of hydrochloric acid such that a total chloride concentration of 4% is achieved upon diluting to 250 ml. Both zirconium and aluminum are determined from this stock solution by comparing peak intensities with standard solutions which bracket the estimated unknown concentrations.

Halide concentrations were determined on the filtrates of the hydroxide precipitates by standard procedures.

The hafnium concentration in zirconium samples was determined by arc spectrographic analysis on oxide samples submitted to the National Spectrographic Laboratories, Cleveland, Ohio.

Acknowledgment. This work was supported in part by National Science Foundation Grant No. GP-9300 and by the Research Committee of the Graduate School from funds supplied by the Wisconsin Alumni Research Foundation. J. W. M. also acknowledges the financial support of an NSF Traineeship (1969-1970). We also acknowledge the contributions of J. Kleppinger and R. Clemmer for certain of the analytical and spectral work and Dr. Eldrys ge Gil and Professor Lawrence Dahl for the single crystal work.

Registry No. $ZrCl_3$, 10241-03-9; $ZrBr_3$, 24621-18-9; ZrI_3, 13779-87-8; $(ZrCl_2)_2 \cdot AlCl_3$, 39472-11-2; $Zr(Cl_2AlCl_2)_2(ClAlCl_3)_2$, 43211-71-8; $Zr(Br_2AlBr_2)_2(BrAlBr_3)_2$, 43211-72-9; $Zr(I_2AlI_2)_2(IAlI_3)_2$, 43211-73-0; $(ZrBr_2)_2 \cdot AlBr_3$, 39472-10-1; $ZrCl_4$, 10026-11-6; $ZrBr_4$, 13777-25-8; ZrI_4, 13986-26-0; $AlCl_3$, 7446-70-0; $AlBr_3$, 7727-15-3; AlI_3, 7784-23-8.

Contribution from the Department of Chemistry,
The University of Wisconsin, Madison, Wisconsin 53706

2,4-, 2,6-, and 3,5-Lutidine Adducts of Zirconium(III) Chloride and Zirconium(IV) Chloride, Bromide, and Iodide

E. M. LARSEN* and T. E. HENZLER[1]

Received April 20, 1973

Solid zirconium(III) chloride reacts with a benzene solution of lutidine (L) to form solid $ZrCl_3(3,5\text{-}L)_2$ and $ZrCl_3(2,4\text{-}L)_{1.2-1.3}$. It does not react with 2,6-lutidine. The small fraction of zirconium(III) in solution appears to undergo an oxidation-reduction reaction in the presence of excess lutidine. Zirconium(IV) chloride, bromide, and iodide react to form $ZrX_4(3,5\text{-}L)_2$, $ZrX_4(2,4\text{-}L)_2$, and $ZrX_4(2,6\text{-}L)$. The product compositions of both the zirconium(III) and zirconium(IV) products are controlled by the steric effects of the methyl groups. A field dependent paramagnetism was observed for the zirconium(III) chloride adducts similar to that observed for the binary chloride itself.

Introduction

The chemistry of trivalent zirconium is relatively unexplored. Fowles and Wiley[2,3] have reported the preparation of $ZrX_3 \cdot 2py$, $2ZrX_3 \cdot 5MeCN$, $2ZrCl_3 \cdot 3L$ (L = 1,10-phenanthroline (phen) and 2,2'-bipyridyl (bipy)), $ZrBr_3 \cdot 2bipy$, and $2ZrI_3 \cdot 3bipy$ by direct reaction of zirconium(III) compounds with the ligand. Wasmund[4] reduced zirconium tetrachloride with sodium in pyridine to prepare the zirconium(III) pyridine adduct. By either route, the products possess unusual stoichiometries[2,3] or rather unsatisfactory[4] analyses suggesting that further work is necessary in the reduced state chemistry of zirconium.

