Contribution from the Department of Chemistry,
Michigan State University, East Lansing, Michigan 48823

The Preparation and Characterization of a Series of Chloroalkoxobis(cyclopentadienyl)zirconium(IV) and Dialkoxobis(cyclopentadienyl)zirconium(IV) Compounds

By Donald R. Gray and Carl H. Brubaker, Jr.*

Received December 14, 1970

A new series of zirconium(IV) compounds of the type $Cp_2Zr(OR)_nCl_{2-n}$ (n = 1, 2; R = CH_3, C_2H_5, 2-C_3H_7; Cp = π-C_5H_5) were prepared by allowing the appropriate alcohol and triethylamine to react with Cp_2ZrCl_2 in THF. The nmr, ir, and far-ir spectra were studied and correlated with basicities. The nmr exhibited chemical shift trends opposite to those expected by invoking basicity arguments. Hydrolysis reactions were studied. $Cp_2Zr(OC_3H_7)Cl$ was found to be capable of activating molecular nitrogen.

Introduction

The present study is concerned with the series of zirconium compounds of the form $(C_5H_5)_2Zr(OR)_xCl_{2-x}$ (x = 1, 2; R = CH_3, C_2H_5, 2-C_3H_7). Some of these compounds (x = 1; R = C_2H_5, i-C_3H_7)[1] have been previously reported. We have now prepared and characterized the complete series. The ir, far-ir, and nmr spectra have been measured.

Organometallic compounds of titanium[2,3] and zirconium[4] have been found to be capable of activating molecular nitrogen. The 2-propoxide derivatives of the present series were investigated as possible agents in the nitrogen-fixation process.

Experimental Section

Materials.—Methanol was dried by distillation in the presence of magnesium. The magnesium was activated with iodine according to the method of Lund and Bjerrum.[5] Absolute ethanol was dried by distillation in the presence of sodium ethoxide and diethylphthalate. 2-Propanol was dried by distillation in the presence of sodium 2-propoxide.

Zirconocene dichloride [$(\pi$-$C_5H_5)_2ZrCl_2$] (henceforth Cp = π-C_5H_5) was obtained from Arapahoe Chemical Co. and used without further purification. Triethylamine was dried over barium oxide and pipetted as needed. Tetrabutylammonium iodide (TBAI) was obtained from Eastman Organic Chemicals. The commercial product was further purified by standard procedures.[6]

Tetrahydrofuran (THF) was refluxed continuously with lithium aluminum hydride and distilled immediately before use. Benzene was refluxed continuously with calcium hydride and distilled immediately before use. Hexane was continuously refluxed in the presence of sodium metal and distilled immediately before use.

Chloromethoxobis(π-cyclopentadienyl)zirconium(IV).—The following method was used for all chloroalkoxo compounds with minor differences noted below. A mixture of methanol (32.2 mmol) and triethylamine (32.2 mmol) in 20 ml of THF was added dropwise to a stirred solution of Cp_2ZrCl_2 (16.1 mmol) in 80 ml of THF. This reaction mixture was allowed to reflux for 3 hr. The dense white precipitate, $(C_2H_5)_3N\cdot HCl$, was removed by filtration. Solvent was removed from the orange-brown filtrate by distillation under vacuum. Seventy milliliters of hexane was added to the remaining amorphous reddish brown mass. This mixture was vigorously stirred for 6 hr and crystals formed. These beige crystals were filtered and dried. Sublimation under vacuum (10^{-1} Torr) at 103° caused pure white crystals to condense on the cold-finger condenser; yield 1.4 g; mp 111–114.5°. *Anal.* Calcd for $ZrClC_{11}H_{13}O$: Zr, 31.69; Cl, 12.32; C, 45.89; H, 4.52. Found: Zr, 31.51; Cl, 12.06; C, 45.35; H, 4.15.

Chloroethoxobis(π-cyclopentadienyl)zirconium(IV).—The initial filtrate was clear yellow. A small amount of solid formed after the bulk of the THF had been removed and was removed by filtration. Removal of the remaining THF by evaporation left a dark brown oil. About 30 ml of hexane was added, and the beige crystals which formed were filtered and dried. This product was purified by sublimation under vacuum (10^{-1} Torr) at 92° and white crystals were obtained; yield ~3 g; mp 72–77°. *Anal.* Calcd for $ZrClC_{12}H_{15}O$: Zr, 30.24; Cl, 11.75; C, 47.77; H, 4.97. Found: Zr, 30.09; Cl, 11.87; C, 47.48; H, 4.78.

