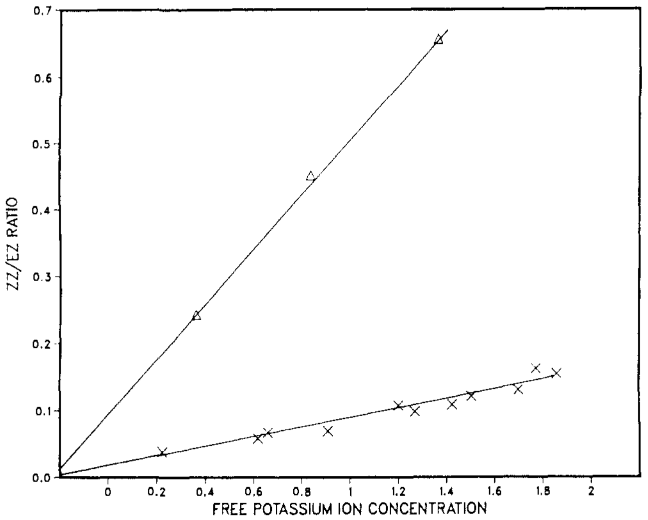
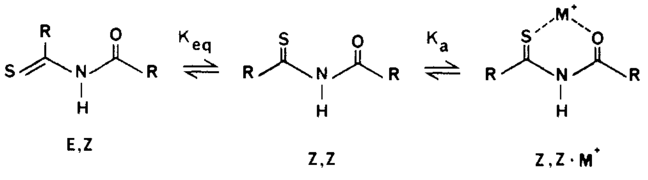


Figure 1. Configurational ratio as a function of free potassium ion concentration (eq 1, $M_{\mathrm{free}} = M - RI(R + 1)$): (×) *N*-acetylthioacetamide (**1**); (△) *N*-propionylthiopropionamide (**2**).

(thiocarbonyl), 24.9 (acetylmethyl), and 34.5 [(thioacetyl)methyl]. Both spectra indicate the presence of a single diastereomer or a rapidly interconverting mixture. That only a single isomer is present is indicated by the essential identity of room temperature spectra to those at −90 °C. At this temperature, rotation about amide and thioamide bonds should be slow on the NMR time scale.[12] Addition of KSCN to solutions of **1** at −90 °C resulted in the appearance of new signals in the ^{1}H NMR spectra at δ 2.58 and 2.23, which must be due to the thioacetyl and acetyl groups, respectively, in (Z,Z)-**1**·M$^+$. Since the chemical shift change for the thioacetyl group is substantial, while that for the acetyl group is negligible, we can conclude that the two species differ in configuration at the thioamide partial double bond and assign the *E*,*Z* configuration to the diastereomer that is present in the absence of alkali-metal cation.



1, R = CH_3
2, R = CH_2CH_3

The behavior of *N*-propionylthiopropionamide was similar except that a small signal (<5%) was observed for the methyl group in (Z,Z)-**2** (δ 2.63) even in the absence of added salt. This is in accord with the postulated assignments since the increased steric interactions between the ethyl group and acyl oxygen atom would be expected to destabilize the *E*,*Z* form relative to the *Z*,*Z* form.[14] Addition of salt led to more dramatic increases in the *Z*,*Z* isomer.

The effect of added metal ion on the configurational equilibrium is illustrated in Figure 1 in which the isomer ratios for **1** and **2** are plotted as a function of the unchelated metal ion concentration (eq 1, $M_{\mathrm{free}} = [M - RI(1 + R)]$):

$$R = K_a'[M - RI(1 + R)] \qquad (1)$$

$$K_a' = K_a K_{\mathrm{eq}} \qquad (2)$$

where R is the observed $Z,Z/E,Z$ ratio, M is the concentration of added salt and I is the concentration of ligand. K_a', the equilibrium constant relating *E*,*Z*- and *Z*,*Z*-**1**·K$^+$ forms, is the product of K_{eq}, the equilibrium constant for *E*,*Z* and *Z*,*Z* isomers in the absence of metal ion, and K_a, the association equilibrium constant for the *Z*,*Z* isomer (eq 2). Linear least squares analysis furnished the equilibrium constant K_a', which is a measure of the complexing ability of the *N*-acylthioamide: **1**, $K_a' = 0.073$; **2**, $K_a' = 0.41$. The complexing ability of the *Z*,*Z* isomer (K_a), which is considerably larger, can be obtained if the equilibrium constant for *E*,*Z* and *Z*,*Z* forms (in the absence of metal ion) is known. While K_{eq} is too small for estimation in the case of **1**, integration of the low-temperature spectrum of **2** indicated that K_{eq} was about 0.05, corresponding to a value of 8.2 for K_a.

