TABLE II

CONDUCTANCES OF SOLUTIONS OF HYDROGEN CHLORIDE AND POTASSIUM CHLORIDE IN FORMAMIDE

C ($\times 10^2$)	Λ	C ($\times 10^2$)	Λ	C ($\times 10^2$)	Λ
3°		20°		40°	
Hydrogen chloride					
0.00	(14.41)	0.00	(24.50)	0.00	(39.40)
4.84	12.39	5.38	21.20	3.28	35.24
6.56	12.07	6.42	21.00	8.04	32.93
13.13	11.42	7.35	20.82	9.79	32.38
26.25	9.99	8.67	20.60	37.15	27.32
52.50	8.40	10.09	20.28	52.51	25.10
		11.77	19.98		
		13.83	19.57		
		15.89	19.21		
		29.93	17.45		
		45.53	15.82		
Theoretical slopes					
8.97		15.23		24.86	
Potassium chloride					
0.00	(16.94)	0.00	(26.38)	0.00	(41.66)
0.52	16.13	0.52	25.31	0.51	40.05
1.04	15.86	1.03	24.81	1.01	39.35
2.60	15.49	2.57	24.22	2.53	38.36
16.13	13.26	15.95	20.87	15.71	33.06
36.40	11.64	36.00	18.42	35.46	29.30
70.78	9.54	70.00	15.33	68.94	24.62
Theoretical slopes					
9.72		15.49		25.18	

ence with the theoretical to nearly 0.01 N, which is shown in these graphs, is unexpected in view of the fact that 0.003 N is the upper limit for similar behavior by the same solutes in water. Furthermore, the difference between these types of solutions becomes much greater if the concentrations are thought of in terms of relative numbers of molecules rather than molarity.

The Kohlrausch plots exhibit much less upward concavity with increased concentration than for these solutes in aqueous solutions; at higher concentrations they tend to approach linearity. This behavior may be produced by an inflection resulting primarily from viscosity effects.

The Walden products for the HCl system at 3, 20 and 40° are 0.942, 0.943 and 0.932. For the KCl system at 5, 20 and 40°, these values are 1.047, 1.016 and 0.987. The conductance-viscosity product for KCl in formamide is markedly less than it is in water (1.34 at 25°) and greater than it is in most organic solvents.

The lower limiting conductance of HCl is evidence that the solvated proton is larger, hence less mobile, than the solvated potassium ion. In addition, the absence of abnormally high cation conductance in the acid solution is proof that the proton does not move through this solvent by some unique mechanism as it does in water. A similar conclusion has been drawn from studies of acids in amine solvents[11] and in dimethylformamide.[12]

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Inorganic Complex Compounds Containing Polydentate Groups. X. Zirconium(IV) Complexes

BY HANS B. JONASSEN AND WINSTON R. DEMONSABERT[1]

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This study[2] was designed to explore by spectrophotometric means the formation of complex ions of zirconium(IV) with the bidentate coördination agent, 1-nitroso-2-naphthol and *o,o'*-dihydroxyazobenzene, a possible tridentate group. A consideration of the structural formula of the latter indicates that coördination to the two hydroxy and the azo groups may be possible.

Experimental

A. **Reagents.**—Zirconium tetrachloride, $ZrCl_4 \cdot 8H_2O$, obtained from the Fairmount Chemical Company was recrystallized six times from concentrated HCl solutions.

The 1-nitroso-2-naphthol, practical grade (melting point 109°), was obtained from the Eastman Kodak Company. This material was dissolved in ethanol and recrystallized with water.

The *o,o'*-dihydroxyazobenzene was prepared by the method of Weselsky and Benedict[3] as modified by Willstätter.[4]

Recrystallization from methyl alcohol produced a golden-yellow product melting at 172° (reported 171–173°). The other reagents were C.P. grade chemicals.

B. **Instruments.**—The Beckman Model G *p*H meter was used in the determination and adjustment of the *p*H of the solutions throughout this study.

All spectrophotometric determinations were made on the Beckman model DU spectrophotometer. Matched ten millimeter Corex cells were used for measurements in the visible range. Matched ten millimeter quartz cells were used with the ultraviolet attachment for measurements in this region of the spectrum.

C. **Spectrophotometric Investigations.** 1. **1-Nitroso-2-naphthol Complexes.**—The absorption spectrum of the zirconium(IV) 1-nitroso-2-naphthol complex was determined using a 50% ethanol solution which was 5×10^{-4} M in 1-nitroso-2-naphthol and 5×10^{-4} M in $ZrOCl_2$. The solution was 1×10^{-1} M in $NaNO_3$ as inert electrolyte. The solution was adjusted to *p*H of 3.5 by the addition of small amounts of M HNO_3.