Although a large variety of organic molecules possessing oxygen ligand atoms are known to form adducts with zirconium(IV) halides, oxygen-containing species did not seem to be the most suitable to study in view of the reducing properties of zirconium(III) and the strength of the zirconium(IV)-oxygen bond. Organic molecules containing nitrogen ligands appeared to be more desirable, especially those with reducing properties. As with the zirconium(III), there have been relatively few adducts prepared with zirconium(IV) halides and compounds with a nitrogen ligand atom. Diadducts, ZrX_4L_2, are known for X = Cl and Br with the unidentate ligands MeCN and EtCN,[5-8] pyridine,[5,6,9] and pyrazine[10] and monoadducts, ZrX_4L, with the bidentate ligands, 2,2'-bipyridyl and 1,10-phenanthroline.[5,9] A triadduct, $ZrCl_4(py)_3$,[9] has also been reported. In this work the 2,4-, 2,6-, and 3,5- isomers of lutidine were used.

Discussion

The Tetrahalide Systems. With the exception of the 2,6-lutidine-zirconium tetrachloride and tetrabromide systems, the syntheses involve the reaction of solid zirconium tetrahalide suspended in benzene with a stoichiometric amount of dissolved ligand. In such a heterogeneous reaction system the reaction rates are slow and the incorporation of unreacted tetrahalide in the product is possible. However, the use of solvents in which the zirconium tetrahalides are soluble, such as acetonitrile and tetrahydrofuran, yields adducts, which, although isolable, are of erratic composition and colored. Some colored organic by-product is obtained even in the benzene systems if excess ligand is present. The amount of such by-product is small since the products obtained are identical, except for color, with those obtained using the stoichiometric amount of ligand, as shown by elemental analysis, X-ray diffraction patterns, and infrared spectra. Zirconium(IV) halides give 1:2 adducts with 2,4- and 3,5-lutidines but only the 1:1 adduct with 2,6-lutidine (Table I).

Except for the two cases cited, the lutidine adducts were recovered as the insoluble component of the reaction system. The insolubility of the products in benzene accounts for the high yields obtained. All the iodides evidenced some slight solubility as seen by the colored supernatant liquor; however,

---

(1) Prepared from the Ph.D. Thesis of T. E. Henzler.

(2) G. W. A. Fowles, B. J. Russ, and G. R. Wiley, *Chem. Commun.*, 646 (1967).

(3) G. W. A. Fowles and G. R. Wiley, *J. Chem. Soc. A*, 1435 (1968).

(4) D. Wasmund, Ph.D. Thesis, Southern Illinois University, 1969, University Microfilms, Inc., Ann Arbor, Mich.

(5) I. R. Beattie and M. Webster, *J. Chem. Soc.*, 3507 (1964).

(6) G. W. A. Fowles and R. A. Walton, *J. Less-Common Metals*, 5, 510 (1963).

(7) G. W. A. Fowles and R. A. Walton, *J. Chem. Soc.*, 2840 (1964).

(8) O. A. Osipov and Yu. B. Kletenik, *J. Gen. Chem. USSR*, 31, 2285 (1961).

(9) T. C. Ray and A. D. Westland, *Inorg. Chem.*, 4, 1501 (1965).

(10) G. W. A. Fowles and R. A. Walton, *J. Chem. Soc.*, 4330 (1964).

Table I. Analytical Data and Physical Properties of the ZrX_4-Lutidine Adducts

		Zr	X	C	H	N	% yield	Color	Thermal props
$ZrCl_4\cdot 2(3,5\text{-L})$	Calcd	20.39	31.70	37.59	4.06	6.26			354-359°^{f}
	Found	20.09	31.10	37.82	4.40	6.24	91	White	
$ZrBr_4\cdot 2(3,5\text{-L})$	Calcd	14.59	51.13	26.90	2.90	4.48			
	Found	14.33	50.94	26.65	3.05	4.49	97	White	220-225°^{a,c} No melting to 325°^{h}
$ZrI_4\cdot 2(3,5\text{-L})$	Calcd	11.22	62.43	20.68	2.23	3.45			
	Found	10.47	62.96	21.02	2.28	3.42	93	Light orange	117°,^{c} 134°,^{a} 204°,^{d} 236°^{f,b} Yellow-orange
$ZrCl_4\cdot 2(2,4\text{-L})$	Calcd	20.39	31.70	37.59	4.06	6.26			165-170°^{b} White → lt brown
	Found	20.43	31.73	36.90	4.10	5.84	100	White	222-230°^{f,g} Dk brown
$ZrBr_4\cdot 2(2,4\text{-L})$	Calcd	14.59	51.13	26.90	2.90	4.48			220-225°$^{a-c}$ White → lt orange
	Found	14.50	51.34	26.79	2.86	4.42	99	White	225-230°^{e,b} Dk brown
$ZrI_4\cdot 2(2,4\text{-L})$	Calcd	11.22	62.48	20.68	2.23	3.45			140°,^{a} 148-185°^{d,b}
	Found	11.31	61.32	20.24	2.45	3.30	98	Bright orange	Yellow → red
$ZrCl_4(2,6\text{-L})$	Calcd	26.81	41.69	24.72	2.67	4.12			80-85°,^{a} 108-113°^{f}
	Found	27.94	39.88	25.04	2.84	4.39	91	White	
$ZrBr_4(2,6\text{-L})$	Calcd	17.61	61.70	16.23	1.75	2.70			103°,^{e} 107-117°^{e,b}
	Found	17.42	60.86	17.13	2.03	2.63	20.6	White	Yellow-orange
$ZrI_4(2,6\text{-L})$	Calcd	12.92	71.90	11.91	1.28	1.98			100-130° Yellow ←→ orange
	Found	12.56	69.24	14.68	1.75	1.95		Bright yellow	140-150°^{b} Black-brown char

