

Chloroalkoxide Complexes of Zinc

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The reaction of sodium methoxide with zinc chloride in methanol has been examined and it is proposed that, depending on the molar ratio of reactants, the following complex ions are produced: $[\text{Zn}(\text{OCH}_3)_4]^{2-}$, $[\text{Zn}(\text{OCH}_3)_3\text{CH}_2\text{OH}]^-$, $[\text{ZnCl}(\text{OCH}_3)_2]^-$, and $[\text{Zn}_2\text{Cl}_4(\text{OCH}_3)_2]^{2-}$. The identity of these complexes is supported by conductometric titration, chemical analysis, and molecular weight determinations. Evidence for the formation of analogous complexes from sodium 2-propoxide is also reported.

In recent years a number of metal alkoxide and alkoxy-containing complex metal ions have been characterized and this general area of chemistry is now developed.² There are a number of literature references to simple zinc alkoxides but the characterization of these has been limited due to their insolubility and apparent polymeric nature.³

The reaction of zinc alkyls with active hydrogen compounds such as alcohols and amines provides a convenient route to replacement derivatives; Coates and Ridley³ have obtained structural information on several of these products. In particular they characterized some alkylzinc alkoxides of the general formula $(\text{RZnOR})_4$. The tetrameric structure, characteristic of the benzene solutions used for cryoscopic molecular weight determination, also persists in the crystalline state. X-Ray structure determination of methylzinc methoxide⁴ shows the zinc atoms to be four-coordinate and to occupy alternate corners of a distorted cube with the oxygen atoms occupying the remaining corners. Reaction of zinc dialkyls with 2 equiv of alcohol leads to insoluble, apparently polymeric zinc alkoxides.

The reaction of metal halides with alcohols provides for a number of cases a useful method of preparation of the metal alkoxides. For some less reactive halides, where the simple reaction fails, the method can be extended by the addition of sodium alkoxide to neutralize the hydrogen chloride produced and force the alcoholysis further toward completion. This expediency also fails, however, in certain cases because of the tendency of some metals to form "double alkoxide" complexes with sodium alkoxide. For still other metallic chlorides, alcoholysis in the presence of sodium alkoxide fails to give the simple metal alkoxides because of the tendency of the metal to coordinate with chloride ion to give mixed chloroalkoxide complexes.

Gut⁵ has recently demonstrated the existence of a reaction involving 1.5 equiv of methoxide per zinc atom by potentiometric titration of zinc chloride in methanol with methanolic lithium methoxide. It was proposed that the zinc complex formed also contained chloride ion since zinc methoxide is not soluble in methanol. The potentiometric titration with additional methoxide showed no evidence for any 2:1, 3:1, or 4:1 complexes even though Meerwein and Bersin⁶ reported the preparation of $\text{KZn}(\text{OMe})_3$ in concentrated solution. In the presence of tetramethylammonium chloride, the titration of zinc chloride with lithium methoxide produced a precipitate.

Experimental Section

Commercial reagent grade methanol was dried⁷ over magnesium methoxide. Freshly cut sodium was washed in dry methanol and transferred in a glove bag containing dry nitrogen to a flask of dry methanol. The concentration was determined by the gravimetric⁸ estimation of sodium.

Reagent grade powdered zinc chloride was dried over phosphorus pentoxide in a vacuum desiccator and washed three times with dry methanol and finally dissolved in dry methanol. The zinc content was determined gravimetrically.⁹

2-Propanol was dried by refluxing over magnesium¹⁰ for 24 hr.

Sodium 2-propoxide and zinc chloride solutions in 2-propanol were prepared and estimated by the same techniques used for the methanolic solutions.