Chloro(2-propoxo)bis(π-cyclopentadienyl)zirconium(IV).—The THF was then removed from the filtrate by evaporation, and a dark brown liquid remained. Thirty milliliters of hexane was added to this liquid; a very small quantity of crystals formed and was removed by filtration. The hexane was removed by evaporation. The resulting dark brown oil was sublimed under vacuum (10^{-1} Torr) at 86°. A large quantity of white crystals formed on the cold-finger condenser; yield ~3 g; mp 81–82.5°. *Anal.* Calcd for $ZrClC_{13}H_{17}O$: Zr, 28.88; Cl, 11.23; C, 49.44; H, 5.38. Found: Zr, 29.21; Cl, 11.21; C, 48.90; H, 5.07.

Dimethoxobis(π-cyclopentadienyl)zirconium(IV).—The following method was used for all dialkoxo compounds with minor differences noted below. A solution of methanol (83.6 mmol) and triethylamine (41.8 mmol) in 10 ml of THF was added dropwise to a solution of $CpZrCl_2$ (20.9 mmol) in 80 ml of THF. The $(C_2H_5)_3H\cdot HCl$ was removed by filtration. A brown oil remained after the solvent was removed from the filtrate. Thirty milliliters of hexane was added to the remaining oil, and beige crystals formed. The crystals were removed by filtration. The filtrate was evaporated and the remaining solid was dried. The resulting brown solid was sublimed under vacuum (10^{-1} Torr) at 85°. Pale yellow crystals of product formed on the cold-finger condenser; yield ~1.4 g; mp 63.68°. *Anal.* Calcd for $ZrC_{12}H_{16}O_2$: Zr, 32.19; C, 50.86; H, 5.65. Found: Zr, 32.20; C, 48.91; H, 5.11.

Diethoxobis(π-cyclopentadienyl)zirconium(IV).—Additional $(C_2H_5)N\cdot HCl$ formed after most of the THF had been removed from the filtrate. This solid was removed by filtration, and the remaining THF was removed from the filtrate by evaporation. The resulting oil was sublimed under vacuum (10^{-1} Torr) at 92°. Proton magnetic resonance spectroscopy showed the sublimation product was a mixture of $Cp_2Zr(OC_2H_5)_2$, $Cp_2Zr(OC_2H_5)Cl$, and $Zr(OC_2H_5)_4$. The desired product, $Cp_2Zr(OC_2H_5)_2$, was isolated by resubliming it from this mixture at 55° and 10^{-1} Torr. The crystalline product was pale yellow; yield ~0.5 g; mp 52–57°. *Anal.* Calcd for $ZrC_{14}H_{20}O_2$: Zr, 29.30; C, 54.00; H, 6.42. Found: Zr, 29.01; C, 52.06; H, 6.01.

Di(2-propoxo)bis(π-cyclopentadienyl)zirconium(IV).—After most of the THF was removed by evaporation, 25 ml of hexane was added, and the small quantity of resulting crystals was separated by filtration. The hexane was removed by evaporation and a yellow-brown solid remained. Vacuum sublimation at 68° produced white crystals on the cold-finger condenser; yield ~1.5 g; mp 110–116.5°. *Anal.* Calcd for $ZrC_{16}H_{24}O_2$: Zr, 26.88; C, 56.62; H, 7.07. Found: Zr, 26.92; C, 56.29; H, 7.36.

---

[1] E. M. Brainina, R. Kh. Freidlina, and A. N. Nesmeyanov, *Dokl. Akad. Nauk SSSR*, **154**, 1113 (1964).

[2] M. E. Vol'pin and V. B. Shur, *Nature (London)*, **209**, 1236 (1966).

[3] E. E. van Tamelen, D. Seeley, S. Schneller, H. Rudler, and W. Cretney, *J. Amer. Chem. Soc.*, **92**, 5251 (1970).

[4] D. R. Gray and C. H. Brubaker, Jr., *Chem. Commun.*, 1239 (1969).

[5] H. Lund and J. Bjerrum, *Ber. Deut. Chem. Ges. B*, **64**, 210 (1931).

[6] C. K. Mann, *Electroanal. Chem.*, **3**, 132 (1969).