We attribute the major difference in complexing abilities of **1** and **2** to the greater ease with which **2** adopts the *Z*,*Z* form. This is likely due to increased steric interactions between the carbonyl oxygen and an ethyl group as opposed to a methyl group. The same factor is responsible for the preference of *N*-acetylpropionamide for the *E*,*Z* configuration as opposed to the *Z*,*E* configuration.[14]

In order to obtain an estimate of the difference in complexing ability between amide sulfur and amide oxygen we examined the complexing ability of *N*-acetylacetamide (**3**) under the same conditions. Since there is a substantial amount of the *Z*,*Z* isomer in equilibrium even in the absence of metal ion, eq 1 is not valid, and eq 3 was used: $K_a' = 20$, $K_a = 38$, $K_{\mathrm{eq}} = 0.59$. We can compare the complexation abilities between **1** and **3** using either K_a or K_a'. On either basis it is clear that while the imide is better at complexation, thioamide sulfur does have significant ability to complex alkali metal cations.

$$K_a = \frac{(R - K_{\mathrm{eq}})(R + 1)}{K_{\mathrm{eq}}[M(R + 1) - I(R - K_{\mathrm{eq}})]} \qquad (3)$$

Registry No. 1, 3542-00-5; **2**, 99797-96-3; KSCN, 333-20-0; K$^+$, 24203-36-9.

---

[12] The coalescence temperature for interconversion of amide torsional isomers in *N*-acetylacetamide is well above temperature: $T_c = -60$ °C, $\Delta G_c^{*} = 10.8$ kcal/mol.[13]

[13] Noe, G. A.; Raban, M. *J. Am. Chem. Soc.* **1975**, *97*, 5811.

[14] Raban, M.; Keintz, R.; Haritos, D. P.; Greenblatt, J. *J. Org. Chem.* **1980**, *45*, 2672.

[15] This equation is valid when $M^+ >> I$. At low metal ion concentrations there is a considerable amount of triple ion[16] $((Z,Z)\text{–}\mathbf{3})_2\cdot\mathrm{M}^+$ present. In order to obtain an estimate for K_a in this concentration range, we assumed that the second association constant, $K_a{}^2 = [(Z,Z)_2\cdot\mathrm{M}^+]/[((Z,Z)\cdot\mathrm{M}^+)(Z,Z)]$ was equal to the first (K_a). The value quoted is an average of four determinations which were in good agreement.

[16] Raban, M.; Yamamoto, G. *Inorg. Nucl. Chem. Lett.* **1976**, *12*, 949.

Decyclization of Crown Ethers. Ring-Opening Reaction of 18-Crown-6 with $ZrCl_4$

Horst Prinz, Simon G. Bott, and Jerry L. Atwood*

Department of Chemistry, University of Alabama
University, Alabama 35486

Received July 18, 1985

We have previously reported that $AlCl_3$ reacts with crown ethers in aromatic solvents to form $[AlCl_2\cdot\text{crown ether}][AlCl_4]$.[1] The ionic substance shows the two-phase effect (liquid clathrate) in an excess of aromatic.[2] Since it would be desirable to have access to liquid clathrates based on early-transition-metal ions, we have carried out the reaction of group IVB (group 4)[13] halides with 18-crown-6. $TiCl_4$ reacts to form the adduct, $TiCl_4\cdot$18-crown-6, in which the crown ether functions as a bidentate ligand.[3] To our surprise, the reaction of $ZrCl_4$ with 18-crown-6 in toluene/THF (15% THF by volume) leads to the formation of an open-ring macrocyclic coordination product of formula [$ZrCl_2\cdot$(OCH$_2$C-

---

[1] $AlCl_3$ and $EtAlCl_2$ react in the same manner: Bott, S. G.; Elgamal, H.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 1796. Atwood, J. L.; Elgamal, H.; Robinson, G. H.; Bott, S. G.; Weeks, J. A.; Hunter, W. E. *J. Inclusion Phenom.* **1985**, *2*, 367.

[2] Atwood, J. L. In *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Academic Press: London, 1984; Vol. 1, pp 375–405.

[3] Bott, S. G.; Prinz, H.; Kynast, U.; Atwood, J. L., unpublished results.