Conductometric Titrations. The conductivity cell was cylindrical, about 4 cm in diameter and 7 cm high. The top was tapered down to an O-ring joint to which could be attached a reflux condenser protected from atmospheric moisture at the opposite end with a tube containing Drierite. The titrant was added from a buret attached through a ground-glass joint and the cell was stirred with a Teflon-coated magnetic bar. The electrodes were 5×7 mm rectangular pieces of thin platinum sheet sealed onto the glass walls on opposite sides of the vessel about 4 cm apart. The titrations were carried out by adding methanolic zinc chloride solutions to methanolic sodium methoxide in the cell. About 20–25 ml of sodium methoxide in different samples ranging from 0.1 to 3.97 *M* was placed in the cell and zinc chloride in the range 2.5–3.28 *M* was added through the buret. Titrations were carried out at both 25 and 60°. The results at the two temperatures were similar except that equilibrium resistance was reached much more quickly at the higher temperature. The titrations at 25° sometimes took several hours due to the slow achievement of equilibrium. Precipitates formed in all titrations except those using the most dilute solutions. Measured resistance was generally in the range of 50–100 ohms. With the reaction mixtures initially up to 1.0 *M* in sodium methoxide the resistance rose smoothly with increasing slope to a sharp well-defined maximum at a sodium methoxide to zinc chloride ratio of 2:1 and then fell smoothly and sharply. The end point at this ratio is the most clearly defined feature of all of the titrations. With the initial sodium methoxide concentration above about 1 *M* there is an initial slow decrease in resistance to a molar ratio near 3:1 and then the increase noted above to the 2:1 ratio point. The initial decrease is most pronounced in the most concentrated titration. In this case, there is also the suggestion of a slight change in slope at the 4:1 ratio point. There is also a difference in the rate of attainment of equilibrium resistance for additions on either side of the 4:1 ratio point of $\text{Na}(\text{OCH}_3)$ to ZnCl_2 .

Ebulliometry. The ebulliometer was of modified Washburn-Cottrell design. The original three-piece design was made in one piece to prevent solvent loss or grease uptake. The boiler, except for a 1-in. length at the bottom left open for heating, was insulated with a vacuum jacket containing a shiny aluminum reflector with a window to allow observation of the thermometer tip.

Superheating was minimized by rapid stirring with a Teflon-covered bar magnet under the three-pronged funnel. A Dymec Model Dy-2801A quartz thermometer was used to measure directly the temperature difference between solvent and solution in the separate boilers heated by the same stirred oil bath. The quartz thermometer probes were fitted into the apparatus through ground-glass joints and machined Teflon sleeves. The temperature differences were reproducible to within a few ten-thousandths of 1°, equilibrium generally being reached in about 15 min.

The apparatus was calibrated with five standard solutions of naphthalene in the concentration range from 0.0650 to 0.1576 *m* and the boiling point elevation constant in this range was calculated to be $0.817 \pm 0.015^\circ$ at 740 mm. In the molecular weight determinations the literature value of 0.83 was used for the molal boiling point elevation constant for methanol at 760 mm.

Osmometry. The molecular weights of several samples, including especially those unstable at elevated temperatures, were determined with a Mechrolab Model 301-A osmometer.

$\text{Na}_2[\text{Zn}(\text{OCH}_3)_4]$. To 40.0 ml of 4.43 *M* sodium methoxide in methanol was added 17.2 ml of 2.5 *M* zinc chloride in methanol. The

solution was refluxed for 1 hr and filtered hot to remove the sodium chloride precipitate. The filtrate, which did not give a silver nitrate test for chloride ion, was evaporated to dryness at 0.1 mm at 50°. The dry mass was analyzed. *Anal.* Calcd: Na, 19.52; Zn, 27.76; C, 20.40; H, 5.13; O, 23.17. Found: Na, 18.51; Zn, 26.53; C, 20.14; H, 5.90; O, 28.90. The molecular weight, ebullioscopic in methanol, assuming complete ionization into two positive and one negative ions, was found to be 236.7; calculated 235.98.

$\text{Na}[\text{Zn}(\text{OCH}_3)_3(\text{CH}_3\text{OH})]$. To 20 ml of 3.97 *M* sodium methoxide in methanol was added 8.0 ml of 3.28 *M* methanolic zinc chloride. The mixture was refluxed and filtered hot. The filtrate did not give a silver nitrate test for chloride. The filtrate was evaporated to dryness at 0.1 mm and 50°. The dry mass was analyzed. *Anal.* Calcd: Na, 10.77; Zn, 30.63; C, 22.51; H, 6.13; O, 29.99. Found: Na, 12.25; Zn, 31.74; C, 20.09; H, 5.49; O, 31.09.

The molecular weight, determined ebullimetrically, assuming complete dissociation into one positive and one negative ion, was 225; calculated 213.5.

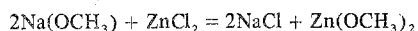
$\text{Na}_2[\text{Zn}_2\text{Cl}_2(\text{OCH}_3)_4]$. Five milliliters of zinc chloride (3.26 *M*) in methanol was pipetted into a flask containing 10.65 ml of methanolic solution (4.59 *M*) of sodium methoxide. This mixture was refluxed for about 2 hr and filtered hot under nitrogen. The filtrate was evaporated to dryness at room temperature under vacuum (0.05 mm).