Continuous variation and saturation studies[5] were made at 480 mμ on a series of a similar solution.

2. ***o,o'*-Dihydroxyazobenzene Complexes.**—The absorption spectrum of a 50% ethanol solution 1.5×10^{-4} M in *o,o'*-dihydroxyazobenzene and in $ZrOCl_2$ was determined from 250 to 600 mμ. An inert electrolyte concentration in $NaClO_4$ was maintained at 3×10^{-2} M. The solution was allowed to stand for 40–48 hours to reach equilibrium. Nitrogen was bubbled through the solution before and after mixing.

Continuous variation and saturation studies were made on similar solutions.

A. Studies of Zirconium(IV) with 1-Nitroso-2-naphthol. 1. Spectral Studies.—Figure 1 shows that the regions from 450 to 500 mμ and 270 to 300 mμ are best suited for continuous variation studies.

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[11] L. F. Audrieth and J. Kleinberg, "Non-aqueous Solvents," John Wiley and Sons, New York, N. Y., 1953, p. 77.

[12] L. R. Dawson, M. Golben, G. R. Leader and H. K. Zimmerman, Jr., *J. Electrochem. Soc.*, **99**, 28 (1952).

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(4) R. Willstätter and M. Berg, *Ber.*, **39**, 3492 (1906).

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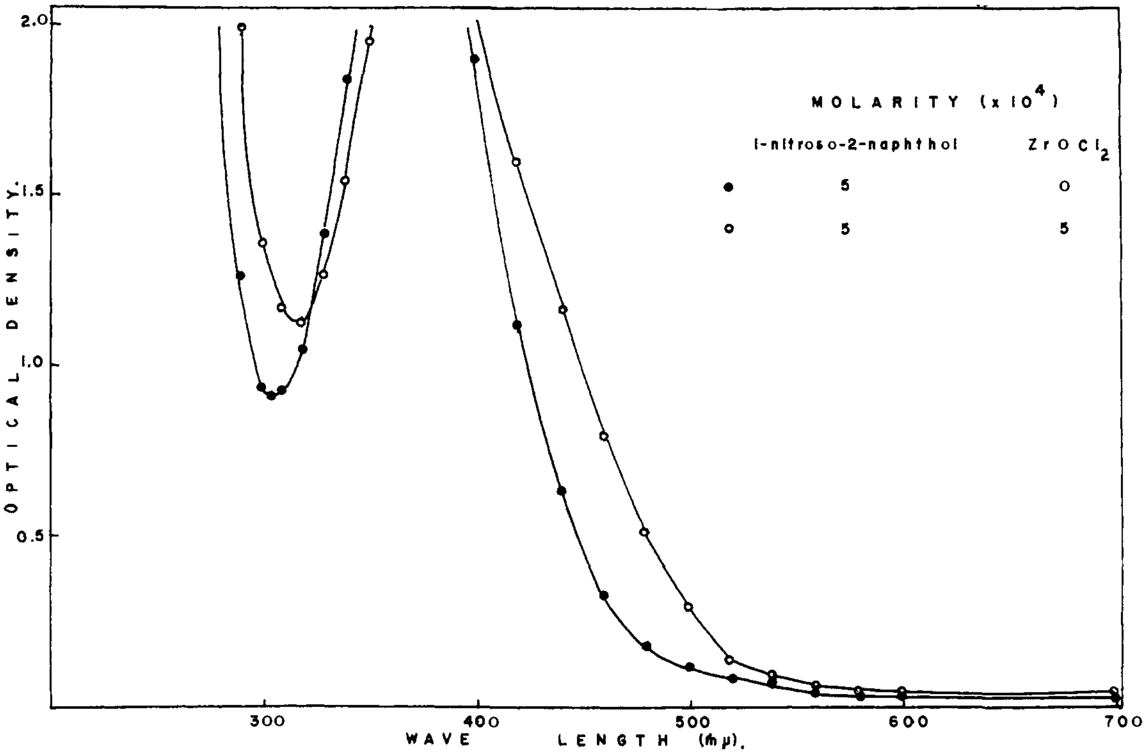

Fig. 1.—Absorption spectra of 50% ethanol solutions of 1-nitroso-2-naphthol and 1:1 mixture of $ZrOCl_2$ and 1-nitroso-2-naphthol; pH 3.5; inert electrolyte = 1.1 M $NaNO_3$; temp., 32°; path length of cell = 1 cm.; O.C. = log (1/transmittance).