0002-7863/86/1508-2113$01.50/0

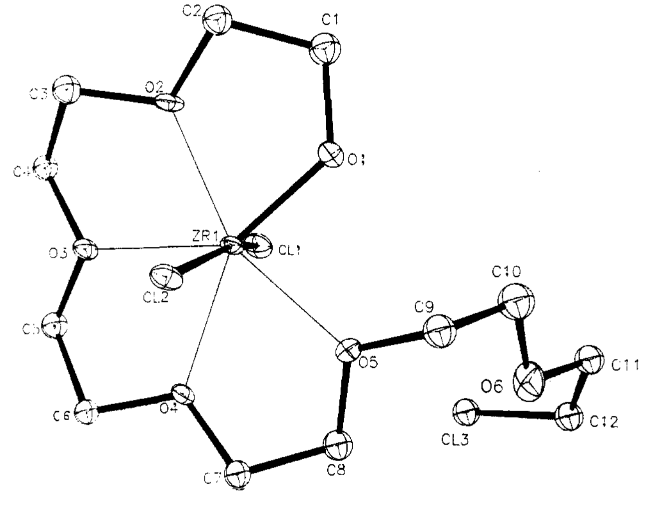


Figure 1. View of the $[ZrCl_2\cdot(OCH_2CH_2)_5OCH_2CH_2Cl]^+$ cation.

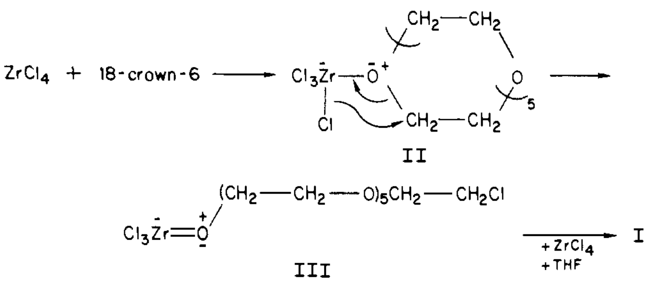
$H_2)_5OCH_2CH_2Cl][ZrCl_5(THF)]$ (I).[4]

The structure of the novel cation is shown in Figure 1. The zirconium atom is seven-coordinate, with the macrocycle filling the five equatorial sites. The Zr–O(1) interaction is a full covalent bond at 1.93 (2) Å.[5,6] The remainng Zr–O lengths range from 2.24 to 2.33 Å and are typical for donor–acceptor bonds.[7] The five zirconium-bonded oxygen atoms are planar to within 0.08 Å, and the Zr atom lies 0.03 Å out of the plane.

The macrocycle appears to be quite similar to 15-crown-5 in its ability to coordinate the metal.[8] The O···O separations, 2.49 to 2.65 Å, are close to those found in complexes of the crown ether with the exception of O(1)···O(5) at 2.72 Å. O(6) is not needed to fill out the coordination sphere of the zirconium, and it does not interact with the metal. The terminal chlorine atom exhibits high thermal motion, but the Cl–C bond length of 1.71 Å is near the ideal value (the high esd notwithstanding).

The transfer of halide from an early transition metal to a hydrocarbon has precedent in the pyrolysis of the diethyl ether complexes of $NbCl_5$ and $TaCl_5$ to give ethyl chloride and metal oxy trihalides.[9] This information, combined with the known propensity of $ZrCl_4$ to break C–O bonds in donor complexes because of the strength of the Zr–O bond,[10] has led us to propose the reaction pathway shown in Scheme I. First, an oxygen atom of the crown ether adds in a donor fashion to the zirconium atom forming II. In the second step one can envision the transfer of a chlorine atom to the α-carbon with breakage of the C–O bond to give III. In the third step a chloride ion is abstracted from the zirconium atom containing a partial negative charge by a $ZrCl_4$ unit in the presence of THF. Note that this is offered only as a reasonable possibility.

Scheme I



The anion is an interesting species. The $[ZrCl_6]^{2-}$ ion is well-known, but the only reference to a $ZrCl_5^-$ species is an infrared spectrum attributed to $[PCl_4][ZrCl_5]$.[11] However, the corresponding titanium-continuing anion was recently reported.[12] The geometry about the zirconium atom is a nearly perfect octahedron. The Zr–Cl lengths range from 2.388 (8) to 2.452 (7) Å. These values compare favorably with both the literature values and with the 2.434 (8) Å distance found in the cation.

Acknowledgment. We are grateful to the National Science Foundation and to the Department of Energy for support of this research. Thanks are also offered to Dr. U. Kynast for recording and interpreting the IR data.

