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A Direct Nuclear Magnetic Resonance Cation Hydration Study of Zirconyl Perchlorate and Zirconyl Nitrate Solutions in Water-Hexamethylphosphoramide-Acetone Mixtures

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Studies by a wide variety of classical and spectroscopic techniques have demonstrated the complexity of aqueous solutions of zirconium salts.³⁻¹¹ There is little evidence for the existence of the monomeric Zr^{4+} or ZrO^{2+} ions in solution at moderate to high zirconium concentrations. Rather the dominant species appears to be the ZrO^{2+} ion in a polymeric form of some kind. Since direct, low-temperature nuclear magnetic resonance (nmr) techniques have been extremely valuable for determining cation hydration numbers and the extent of complex formation in numerous diamagnetic and paramagnetic metal ion solutions,¹²⁻¹⁶ a similar approach was carried out with aqueous $ZrO(ClO_4)_2$ and $ZrO(NO_3)_2$ solutions. In spite of the complexity of these solutions, it was anticipated that a quantitative measure of the average hydration state of the zirconium species would be obtained.

The samples were prepared by the addition of a measured volume of cold acetone (-78°) to a weighed amount of aqueous zirconyl salt (Research Inorganic) stock solution, the concentration of which had been determined by passage through a Dowex 50W-X8 ion-exchange resin and titration of the resultant solution. Repeated titrations verified the stability of these pure aqueous stock solutions for a period of weeks. Reproducible hydration results were obtained with different stock solutions. The concentration of the

stock solution also was checked by an nmr area method with solutions containing known amounts of acetone. The water concentration was determined by a comparison of the area of this peak to that of acetone. To minimize the possibility of decomposition in the presence of acetone, the samples were kept at Dry Ice-acetone temperature until the spectra could be recorded, usually within a few hours of preparation. Measurements repeated within 1 week with the same sample gave identical hydration results.

The nmr experiments were made with a Varian HA-100 spectrometer, equipped with a variable-temperature accessory and a probe and radiofrequency unit for studying ^{31}P nuclei at 40.5 MHz. The method¹²⁻¹⁶ consists essentially of cooling the sample in the spectrometer probe to slow proton and ligand exchange and permits the observation of resonance signals for bulk and bound solvent molecules. A typical water pmr spectrum is shown in Figure 1 for a $ZrO(ClO_4)_2$ solution in a water-acetone mixture. All spectra, 1H and ^{31}P , were recorded at approximately -70° , in spite of the fact that bulk and bound hexamethylphosphoramide (HMPT) peaks were observable at ambient temperature. This procedure was consistent with the desire to keep the samples cold. The most significant feature of the spectrum in Figure 1 is the appearance of the two bound water signals, of essentially equal area, displaced downfield from the bulk water peak by 240 and 340 Hz. This pattern prevailed in the spectra of all solutions with the following significant changes. The addition of nitrate ion as nitric acid produced a selective intensity decrease of the high-field bound water peak, whereas the presence of HMPT resulted in an intensity decrease of both coordinated water peaks.

The ZrO^{2+} solvation numbers in a variety of solutions are summarized in Table I. The water and HMPT proton signal areas and, consequently, the solvation numbers were measured with a precision of 5-10%. As indicated in the table, bulk and bound HMPT methyl group doublets separated by ~ 18 Hz were observed at the higher mole ratios of base to salt listed. At 1:1 and 2:1 HMPT:salt mole ratios, only one set of doublets was seen, and from their resonance position they were assigned to bound ligand molecules. The ^{31}P nmr spectra of these solutions showed two signals at the low mole ratios of base to salt, each presumably arising from bound HMPT molecules. The appearance of a large bulk HMPT ^{31}P peak at the 6:1 and 8:1 mole ratios produced extensive overlap and precluded an area evaluation.

The data in Table I clearly reveal an average cation hydration number of about 4. Numerous prior studies have demonstrated the inert nature of acetone and the inability of perchlorate anion to form inner-shell complexes in diamagnetic salt solutions of this type.¹²⁻¹⁶ The addition of $HClO_4$ produced no significant change in the hydration number, ruling out hydrolysis and contact ion pairing as contributing processes. Also, the total solvation number remained unchanged in the water-HMPT mixtures, indicating the presence of the same principal species throughout. Thus, it may be concluded that the data of Table I reflect solvation only by water and HMPT and complex formation with nitrate ion when this species is present. On this basis it is difficult to interpret the hydration number value of 4 and the nonequivalence of the bound water molecules in

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Table I. Proton Magnetic Resonance Cation Coordination Number Data for Water-HMPT-Acetone Mixtures of $ZrO(ClO_4)_2$ and $ZrO(NO_3)_2$