Tetraethoxozirconium(IV).—A solution of ethanol (73.8 mmol) and triethylamine (37.0 mmol) in THF was added to a solution of Cp_2ZrCl_2 (18.5 mmol) in THF. This mixture was allowed to reflux for 2 hr. The precipitate, $(C_2H_5)_3N \cdot HCl$, was separated by filtration. Sublimation under vacuum (10^{-1} Torr) at 165° produced white crystals of product on the cold-finger condenser; yield ~1 g; mp 172–180°. The physical data agreed with those given by Bradley and Wardlaw[7] for $Zr(OC_2H_5)_4$ prepared by a different method. *Anal.* Calcd for $ZrC_8H_{20}O_4$: Zr, 33.62. Found: Zr, 34.14.

Tetra(2-propoxo)zirconium(IV).—This compound was prepared in doubtful purity by continued sublimation of the residue from the $Cp_2Zr(OC_3H_7)_2$ preparation (see above). All of the $(Cp_2)_2Zr(OC_3H_7)_2$ had sublimed at 90°. Further sublimation produced white crystals of product $Zr(OC_3H_7)_4$; yield ~0.5 g; mp 180–200° dec. The infrared spectrum agreed closely with that reported by Bradley[8] and Lynch.[9] *Anal.* Calcd for $ZrC_{12}H_{28}O_4$: Zr, 27.87. Found: Zr, 28.52.

Hydrolysis Reactions.—These reactions were simply performed by exposing the compounds to air. This treatment was generally sufficient to cause almost total hydrolysis to occur in about 30 min. A more efficient method, ensuring that complete hydrolysis had taken place, involved placing the samples in air saturated with water vapor. This was accomplished by filling the bottom section of a desiccator with water, placing the samples (in open vials) on the plate, and closing the desiccator lid. The sample vials were periodically removed, placed in a vacuum desiccator, which was evacuated several times, and weighed until further exposure to water vapor caused no further weight loss.

Infrared Spectra.—Nuclear magnetic resonance spectra were recorded with a Varian A56/60D analytical nmr spectrometer. The nmr tubes were filled with sample in an inert-atmosphere box. All measurements were made with samples dissolved in deuterated benzene.

Polarography.—Attempts to obtain polarograms were made with a Sargent Model XV polarograph. Tetrahydrofuran was used as the solvent, and tetrabutylammonium iodide (TABAI) was the supporting electrolyte. To obtain a 0.1 *N* solution of TBAI in THF it was necessary to maintain a temperature of 55°. A dropping mercury–saturated calomel electrode pair was employed. A three-compartment cell was used to ensure that no aqueous solution would diffuse into the sample.

Nitrogen Fixation.—Nitrogen-fixation experiments similar to those reported earlier[4] were attempted with $Cp_2Zr(OC_3H_7)Cl$ and $Cp_2Zr(OC_3H_7)_2$.

Analyses.—Carbon and hydrogen analyses were performed by Spang Microanalytical Laboratories and by the microanalytical laboratory of the Institute of Water Resources at Michigan State University. Because of extreme sensitivity to moisture, the complexes were very difficult to handle and the analyses reported were a result of experimenting with several handling techniques. Identical samples frequently gave different results, and the reported C and H analyses may not be totally reliable.

Zirconium was analyzed by precipitation of zirconium cupferrate and was ignited and weighed as ZrO_2. Chloride was determined by a differential potentiometric titration with a standard silver nitrate solution.

Technique.—Practically all the compounds dealt with in this research were extremely sensitive to oxygen and/or water vapor. All reactions and manipulations were performed in an atmosphere of dry nitrogen. Glove box and Schlenk vessel techniques[10] were used extensively. The compounds were stored in closed vials in an inert-atmosphere box. Manipulations included preparation of Nujol mulls for infrared measurements, filling of nuclear magnetic resonance tubes, and scraping sublimation products from cold-finger condensers.

Results and Discussion

All of the compounds prepared in this study were stable if stored in an atmosphere of dry nitrogen. They are assumed to be structurally similar to the somewhat distorted tetrahedron of Cp_2ZrCl_2.

The nmr absorptions of the compounds are shown in Table I. The chemical shift results are noteworthy.