[a] Appears damp. [b] Color change. [c] Shrinks. [d] Melts, plastic (no flow). [e] Melts, semifluid. [f] Melts, liquid. [g] Melting incomplete. [h] Heating stopped.

the solubility was not sufficiently high to provide an attractive route for recovery of a product. In the 2,6-lutidine system with zirconium tetrachloride and zirconium tetrabromide, under the concentration and temperature conditions used, the tetrachloride was completely soluble in the lutidine-benzene mixture revealing only a miniscule amount of residue, and the bromide system resulted in a saturated solution from which the product was obtained. The favorable solubility of the 1:1 adducts of 2,6-lutidine compared with the insolubility of the 2:1 adducts of 3,5- and 2,4-lutidine was surprising.

The infrared spectra (Table II), in spite of their complexity and the problem of sorting shifted from nonshifted bands, do reveal some information regarding the structural features of the adducts. Pyridine and pyridine-metal halide spectra are used as models for the lutidine systems. Gill[11] and Clark[12] have presented extensive data to show that two of the lowest ring vibrations of pyridine, which in the liquid are at 405 cm^{-1} (16b out-of-plane deformation) and 604 cm^{-1} (6a in-plane deformation), shift significantly toward higher frequencies upon coordination to a metal ion. In 2,4-lutidine and 2,6-lutidine these ring frequencies have been identified[13] as occurring at 197 and 200 and 518 and 555 cm^{-1}, respectively. We assign the band at 536 cm^{-1} in the spectrum of liquid 3,5-lutidine to the 6a mode. In agreement with Clark and Gill, the 6a mode in the lutidine adducts of zirconium tetrachloride are shifted toward higher frequencies compared to the free ligand, namely 546 (2,4-L), 573 (2,6-L), and 545 cm^{-1} (3,5-L). Similar positive shifts are seen in the spectra of the bromide and iodide adducts. The frequencies associated with the out-of-plane deformation probably are out of the range of our instrument, although it is conceivable that the bands in the adduct spectra between 300 and 250 cm^{-1} contain a shifted 16b ring mode. Fowles,[14] in addition to the shift in the ring modes, observed negative shifts for modes associated with carbon-hydrogen frequencies in dipyridine adducts of niobium tetrachloride and tantalum tetrachloride and tetrabromide. We were unable to confirm unambiguously similar shifts for the lutidine adducts under consideration here. However, this fact should not negate the conclusion that lutidine is bound to zirconium in these compounds.

The infrared spectra of the 3,5-lutidine adducts of all three tetrahalides are very similar as are the spectra of the corresponding 2,4-lutidine products. There is an important exception, namely the presence of a strong band at 337 cm^{-1} in the 3,5-lutidine complex and a strong band at 340 cm^{-1} in the 2,4-lutidine complex of the chloride, which are missing from the spectra of the corresponding bromide and iodide complexes. These bands are presumably due to a Zr-Cl mode. The presence of a single strong band in this region represents a substantial change from the spectrum of zirconium tetrachloride[15] which consists of two groups of strong bands between 431 and 388 and 305 and 271 cm^{-1}. If in fact this absorption is the only Zr-Cl mode, then we must conclude that the metal ion site symmetry in the adduct is higher than in the tetrachloride itself where it is known[16] to be a distorted octahedron consisting of one pair of terminal chlorides and two pairs of cis nonequivalent bridging chlorides. We conclude that a molecular CN 6 structure for $ZrCl_4\cdot 2L$ is likely with the trans structure favored over the cis structure in contrast to what appears to be the case for the pyridine adduct.[9]

