22,23</sup> and the slight preference for DMSO exhibited by Cr<sup>3+</sup> in aqueous mixtures.<sup>7</sup>

The separations of the bulk and coordinated water (~380 Hz) and DMSO (~35–40 Hz) signals provide an estimate of the exchange rates, if the relationship  $\tau \simeq 10/2\pi\Delta\nu$  can be used to approximate the lifetime of a solvent proton in the cation solvation shell.<sup>27</sup> If so, at -80 to -100°,  $\tau$  is roughly  $4 \times 10^{-3}$  sec for water protons and  $4 \times 10^{-2}$  sec for DMSO molecules. Since the separate DMSO signals are observable at slightly higher temperatures, ~-60°, the ligand exchange rate is slower than this estimate.

Within the range of salt and solvent concentrations necessitated by solubility and the low temperatures of study, the data of Table II illustrate several aspects of the complexing process in UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> solutions. The estimates of the amount of NO<sub>3</sub><sup>-</sup> complexed, precise to

~10%, were based on the water and DMSO solvation number results and the conclusion of a previous study that the UO<sub>2</sub><sup>2+</sup>-NO<sub>3</sub><sup>-</sup> bonding is bidentate.<sup>19</sup> Thus, a solvation number of 2 would correspond to the replacement of two solvent molecules by one NO<sub>3</sub><sup>-</sup> ion. The results confirm the observation noted for ClO<sub>4</sub><sup>-</sup> solutions that DMSO is much more effective than water in solvating the UO<sub>2</sub><sup>2+</sup> ion. In all solutions, most of the DMSO was complexed at the expense of water and even NO<sub>3</sub><sup>-</sup>. With no DMSO present, the UO<sub>2</sub><sup>2+</sup> ion hydration number varied from 2 to 0 (complete NO<sub>3</sub><sup>-</sup> complexing) for UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> solutions over the water-acetone range of Table II.<sup>19</sup> Thus, from the data of Table II, it appears that solvation of UO<sub>2</sub><sup>2+</sup> by DMSO is more favorable than complexing of this cation by NO<sub>3</sub><sup>-</sup>. As anticipated, when the acetone concentration was varied for a specific H<sub>2</sub>O:DMSO:UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> mole ratio, complexing by NO<sub>3</sub><sup>-</sup> ion increased with a lowering of dielectric constant.

The coordinated water pattern of Figure 2 was obtained in all systems of Table III for which these signals were intense enough to be observed. This pattern reflects the complexity of the Cl<sup>-</sup> solutions and it is not readily interpretable in terms of simple successive monomeric UO<sub>2</sub><sup>2+</sup>-Cl<sup>-</sup> complexes. The features of interest in Figure 2 and other Cl<sup>-</sup> solution spectra are (1) the position of the broad signal at lowest field, ~560 Hz downfield from internal acetone, corresponds roughly to the resonance position of the coordinated water peak in ClO<sub>4</sub><sup>-</sup> (Figure 1) and NO<sub>3</sub><sup>-</sup> solutions, (2) the intensities of the remaining two signals were the same within the limits of measurement, and the areas decreased by the same amount when DMSO and Cl<sup>-</sup> were added, and (3) the position of the doublet varied over a ~30-Hz range with DMSO concentration. Unfortunately, this last measurement could not be made with the bound water peak at lowest field since it was too broad to be

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observable. However, the position of the coordinated water peak was invariant with composition in the  $\text{ClO}_4^-$  and  $\text{NO}_3^-$  solution spectra. Assuming all the  $\text{Cl}^-$  is complexed in the form of monomeric species only, these points and the observation of a solvation number of  $\sim 3$  in the 1:1  $\text{Cl}^-$ - $\text{UO}_2^{2+}$  solution of Figure 2 are consistent with the presence of roughly equal amounts of  $\text{UO}_2(\text{H}_2\text{O})_4$  and  $(\text{H}_2\text{O})_2\text{UO}_2\text{Cl}_2$ . The tetrahydrate would give rise to the low-field broad peak of Figure 2, and the two isomers of the dichloro complex, if equally stable, would be responsible for the doublet. However, no firm conclusions can be drawn without the support of other types of experimental data.