TABLE I

PROTON NMR CHEMICAL SHIFTS FOR $Cp_2Zr(OR)_nCl_{2-n}$ AND $Zr(OR)_4$[a]

Compound	$\tau(C_5H_5)$, ppm	$\tau(CH_3)$, ppm	$\tau(CH_2)$, ppm
Cp_2ZrCl_2	4.09	. . .	
$Cp_2Zr(OCH_3)Cl$	4.05 (10)	6.35 (2.7)	
$Cp_2Zr(GCH_3)_2$	4.02 (10)	6.23 (5.7)	
$Cp_2Zr(OC_2H_5)Cl$	4.01 (10)	9.00 (2.8)	6.14 (1.9)
$Cp_2Zr(OC_2H_5)_2$	4.00 (10)	8.89 (6.4)	6.07 (3.8)
$Zr(OC_2H_5)_4$	. . .	8.64	5.73
$Cp_2Zr(OC_3H_7)Cl$	4.05 (10)	9.00 (5.9)	
$Cp_2Zr(OC_3H_7)_2$	4.01 (10)	8.92 (12)	
$Zr(OC_3H_7)_4$	. . .	8.65	

[a] TMS used as internal standard; all spectra were run at 35°. Solvent used was perdeuterated benzene. Relative intensities are given in parentheses.

Nesmeyanov has studied the nmr of the series of compounds $CpTi(OC_2H_5)_nCl_{3-n}$ (n = 0–3).[11] His results show that the chemical shifts of the ring, methyl, and methylene groups move to higher frequencies as n increases. This trend is explained by invoking basicity arguments. As the ethoxide groups are replaced by the less basic chloride ligands, the electron density is decreased about the Cp ring and the methylene and methyl groups of the ethoxide ligand. The result is a shift toward lower frequencies in the nmr spectrum.

Nesmeyanov's results are significant because the exactly opposite effect is seen with the zirconium compounds (see Table I). As the number of alkoxide groups is decreased, the chemical shifts of the ring and alkoxide resonances increase. The basicity argument cannot be used to explain this apparently anomalous behavior. The primary differences between the Nesmeyanov work and the present zirconium work are (1) the central metal and (2) the number of cyclopentadienyl rings bonded to the central metal.

Wales[12] has reported an nmr study of a similar series, $Cp_2Ti(SR)_nCl_{2-n}$ (n = 0–2). Because this series contains two Cp rings, the analogy to the zirconium series may be more valid than the Nesmeyanov series. However, Wales' results show the same trends in chemical shifts as the Nesmeyanov compounds show. The presence of thioalkoxide groups rather than alkoxide groups makes the comparison questionable.

It is possible that benzene solvent effects may, in part at least, account for the anomaly in the chemical shifts.

Until additional work is done with zirconium series, it is futile to attempt an explanation of the anomalous chemical shift behavior. Similar behavior has been noted by Druce, *et al.*,[13] for the titanocene and zirconocene series Cp_2MX_2 (X = F, Cl, Br, I). The trend in Cp proton chemical shifts (τ) (Cl > Br > I) is opposite to that expected from simple basicity arguments. The possibility of an overriding trend in $p\pi \rightarrow d\pi$ bonding is given as a rationalization for this effect. The study of the series of compounds $Cp_2Ti(OR)_nCl_{2-n}$ and $CpZr(OR)_nCl_{3-n}$, neither of which has been characterized, should help clarify this matter.

---

(7) D. C. Bradley and W. Wardlaw, *J. Chem. Soc.*, 280 (1951).

(8) C. G. Barraclough, D. C. Bradley, J. Lewis, and I. M. Thomas, *ibid.*, 2601 (1961).

(9) C. T. Lynch, K. S. Mazdiyasni, J. S. Smith, and W. J. Crawford, *Anal. Chem.*, **36**, 2332 (1964).

(10) S. Herzog, J. Dehnert, and K. Luhder in "Techniques of Inorganic Chemistry," Vol. III, H. B. Jonassen and A. Weissberger, Ed., Interscience, New York, N. Y., 1968.

(11) A. N. Nesmeyanov, E. I. Fedin, P. V. Petrovskii, A. A. Dubovitskii, O. V. Nogina, and N. A. Lazareva, *Dokl. Akad. Nauk SSSR*, **163**, 659 (1965).

(12) R. S. P. Coutts, J. R. Surtees, J. M. Swan, and P. C. Wales, *Aust. J. Chem.*, **19**, 1377 (1966).

(13) P. M. Druce, B. M. Kingston, M. F. Lappert, T. R. Spalding, and R. C. Srivastava, *J. Chem. Soc. A*, 2106 (1969).