A continuous variation study at constant inert electrolyte concentration indicated the presence of a 1:1 complex at 480, 500 and 290 mμ. The stability constants of the complex were calculated by the saturation method[5] at the wave length of 420 mμ.

Using the Turner and Anderson[6] method the same values (Table I) were obtained.

B. *o,o*′-Dihydroxyazobenzene and Zirconium (IV).—From the absorption curve of a 50% ethanol solution of $ZrOCl_2$ and *o,o*′-dihydroxyazobenzene, three wave length regions (Fig. 2) were found suitable for continuous variation studies: 250 to 280, 300 to 420, and 460 to 550 mμ. Studies in these regions indicate the presence of a 1:1 complex at constant inert electrolyte concentration.

Saturation study techniques and Turner's and Anderson's method of "equal optical density"[6] were applied and gave the same pK values (Table I).

TABLE I

THERMODYNAMIC DATA OF ZIRCONIUM(IV) COMPLEXES

Complexing agent	Temp., °C.	pK
2-Nitroso-1-naphthol	30.5	4.1 ± 0.05
1-Nitroso-2-naphthol	32.0	3.6 ± .05
o,o′-Dihydroxyazobenzene	32.0	5.0 ± .05

The decrease in stability in the 1-nitroso-2-naphthol complex as compared to the 2-nitroso-1-naphthol[2] is to be expected from a comparison of the reactions of α- and β-naphthols.

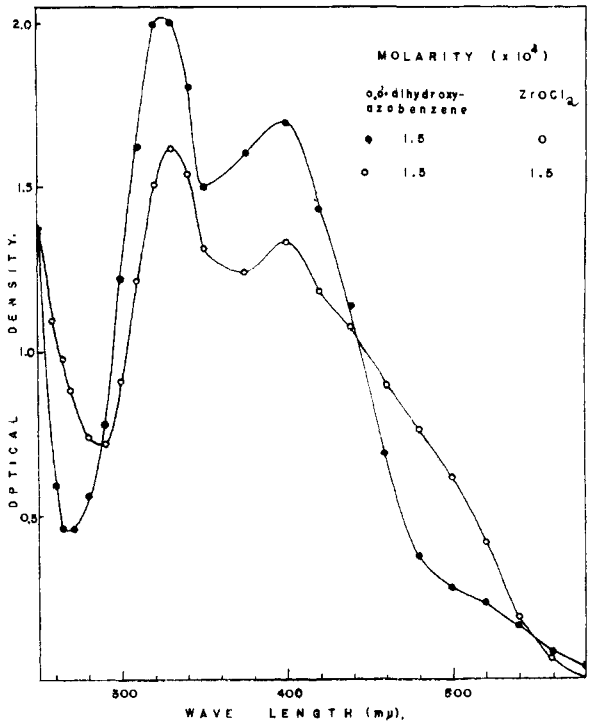

Fig. 2.—Absorption spectra of 50% ethanol solutions of *o,o*′-dihydroxyazobenzene and its 1:1 mixture of $ZrOCl_2$; inert electrolyte = 3 × 10^{-2} M $NaClO_4$, temp., 32°; path range = 1 cm.; O.D. = log (1/transmittance).

For the 1:1 Zr(IV) *o,o*′-dihydroxyazobenzene

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[6] S. E. Turner and R. C. Anderson, THIS JOURNAL, **71**, 912 (1949).

complex, further investigations are necessary in order to establish the existence of a tridentate linkage.

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The Preparation of Lanthanum Titanium Oxide, $LaTiO_3$[1]

BY MICHAEL KESTIGIAN AND ROLAND WARD

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Ternary oxides of the general formula $LaMO_3$ have been described for all of the 1st Period transition elements from vanadium to cobalt, inclusive. These compounds all have the perowskite-type structure.[2–5]

The manganese compound always contains some tetravalent manganese which suggests that some of the lanthanum positions in the lattice are vacant.[3]

Prior investigations of the lanthanum–titanium system appear to have been confined to tetravalent titanium. Among a number of solid phases which have been reported is $La_{2/3}TiO_3$ which is said to have a defect perowskite structure with one third of the lanthanum positions vacant.[3,6] It was an obvious possibility that the compound $LaTiO_3$ should be formed under the proper experimental conditions. This paper deals with the synthesis of the compound and its characterization.