In the DMSO solutions containing a 1:1 and 1.5:1 mole ratio of  $\text{Cl}^-$  to  $\text{UO}_2^{2+}$ , the water contribution to the cation solvation shell decreases. The corresponding decrease in the signal intensity made signal integrations very difficult. In these systems the estimates of the amount of  $\text{Cl}^-$  complexed are in doubt, perhaps by as much as 0.1–0.2 unit. At higher  $\text{Cl}^-$  concentrations, when essentially all the water had been replaced in the solvation shell by DMSO and anion, the estimates are more reliable since only the integrations of the sharper DMSO peaks are involved. In all cases, however, it is clear that the presence of DMSO decreases the extent of  $\text{UO}_2^{2+}$ - $\text{Cl}^-$  complex formation. Up to a  $\text{Cl}^-$ : $\text{UO}_2^{2+}$  mole ratio of 4:1,  $\text{Cl}^-$  is completely complexed in similar solutions containing no DMSO.<sup>19</sup> The data of Table III demonstrate that when DMSO is present, the order of binding to  $\text{UO}_2^{2+}$  is  $\text{DMSO} > \text{Cl}^- > \text{H}_2\text{O} > \text{acetone}$ , a trend similar to that observed in the  $\text{NO}_3^-$

solutions. This order parallels the relative basic strengths generally quoted for these species.<sup>23</sup>

It is interesting that only one signal is observed for bound DMSO in the spectra corresponding to the solutions of Tables I–III. This observation may mean that only one DMSO solvation complex, perhaps  $\text{UO}_2(\text{DMSO})_4^{2+}$ , is present in each case, intramolecular exchange is very rapid, or the chemical shifts of the DMSO molecules in different environments are the same. The ion-exchange studies of King, *et al.*, demonstrated the presence of mixed solvation complexes in several solvent systems,<sup>3–7</sup> including water–DMSO solutions of  $\text{Cr}^{3+}$ ,<sup>7</sup> and by analogy, one might reasonably assume that species of similar composition are present here. It is not possible to distinguish unambiguously between the remaining two possibilities. Since the multiple signal pattern of Figure 2 may arise either from a combination of complexes such as those previously mentioned or from water molecules in the same complex, the intramolecular exchange rate cannot be estimated. Most likely, however, only small shift variations would result for bound DMSO molecules in different environments, since the methyl groups are far removed from the complexing interaction site in the DMSO molecule, the oxygen atom unshared electron pair.

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## Competitive Reductions of Cobalt(III) Complexes by Chromium(II)

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Relative rates of reduction by chromous ion of cobalt(III) complexes containing bridging groups have been determined by a method involving competing reactions. The technique exploits the competition of two potential bridging ligands (either in separate ions or in the same ion) for  $\text{Cr}^{2+}$  and treats the experimental data by means of a rate expression for competing reactions. For the system  $\text{Co}(\text{NH}_3)_5\text{L}^{2+}$ - $\text{Cr}^{2+}$ , relative rates of 2.75:1.89:1.51:1.00:0.88, at  $\mu = \sim 2 \times 10^{-2} M$ , are obtained for the iodo, bromo, chloro, fluoro, and azido complexes, respectively; at  $\mu = 0.1 M$  the relative rates for the iodo through the fluoro complexes are 4.3:2.6:1.8:1.00. The calculated interrelationships of these relative rates have been confirmed by  $\text{Cr}^{2+}$  competitive reductions of the requisite pairs of  $\text{Co}(\text{NH}_3)_5\text{L}^{2+}$  ions as well as the reduction of a solution containing the three ions  $\text{Co}(\text{NH}_3)_5\text{I}^{2+}$ ,  $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ , and  $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ . When two different halides are present in the same complex, as in *cis*- and *trans*- $\text{Co}(\text{en})_2\text{BrCl}^+$ , the relative preference of  $\text{Cr}^{2+}$  for  $\text{Br}^-$  over  $\text{Cl}^-$  is reduced from 1.26 (for the pentaammine system) to values of 1.14 and 1.00 for these *cis* and *trans* complexes, respectively. When  $\text{Cr}^{2+}$  reacts with a mixture of  $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$  and *trans*- $\text{Co}(\text{en})_2(\text{NO}_2)\text{Cl}^+$ , the rate of the reaction with chloride acting as the bridging group becomes greater than the rate of the reaction with bromide acting as the bridging group.

### Introduction

Several studies<sup>1–4</sup> show that in the reactions of chro-

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mous ion with both chromium(III) and cobalt(III) complexes of the general formula  $\text{M}(\text{NH}_3)_5\text{L}^{2+}$ , where  $\text{L}^- = \text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ , etc., the electron-transfer process proceeds *via* a bridged transition state in which L functions as a bridging group and then appears in the coor-