The 3,5-lutidine adducts possess some properties the other adducts do not. For instance, these compounds are ther-

---

(11) N. S. Gill, R. H. Nuttall, D. E. Scaife, and D. W. A. Sharp, *J. Inorg. Nucl. Chem.*, **18**, 79 (1961).

(12) R. J. H. Clark and C. S. Williams, *Inorg. Chem.*, **4**, 350 (1965).

(13) K. C. Medhi and D. K. Mukherjee, *Spectrochim. Acta*, **21**, 895 (1965).

(14) M. Allbutt, K. Feenan, and G. W. A. Fowles, *J. Less-Common Metals*, **6**, 299 (1964).

(15) J. Weidlein, U. Muller, and K. Dehnicke, *Spectrochim. Acta, Part A*, **24**, 253 (1968).

(16) B. Krebs, *Angew. Chem., Int. Ed. Engl.*, **8**, 146 (1969).

Table II. Infrared Spectra of Lutidine Adducts of Zirconium Tetrahalides

$ZrCl_4(2,6\text{-}L)$	$ZrBr_4(2,6\text{-}L)$	$ZrI_4(2,6\text{-}L)$	$ZrCl_4(3,5\text{-}L)_2$	$ZrBr_4(3,5\text{-}L)_2$	$ZrI_4(3,5\text{-}L)_2$	$ZrCl_4(2,4\text{-}L)_2$	$ZrBr_4(2,4\text{-}L)_2$	$ZrI_4(2,4\text{-}L)_2$
	1390 w	1397 m	1392 m	1390 m	1388 w			
		1370 m	1380 sh	1381 sh	1382 w	1375 w	1378 vw	1370 w
			1341 w	1342 w	1343 w	1340 w	1347 vw	1340 w
						1310 s	1316 w	1308 m
							1312 sh	
1278 w	1272 w		1282 w	1284 w	1278 w	1275 sh	1279 w	1275 w
			1253 vw				1271 w	
1210 vs	1225 w				1224 vw	1240 sh		1226 vw
1171 s	1170 sh	1168 w	1170 s	1169 m	1164 s	1193 w	1191 w	
	1165 m		1146 s	1143 m	1140 s	1155 vw		
1108 w	1106 s	1107 w				1117 vw		1116 w
1100 sh								
1041 sh			1047 vw	1046 w	1045 w	1039 sh		
1028 s	1028 s	1025 m	1033 vw	1035 sh	1033 sh		1020 w	1025 m
1015 sh	997 w	996 w				1011 s	1010 m	1014 m
974 w	971 w			971 w		987 sh	987 vw	982 w
								966 w
						925 m	927 m	925 m
			866 s	865 m	863 s	895 m	891 m	885 w
								873 w
						817 vs	819 s	818 s
784 vs	773 vs	780 s	770 vs	765 m	760 vs	740 sh		755 vw
721 w	729 w	729 w	722 w	720 w	718 w	721 w	722 w	720 w
708 sh		720 w						
	685 sh	681 sh	697 s	695 m	695 s			
661 vw	672 w	675 sh			675 w	662 w		676 w
630 vw								
581 sh								
573 m	580 m	579 w						
564 sh	561 vw							
			545 vw	542 w	540 w	546 m	543 m	542 sh
			542 vw	538 sh	538 sh	542 sh		537 m
								520 vw
455 sh	448 vw	446 vw				458 m	459 m	
			426 vw					
	433 vwb					446 w	443 w	442 m
								428 vw
412 sh	411 vw	408 vw						
382 sh			355 sh	332 vw	320 wb	342 sh		
346 sb		340 vw	340 s			337 s		
		333 vw						
	321 m	319 vw						
		308 vw	309 vw			308 sh	311 vw	
295 sb	295 sh		292 w	289 sh	286 w	295 sh		290 sh
	286 sh		285 w			283 sh		283 w
	275 sh	271 w		268 sh			270 sh	
	259 vs			250 vs			260 sh	
							<250 vs	