| Salt | Mole ratios | | | ZrO^{2+} coord no. | | |
|----------------|-----------------------|-----------|--------------------------|----------------------|--------------------|-------|
| | Salt:H ₂ O | Salt:HMPT | H ₂ O:acetone | H ₂ O | HMPT | Total |
| $ZrO(ClO_4)_2$ | 1:10 | | 1:10 | 3.6 | | 3.6 |
| | 1:13 | | 1:10 | 3.7 | | 3.7 |
| | 1:12 ^a | | 1:10 | 3.8 | | 3.8 |
| | 1:15 ^a | | 1:10 | 4.0 | | 4.0 |
| | 1:20 | | 1:3 | 3.8 | | 3.8 |
| | 1:20 | | 1:5 | 3.6 | | 3.6 |
| | 1:20 | | 1:10 | 4.1 | | 4.1 |
| | 1:10 | 1:1 | 1:10 | 2.6 | (1.0) ^b | (3.6) |
| | 1:10 | 1:2 | 1:10 | 1.7 | (2.0) ^b | (3.7) |
| | 1:10 | 1:6 | 1:10 | 1.6 | 2.0 | 3.6 |
| | 1:10 | 1:8 | 1.5 | 2.8 | 4.3 | |
| $ZrO(ClO_4)_2$ | Salt:HNO ₃ | | | | | |
| | 1:10 | 1:0.2 | 1:5 | 3.5 | | 3.5 |
| | 1:10 | 1:0.5 | 1:5 | 2.8 | | 3.0 |
| | 1:10 | 1:1 | 1:5 | 2.4 | | 2.4 |
| | 1:12 | 1:1.5 | 1:5 | 1.8 | | 1.9 |
| | 1:13 | 1:2.5 | 1:5 | 1.3 | | 1.5 |
| $ZrO(NO_3)_2$ | 1:16 | 1:4 | 1:5 | (Overlap) | | |
| | 1:10 | | 1:5 | 1.9 | | 1.9 |

^a The solution was acidified to a 1:1 mole ratio of HClO₄ to salt.

^b Only one set of HMPT signals was observed (see text).

$ZrO(ClO_4)_2 \cdot H_2O : A$
1 : 10 : 100
 $t = -70^\circ$

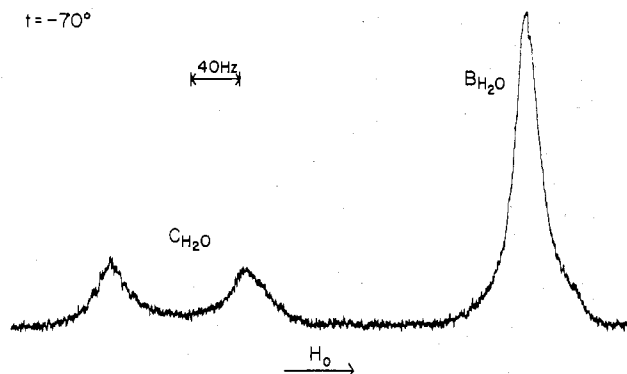


Figure 1. The water nmr spectrum of an aqueous-acetone solution of $ZrO(ClO_4)_2$, recorded on a Varian HA-100 spectrometer. The signals arising from bulk (B_{H_2O}) and coordinated (C_{H_2O}) water molecules are labeled. The mole ratios of all species also are shown.

terms of a simple monomeric ZrO^{2+} species.

In view of the propensity of zirconyl salts to form higher ionic aggregates,³⁻¹¹ polymeric species probably are present here. For example, the species generally proposed are a linear trimer, $Zr_3(OH)_4(H_2O)_{10}^{8+}$, and a cyclic tetramer, $Zr_4(OH)_8(H_2O)_{16}^{8+}$, each with bridging hydroxyl groups. The trimer is not consistent with the observation of two bound water signals of equal area but gives a hydration number of 4. The tetrameric structure^{6,8} accounts for these facts if the assumption is made that only the bound water molecules are observed. Rapid proton exchange, for example, could account for the lack of a pmr signal for the hydroxyl groups.

The presence of such species also can account for the HMPT and NO_3^- solution results. The more basic HMPT was added to ascertain the structural nature of the complex which would result from the substitution of water molecules in the solvation shell of the central metal ion.¹⁷ Although the size of the HMPT molecule prevented the replacement of more than two or three water molecules, the substitu-

tion occurred randomly as seen by the simultaneous decrease of both bound water peaks. However, the ^{31}P nmr spectra described previously show that this ligand also experiences two environments in the solvation shell. Complex formation by the nitrate ion occurs in a more interesting fashion. The selective displacement of one pair of bound water molecules by bidentate complexing proceeds quite readily. The replacement of the second set, however, is a more difficult process and it does not take place completely even at high mole ratios of NO_3^- to salt. The need to accommodate bidentate binding, the charge on the anion, and steric requirements would produce interaction at specific sites in the complex.

In general the cation hydration numbers and the nmr spectra exhibited by aqueous solutions of zirconyl perchlorate and nitrate can be interpreted most reasonably in terms of a metal ion polymer. Although a detailed structural analysis is not possible using only nmr data, they do establish the important criterion of an average of four tightly bound water molecules per metal ion. Any proposed structure based on other types of experimental data for comparable solutions must be consistent with this result.

Registry No. $ZrO(ClO_4)_2$, 15607-09-7; $ZrO(NO_3)_2$, 13826-66-9; H_2O , 7732-18-5; HMPT, 680-31-9; HNO_3 , 7697-37-2; acetone, 67-64-1.

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Reaction of Nitric Oxide with Some Halides of Molybdenum

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We have recently reported the use of the molybdenum-nitrosyl complexes $MoX_2(NO)_2L_2$ ($X = Cl, Br, I$; $L = C_5H_5N, Ph_3P, Ph_3PO, Ph_3As$) as homogeneous olefin disproportionation catalyst precursors.^{1,2} In the course of these studies, it was observed that catalytic activity for a number of molybdenum compounds could be initiated or considerably enhanced by exposure to nitric oxide prior to the addition of the organoaluminum cocatalyst.^{1,2} For example, a mixture of $MoOCl_3$ and $(CH_3)_3Al_2Cl_3$ in chlorobenzene failed to disproportionate 1-pentene (only slight double-bond isomerization was observed). Treatment of the $MoOCl_3$ with 25 psig of nitric oxide before the addition of $(CH_3)_3Al_2Cl_3$ resulted in a 63% conversion to disproportionation products.

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