Supplementary Material Available: Tables of bond distances and angles, final fractional coordinates, thermal parameters, observed and calculated structure factors, and IR absorptions with tentative assignments (17 pages). Ordering information is given on any current masthead page.

---

[4] A solution of18-crown-6 (1.59 g, 6 mmol) in toluene was added to a suspension of $ZrCl_4$ (1.40 g, 6 mmol) in toluene. THF was added up to 15% by volume, and the tube was sealed and heated to 100 °C for 24 h. Upon cooling to room temperature, colorless, air-sensitive crystals formed in ca. 25% yield. The crystals belong to the triclinic space group $P\bar{1}$; cell constants, $a = 7.238$ (7) Å, $b = 13.754$ (6) Å, $c = 16.378$ (9) Å, $\alpha = 105.52$ (4)°, $\beta = 91.17$ (4)°, $\gamma = 98.17$ (4)° with two formula units per unit cell and $D_c = 1.72$ g cm^{-3}. Least-squares refinement based on 1751 observed reflections led to a final $R = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.068$. The details of data collection and refinement are as given in Holton et al.: Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 45. An empirical absorption correction was done according to Churchill and Hollander: Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1978**, *17*, 1957. Anisotropic thermal parameters were used for Zr, Cl, and O atoms. Hydrogen atoms were not located.

[5] Atwood, J. L.; Rogers, R. D.; Bynum, R. V. *Acta Crystallogr., Sect. C* **1984**, *C40*, 1812 and references therein.

[6] The Zr–O stretch in the IR corresponding to the covalent linkage appears as a very strong band at 750 cm^{-1}. A complete listing of IR absorptions may be found in the supplementary material.

[7] The Zr–O lengths are 2.24 (1), 2.25 (1), 2.33 (1), and 2.24 (1) Å for O(2) to O(5), respectively. They may be compared with the Zr–O distance in the anion of 2.24 (2) Å.

[8] Although there is no related complex between 15-crown-5 and $ZrCl_2^{2+}$, comparisons can be made with regard to 15-crown-5·$AlCl_2^+$ (ref 1) and 15-crown-5·$YbCl_2^+$ (Atwood, D. A.; Bott, S. G.; Atwood, J. L., unpublished results).

[9] Cowley, A.; Fairbrother, F.; Scott, N. *J. Chem. Soc.* **1958**, 3133.

[10] Early transition metal halides are known to cleave a C–O bond in THF. For a recent account, see: Bartmann, E. *J. Organomet. Chem.* **1985**, *284*, 149.

[11] Demiray, A. F.; Brockner, W. *Monatsh. Chem.* **1980**, *111*, 21.

[12] Sobota, P.; Utko, J.; Lis, T. *J. Chem. Soc., Dalton Trans.* **1984**, 2077.

[13] In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III→3 and 13.)

Thermally Activated Magnesium Oxide as a Selective Deuteration Catalyst under Mild Conditions

M. Fazlul Hoq and Kenneth J. Klabunde*

Department of Chemistry, Kansas State University
Manhattan, Kansas 66501

Received October 18, 1985

Alkaline-earth oxides are readily available materials that possess remarkable chemical properties when thermally activated. Basic sites (H^+ abstraction sites),[1] reducing sites[2,3] (electron-transfer sites), and radical sites (H· abstraction sites)[4] have all been utilized on the surface of high surface area polycrystalline MgO.

Due to this wealth of interesting chemistry and the abundance of MgO and CaO, we have initiated a program involving the use of these materials as catalysts and/or stoichiometric reagents for carrying out organic/inorganic syntheses.[5] In this paper we report on MgO as a catalyst for carrying out selective hydrocarbon–D_2 exchange.

Hydrogen–deuterium exchange reactions over metal oxide catalysts have been observed before. Hall and co-workers[6] and

---

[1] Utiyama, M.; Hattori, H.; Tanabe, K. *J. Catal.* **1978**, *53*, 237–242.

[2] Tanabe, K. *Solid Acids and Bases*; Academic Press: New York, 1970.

[3] Morris, R. M.; Klabunde, K. J. *Inorg. Chem.* **1983**, *22*, 682–687.

[4] Driscoll, D. J.; Martir, W.; Wang, J. X.; Lunsford, J. H. *J. Am. Chem. Soc.* **1985**, *107*, 58–63.

[5] Lin, S. T.; Klabunde, K. J. *Langmuir* **1985**, *1*, 600–605.

[6] Larson, J. G.; Hall, W. K. *J. Phys. Chem.* **1965**, *69*, 3080–3089.

0002-7863/86/1508-2114$01.50/0