In order to determine the degree of possible polymerization of the complex zinc anion, ebullimetric measurements were carried out on dilute solutions made up in 2:1 molal ratio of sodium methoxide and zinc chloride. For solutions made up to be 0.0916, 0.0456, and 0.0305 *m* in sodium methoxide (each containing 0.5 equiv of zinc chloride) the observed boiling point elevations in methanol were 0.1335, 0.0683, and 0.0660°, respectively. At these concentrations, sodium chloride did not precipitate. Assuming complete ionization of the 2 equiv of sodium chloride and the 2 equiv of sodium zinc complex expected to be formed, the calculated boiling point elevations would be 0.132, 0.0663, and 0.0504°, respectively.

If the complex zinc anion were monomeric instead of dimeric, the calculated values would be 0.1512, 0.0757, and 0.0504°, respectively. The observed values are in reasonably close accord with those calculated on the assumption of the dimeric zinc anion structure.

Discussion

The formation of the 2:1 complex is the most prominent feature of the reaction between sodium methoxide and zinc chloride in methanol. This product has a reasonable methanol solubility since it remains in solution when formed at 25° from a solution 0.1 *M* in sodium methoxide. Zinc methoxide formed by the decomposition of zinc diethyl with methanol is so insoluble that the filtrate does not give the 8-hydroxyquinoline test for zinc. The molecular weight determinations indicate that the complex zinc anion is dimeric with the formula $\text{Na}_2[\text{Zn}_2\text{Cl}_2(\text{OCH}_3)_4]$. It does not seem to be sufficiently stable to air to permit conventional elemental analysis. It is interesting to recall that, during ebullimetric studies, it was always noticed that the mixture of sodium methoxide and zinc chloride showed a transitory milkiness. This suggests the probable sequence of reactions

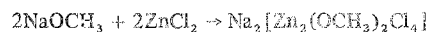


Elemental analyses and molecular weight determinations on the 4:1 complex are consistent with its formulation as disodium tetramethoxyzincate, expected by analogy with the formation of zincate salts from strongly basic aqueous solutions

of zinc hydroxide. It is noted that the conductometric titrations give only minimal evidence even in concentrated solutions for the existence of this complex.

The conductometric titrations in concentrated solution indicate the existence of a 3:1 complex similar in composition to the potassium salt obtained by Meerwein and Bersin. The absence of chloride and the elemental analyses for C, H, O, and Zn (as ZnO residue after combustion) are consistent with its formulation as $\text{Na}[\text{Zn}(\text{OCH}_3)_3\text{CH}_3\text{OH}]$. The molecular weight determination is also in agreement with the formulation of the complex anion as monomeric containing one methanol molecule to give the zinc atom a coordination number of 4. Its beryllium analog $\text{Na}[\text{Be}(\text{OCH}_3)_3\text{CH}_3\text{OH}]^{11}$ is already known.

The conductometric curves for titration with concentrated solutions at higher temperature show a slight break in the 1:1 molar region of reactants. The existence of this complex is also indicated by the fact that the 2:1 complex which precipitates on first addition of zinc chloride will, with sufficient added zinc chloride to give the 1:1 complex, slowly go into solution. If a solution of the 1:1 complex is made from ZnCl_2 and Na_2OCH_3 each at 0.0446 *m* concentration, the osmometric determination indicates a 0.066 *m* solution. This result favors formulation of the 1:1 complex as a dimer



The complex ionic structure might involve each zinc as four-coordinated, attached to two chlorides and two methoxides, with the latter forming bridges between the zinc atoms.

Reaction of ZnCl_2 with Sodium 2-Propoxide. When zinc chloride, 0.928 *M* in 2-propanol, was added to 0.241 *M* sodium 2-propoxide in 2-propanol in the conductivity cell, considerable precipitation took place but sharp breaks in the conductance curve were evident at 4:1, 3:1, and 2:1 mole ratios of sodium methoxide to zinc chloride. Thus the results appear quite analogous to those with sodium methoxide except for the lack of evidence for the 1:1 complex. Some complex of a Na:Zn ratio lower than 2:1 appears to exist because a severalfold excess of zinc chloride causes the initial precipitate formed on addition of zinc chloride to the alkoxide to dissolve.

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Registry No. $\text{Na}_2[\text{Zn}(\text{OCH}_3)_4]$, 52827-32-4; $\text{Na}[\text{Zn}(\text{OCH}_3)_3(\text{CH}_3\text{OH})]$, 52827-33-5; $\text{Na}_2[\text{Zn}_2\text{Cl}_2(\text{OCH}_3)_4]$, 52873-48-0; $\text{Na}_2[\text{Zn}_2(\text{OCH}_3)_2\text{Cl}_4]$, 52827-34-6.

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