The infrared spectra (3500–700 cm^{-1}) of the compounds all show absorptions characteristic of π-bonded cyclopentadienyl groups (3100, 1020–1010, 850–840–815 cm^{-1}). These absorptions exhibit very small shifts as n changes from 0 to 2. The absorptions characteristic of the bound alkoxide ligands are listed in Table II. A study of the table shows that small shifts occur in the OR bands as n goes from 1 to 2. The unassigned bands in the 730–770-cm^{-1} region, however, undergo larger shifts to lower frequencies as n changes from 1 to 2. These bands are absent in the spectra of the pure alcohols and the Cp_2ZrCl_2. It is reasonable, therefore, to assume that they arise from the Zr–O bond. The presence of a chloride ligand should decrease the electron density about the central metal, thus allowing a stronger Zr–O bond to be formed, and is consistent with the observed shift to higher frequency of the Zr–O bond assignment as chloride replaces alkoxide in each case. The Zr–O stretching frequencies are found at much lower frequencies, and the vibration in the 730–770-cm^{-1} region is possibly a bending mode.

TABLE II

CHARACTERISTIC FREQUENCIES (CM^{-1}) OF ALKOXIDE GROUPS IN $Cp_2Zr(OR)_nCl_{2-n}$[a]

Compound	C–H str	C–H bend	C–O str	C–O bend	C–C str	Unassigned (Zr–O) (?)
$Cp_2Zr(OCH_3)Cl$	2805		1120			762
$Cp_2Zr(OCH_3)_2$	2800		1120			730
$Cp_2Zr(OC_2H_5)Cl$		1072	1130–1122		920	763
$Cp_2Zr(OC_2H_5)_2$		1070	1140–1122		913	732
$Cp_2Zr(OC_3H_7)Cl$	2600	1330		1161–1137		765
$Cp_2Zr(OC_3H_7)_2$	2600	1329		1163–1136		740

[a] All spectra run as Nujol mulls.

The far-infrared (700–250 cm^{-1}) absorptions of the compounds are given in Table III. The important features of these spectra are the probable assignments and observed shifts in the Zr–O and Zr–Cp stretching frequencies. The assignments were made by comparing the spectra of $Cp_2Zr(OR)_nCl_{2-n}$ with the spectrum of Cp_2ZrCl_2. From Table III it is seen that the Zr–O and the Zr–ring frequencies are shifted to lower frequencies as chloride ions are successively replaced by alkoxide ions and are once again consistent with basicity arguments. The Zr–O and Zr–ring bonds are equally affected by the presence or absence of chloride ligands.

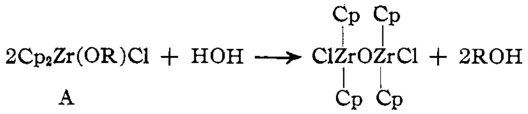
TABLE III

FAR-INFRARED ABSORPTIONS (CM^{-1}) OF Zr–O AND Zr–Cp BONDS

Compound	Zr–O str	Zr–Cp str	Compound	Zr–O str	Zr–Cp str
Cp_2ZrCl_2	. . .	359	$Zr(OC_2H_5)_4$	(520, 472, 421)	. . .
$Cp_2Zr(OCH_3)Cl$	507	342	$Cp_2Zr(OC_3H_7)Cl$	572	344
$Cp_2Zr(OCH_3)_2$	482	329	$Cp_2Zr(OC_3H_7)_2$	560 (453, 435)	315
$Cp_2Zr(OC_2H_5)Cl$	532	338	$Zr(OC_3H_7)_4$	(570, 516, 463)	. . .
$Cp_1Zr(OC_2H_5)_2$	521	318			

If the compounds are hydrolyzed by exposure to air saturated with water vapor, they lose weight rapidly. No physical change can be visibly observed, but the melting points change from relatively low values (above) to values in the range of 300° or greater. The infrared spectra undergo marked changes.