Experimental

Products which gave X-ray diffraction patterns containing the lines of a cubic perowskite were obtained by heating the mixture of composition La_2O_3:$2TiO_2$ at 1200° for prolonged periods in a hydrogen atmosphere. The samples, however, were not homogeneous under the microscope but consisted of a white and black phase. The same phase with the perowskite structure was prepared by heating stoichiometric mixtures ($La_2O_3 + 3TiO_2 + La$) of lanthanum oxide, titanium dioxide and lanthanum metal *in vacuo* in a sealed silica capsule at 1150°. These products were always contaminated with silicon due to the reaction of the lanthanum metal with the container. A similar procedure using titanium metal as reducing agent gave products which always contained some unreacted titanium metal. The same results were obtained using either lanthanum hydride or titanium hydride as a reducing agent.

The purest products were prepared by the reaction

$$La_2O_3 + Ti_2O_3 \longrightarrow 2LaTiO_3$$

The titanium sesquioxide was prepared according to the method of Friedel and Guerin.[7] C.P. titanium dioxide and freshly prepared titanium tetrachloride were used. Analysis of the preparation by the method of MacCardle and Scheffer[8] gave 66.86% Ti^{+3} compared with the theoretical 66.63% Ti^{+3}. Because of the rapid hydrolysis of lanthanum oxide, it was ignited at 1000° just prior to weighing and mixing with the titanium sesquioxide. The sample was pressed into a pellet and heated in an evacuated silica capsule for 24 hr. at 1180°. The surface of the pellet was removed and the remaining sample reground and reheated at 1220° for 48 hr. in the same manner. The product was homogeneous under the microscope and consisted of small, black, slightly iridescent crystals. The same product was obtained using a slight excess of lanthanum oxide which was removed after the final heating by extraction with 2 *N* hydrochloric acid.

The products were analyzed for titanium and lanthanum by subjecting a sample to fusion with potassium bisulfate containing a few drops of concd. sulfuric acid. The colorless melt obtained in this way was dissolved in 1 *M* sulfuric acid solution from which the titanium was precipitated with cupferron. The lanthanum was precipitated as the oxalate from the solution at *p*H 4. These analyses gave 19.75% Ti and 58.95% La compared with 20.40% Ti and 59.16% La for $LaTiO_3$. The percentage of titanium in the black product was also determined by a modification of the procedure of MacCardle and Scheffer.[8] The use of hydrofluoric acid had to be abandoned because of the precipitation of lanthanum fluoride. The reaction was carried out by heating the sample with 50 ml. of 18 *N* sulfuric acid containing an excess of vanadium(V). The excess vanadium was titrated with standardized Mohr salt solution. These analyses gave 20.58% Ti.

The structure as determined from the X-ray diffraction powder pattern using a camera of radius 107.8 mm. with Cu K_α radiation is the cubic perowskite (a_0 = 3.92 ± 0.01 Å.). The X-ray data are listed in Table I. With short exposures of 3 hr., only the perowskite lines were observed, but with prolonged exposures up to 60 hr. additional weak lines appeared. All of these were identified with the stronger lines of the white product which is formed by heating the black product in air. It is possible that the oxidation may occur during the exposure to X-rays. The density, determined pycnometrically is 6.26 g./cm.^{3} corresponding to 0.97 molecule of $LaTiO_3$ per unit cell.

TABLE I

DETERMINATION OF CELL CONSTANT

I	*d/n*	*hkl*	$h^2 + k^2 + l^2$	a_0 (Å.)
W+	3.92	100	1	3.92
S+	2.78	110	2	3.93
M+	2.27	111	3	3.93
S	1.967	200	4	3.93
W	1.756	210	5	3.93
S	1.603	211	6	3.93
M	1.388	220	8	3.93
W−	1.309	300	9	3.93
M	1.241	310	10	3.92
W−	1.183	311	11	3.92
W	1.134	222	12	3.93
M−	1.040	321	14	3.92
W−	0.979	400	16	3.92
W−	0.948	322, 410	17	3.91
M+ diffuse	0.921	411	18	3.91
M diffuse	0.873	420	20	3.91
M diffuse	0.833	332	22	3.91

Average cell constant 3.92 ± 0.01 Å.

These results show conclusively that the compound corresponds closely to the normal perowskite type. In view of the reported defect structure of the compound $La_{2/3}TiO_3$, we are planning to investigate the range of composition between this and the compound $LaTiO_3$.

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