mally stable and can be sublimed *in vacuo* unchanged; the chlorides and bromides at 320° and the iodide at 230°. The products are clear macroscopic crystals; the chloride and bromide are colorless while the iodide is orange at room temperature. In contrast, the 2,4-lutidine and 2,6-lutidine complexes decompose when heated *in vacuo* yielding tarry brown residues. The fact that the three 3,5-lutidine complexes sublime without significant decomposition is consistent with the proposed molecular structure or one which is easily decomposed and reformed. On the other hand, the insolubility of 2,4-L and 3,5-L products compared to the 2,6 adducts suggests a polymeric structure. We know on the basis of X-ray diffraction powder patterns that the 3,5-lutidine complexes appear to be isostructural; the same cannot be said for the 2,4 or 2,6 adducts. A single crystal X-ray study is clearly required before a more definitive statement about the structural details can be made.

The 1:1 adducts of 2,6-lutidine deserve special comment. To date no complexes of 2,6-lutidine with a coordination number greater than four have been prepared[17-19] with the possible exception of $Cu(NCO)_2 \cdot L$,[20] which may have tetragonal geometry in the solid state. However, the solubility of zirconium tetrachloride and zirconium tetrabromide in a benzene–2,6-lutidine mixture requires the formation of a soluble species with a coordination number greater than four unless some sort of dissociative process accompanies the solution process. A proton nmr of a deuterated benzene solution of $ZrCl_4 \cdot 2,6\text{-}L$ clearly shows the characteristic singlet for the two symmetrical methyl groups, the doublet of the hydrogens in the meta positions and the pair of doublets (which show as a triplet at 100 MHz) due to the hydrogen in the para position. These absorptions are somewhat broader than the corresponding absorptions for free lutidine and are shifted upfield with respect to the same absorptions for free lutidine. There is no evidence for the presence of free lutidine. If the soluble species is a chloride bridged cis dimer, the upfield shifts may be due to the interactions of the ring currents on two adjacent lutidines. The solid state infrared spectrum also shows the shift of the ring in-plane deformation expected upon coordination of the lutidine. There is no question that

---

[17] S. Buffagni, L. M. Vallarino, and J. Quagliano, *Inorg. Chem.*, 3, 480 (1964).

[18] I. S. Ahuja and P. Rastogi, *J. Chem. Soc. A*, 2161 (1970).

[19] D. J. Machin and J. F. Sullivan, *J. Chem. Soc. A*, 658 (1970).

[20] J. Kohout, M. Quasterova-Hvastijora, M. Kohutova, and J. Gazo, *Monatsh. Chem.*, 102, 350 (1971).

the solid state and soluble species contain coordinated lutidine. The infrared spectrum of the tetrachloride adduct also shows two strong absorptions assignable to Zr-Cl modes at 345 and 295 cm^{-1} on the basis of their absence in the spectra of the tetrabromide and iodide adducts. These bands are located in the frequency range where the metal-chlorine modes of zirconium tetrachloride are found[15] but are fewer in number than the tetrachloride bands. The similarity of the spectra suggests that the 2,6 adduct may be a somewhat more symmetrical derivative of the zirconium tetrachloride structure. Here also a six-coordinate bridged dimer in which the lutidines are coordinated such that the methyl groups are in stereochemically equivalent positions is a reasonable structure. There is no basis for extending these conclusions to the bromide and iodide systems at present.

One further observation should be added here to the effect that exposure of the infrared samples to oxygen and water of the air leads to the development of a strong band at 2400 cm^{-1}. This band is characteristic of the lutidinium ion and presumably arises from a reaction of the type

$$ZrX_4 \cdot 2L + H_2O \rightarrow ZrOHX_3 \cdot L + HL^+X^-$$

This band is clearly absent from all the spectra of the tetrahalide complexes and eliminates the possibility that any of the complexes contain a lutidinium ion rather than a lutidine ligand.

Trihalide Systems. The steric effects of the methyl groups are clearly seen in the reactions of benzene solutions of these ligands with zirconium trichloride. The 2,6-lutidine showed no sign of reacting with the trichloride; the two α-methyl groups apparently obstruct the interaction of the nitrogen atom even with the surface zirconium sites.