The infrared spectra and melting points indicate that the end hydrolysis product for each of the three compounds $Cp_2Zr(OR)Cl$ (R = CH_3, C_2H_5, 2-C_3H_7) is the same. Furthermore, the weight loss corresponds to the hydrolysis reaction

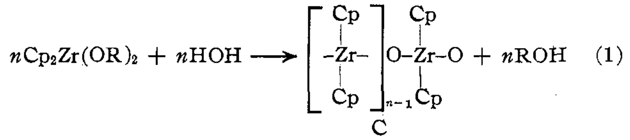


$$\underset{A}{2Cp_2Zr(OR)Cl} + HOH \longrightarrow Cl\overset{Cp}{\underset{Cp}{Zr}}O\overset{Cp}{\underset{Cp}{Zr}}Cl + 2ROH$$

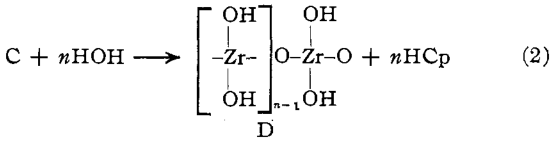
This is the same as noted by Brainina[1] when he performed an elaborate hydrolysis reaction with $Cp_2Zr(OC_2H_5)Cl$.

The infrared spectrum of the hydrolysis products is consistent with the above reaction. The absorption bands of the cyclopentadienyl rings (3100, 1030–1020, 840–810 cm^{-1}) are still present. All bands of the R groups are absent. There are additional strong absorptions at 779 and 752 cm^{-1} which are due to Zr–O–Zr[14,15] bands. The far-infrared region shows the Zr–ring stretching band at 349 cm^{-1} and the lower frequency broader bands characteristic of a Zr–Cl bond.

The hydrolysis of the compounds $Cp_2Zr(OR)_2$ (B) is much different from and less straightforward than the hydrolysis of $Cp_2Zr(OR)Cl$ (A). The weight loss (relative to weight of original product) attending the hydrolysis of B is much greater than the weight loss for A. The hydrolysis of B seems to proceed in two rather ill-defined steps. On the basis of infrared spectral evidence and weight loss calculations, the two steps may be expressed as



$$nCp_2Zr(OR)_2 + nHOH \longrightarrow \underset{C}{\left[-\overset{Cp}{\underset{Cp}{Zr}}-\right]_{n-1}O-\overset{Cp}{\underset{Cp}{Zr}}-O} + nROH \qquad (1)$$



$$C + nHOH \longrightarrow \underset{D}{\left[-\overset{OH}{\underset{OH}{Zr}}-\right]_{n-1}O-\overset{OH}{\underset{OH}{Zr}}-O} + nHCp \qquad (2)$$

The above steps are probably oversimplifications. If the hydrolysis is allowed to proceed for about 30 min, the weight loss corresponds roughly to the weight lost by elimination of alkoxide groups in step 1. The infrared spectrum shows that all bands characteristic of the R groups are absent. The spectrum shows, however, that the cyclopentadienyl absorption bands are superimposed on the broad band characteristic of the Zr–OH bond (very broad centering at 480 cm^{-1}). The spectrum thus indicates that step 2 has already begun. Further hydrolysis results in a slower weight loss until a constant weight is finally observed. This weight loss corresponds roughly to the elimination of HCp as in step 2. The distinctive odor of cyclopentadiene is observed during the latter stage of hydrolysis. The infrared spectrum of D shows no indication of the presence of Cp. Broad bands are observed at 3300, 1480, and 480 cm^{-1}. The former two are indicative of bound OH while the latter is probably due to the Zr–OH bond.

It was hoped that reduction potentials for each of the compounds could be determined. The polarograms were attempted in THF solution. The resistance of THF, however, could not be sufficiently overcome by the presence of supporting electrolyte (TBAI) to obtain

---

(14) A. F. Reid, J. S. Shannon, J. M. Swan, and P. C. Wailes, *Aust. J. Chem.*, **18**, 173 (1965).

(15) E. Samuel, *Bull. Soc. Chim. Fr.*, 3548 (1966).

interpretable polarograms. This work is being continued.

Nitrogen-fixation experiments were attempted by using Cp_2ZrCl_2, $Cp_2Zr(OC_3H_7)Cl$, and $Cp_2Zr(OC_3H_7)_2$. The results (% NH_3) of the nitrogen-fixation experiments for these three compounds are shown as follows: Cp_2ZrCl_2, 2.7, 4.1; $Cp_2Zr(OC_3H_7)Cl$, 1.3; $Cp_2Zr(OC_3H_7)_2$, 0.0.

The yields of ammonia produced are disappointingly small, and any conclusions must be drawn with considerable uncertainty. However, it does appear that the nitrogen-fixing ability of the series decreases as the chloride ligands are replaced by isopropoxide groups. One can only speculate about the effect being related to the ease of the two-electron reduction of Zr(IV)–Zr(II). The speculated "ease-of-reduction" of the series $Cp_2ZrCl_2 > Cp_2Zr(OR)Cl > Cp_2Zr(OR)_2$ may be a result of the relative electron density about the zirconium. As the chlorides are replaced by the more basic alkoxide groups, the electron density about the zirconium should increase and may have the effect of raising the energy of the lowest lying d orbital slightly. Such an effect would make reduction more difficult and would be consistent with the trend seen in the relative nitrogen-fixing abilities of the compounds.

Acknowledgment.—The authors thank the National Institutes of Health for fellowship aid (to D. R. G.) and the National Science Foundation for support under Grants GP-7088X and 17422X.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
STANFORD UNIVERSITY, STANFORD, CALIFORNIA 94305

Mixed-Valence Complexes of Iron(III) with Iron(II) and Mixed-Metal Complexes of Iron(III) with Tin(II) in Aqueous Citrate Media

BY B. BINDER*

Received February 18, 1971

From spectrophotometric absorption data two mixed-valence complexes $Fe^{II}Fe^{III}L^+$ (L^{4-} = citrate ion) and $Fe^{II}Fe^{III}H_2L_2^-$ have been identified in aqueous citrate media. In similar media a mixed-metal complex $Sn^{II}Fe^{III}H_2L_3^{5-}$ has also been found. The formation constant of the last complex has been calculated.

Introduction

As pointed out by Robin and Day,[1] inorganic compounds made up of ions of the same element in two different formal oxidation states constitute an interesting class of substances whose study has been largely neglected. Mixed-valence systems of this kind are of interest because their properties are seldom the sum of the properties of the two metal ions taken separately. One of the most obvious manifestations of this feature is the enhanced optical absorption that usually results when a mixed-valence species is formed. Davidson and coworkers[2] have termed the enhanced absorption "interaction absorption" and have studied the phenomenon in concentrated HCl solutions containing Fe(III) and Fe(II),[3] Sb(V) and Sb(III),[2] and Cu(II) and Cu(I),[3] as well as Sn(IV) and Sn(II).[1] With the copper system[3] they were able to demonstrate that the absorbing species had the empirical formula Cu_2Cl_3; the structure of this compound was postulated to involve a single chloride bridge between the two copper ions. The enhanced absorption apparently results from resonance of a valence electron between the two metal centers.

From a quantitative study of Fe(II)–Fe(III) systems we have found that a number of ligands can bring about interaction absorption at considerably lower concentrations than in the case of chloride ion where 6–12 *M* HCl was required. Among the effective ligands were oxalate, malonate, lactate, glycolate, tartrate, citrate, formate, and glycine. Under similar experimental conditions, Fe(II) and Fe(III) concentrations of 0.03 *M* and ligand concentration of 0.3 *M*, no enhanced absorption was found with acetate, propionate, monochloroacetate, succinate, γ-hydroxybutyrate, and ethylene glycol.

We have also observed what appears to be a similar kind of absorption enhancement when the Fe(II) is replaced by the better electron donor Sn(II) with malonate, tartrate, oxalate, and citrate as ligands. In these media reduction of Fe(III) is slow and the solutions are considerably more intense in color than in the presence of Fe(II).

In this paper we present the results of a quantitative spectrophotometric study of the iron(III)–iron(II)–citrate and the iron(III)–tin(II)–citrate systems. In the former system we were able to identify two mixed-valence complexes which were responsible for the observed interaction absorption; formation constants could not, however, be determined. In the latter case, a single mixed-metal complex predominates; its stability is great enough to permit assessment of its formation constant.

Experimental Section

Reagents and Solutions.—Stock solutions of Fe(II) and Fe(III) were prepared from their perchlorates (G. Frederick Smith Chemical Co.) and were standardized periodically with a standard permanganate solution by the Zimmermann–Reinhardt

---

* Address correspondence to Chemistry Department, Southern Oregon College, Ashland, Oreg. 97520

[1] M. B. Robin and P. Day, *Advan. Inorg. Chem. Radiochem.*, **10**, 247 (1967), and references therein.

[2] J. E. Whitney and N. Davidson, *J. Amer. Chem. Soc.*, **71**, 3809 (1949).

[3] H. M. McConnell and N. Davidson, *ibid.*, **72**, 3168, 5557 (1950).