The 2,4- and 3,5-lutidines on the other hand clearly undergo two reactions simultaneously with the trichloride. One is the incorporation of the lutidine into the solid phase to yield an insoluble zirconium trichloride adduct. The other reaction is one which transfers some zirconium(III) into the solution phase as a green solution in the 3,5-lutidine case and a ruby red solution in the 2,4-lutidine case.

The change in composition of the solid phase is observed as a slow change of the insoluble green crystals to insoluble maroon and orange adducts of 3,5- and 2,4-lutidine, respectively. The change in composition is accompanied by a decrease in the intensity of the solution phase color as the benzene-lutidine solution is filtered and recycled through the vapor phase. The final solution in contact with the adduct shows no visible color. The composition of the solid phase with 3,5-lutidine shows the incorporation of 2 mol of 3,5-lutidine per mole of zirconium trichloride in the solid phase, while a maximum of 1.3 mol of 2,4-lutidine per mole of trichloride are taken up over a period of 30 days. While the X-ray diffraction patterns of the adducts compared with the pattern of zirconium trichloride itself make it clear that significant structural changes occurred upon adduct formation, we view the reaction as one in which the lutidine is inserted into the solid between chains of $ZrCl_6$ octahedra in a fashion not unlike the formation of intercalation compounds of transition metal chalcogenides.[21] The difference in the stoichiometry of the lutidine adducts reflects the ease of diffusion of the ligand and/or accessibility of the ligand nitrogen to the zirconium(III). Thus, the least sterically hindered lutidine (3,5-L) yields the 1:2 adduct, while the most sterically hindered lutidine (2,6-L) does not penetrate the zirconium(III) chloride structure at all. Whether CN 6 is maintained upon adduct formation by breaking metal-chlorine bonds or whether a higher coordination number species is formed is not clear. Evidence for at least partial preservation of the zirconium(III) structure comes from the spectral and the magnetic properties.

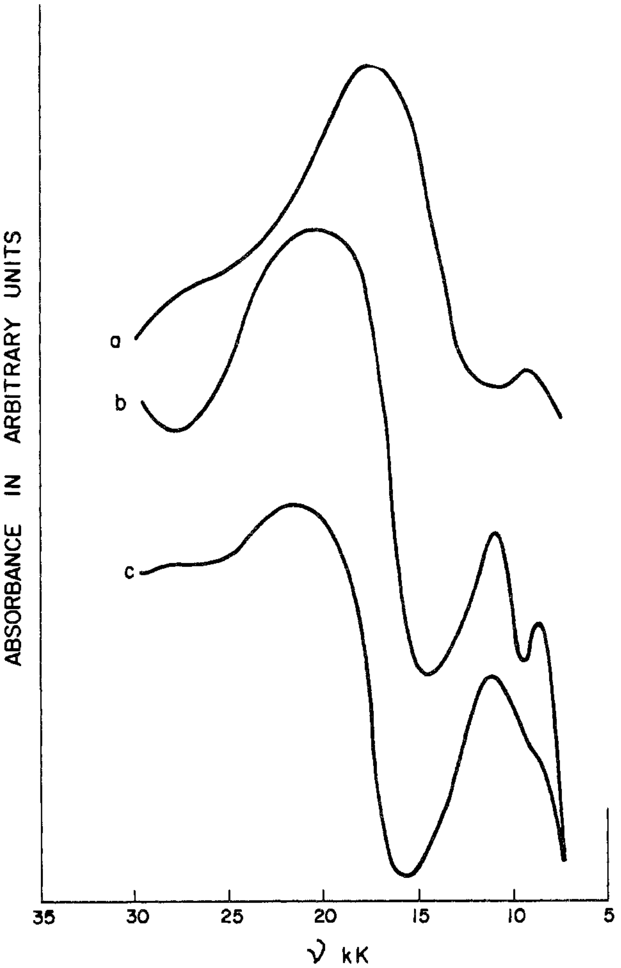


Figure 1. Reflectance spectra of (a) $ZrCl_3$ diluted with anhydrous magnesium sulfate, (b) $ZrCl_3(2,4\text{-}L)_{1.3}$, (c) $ZrCl_3(3,5\text{-}L)_2$.

The infrared spectrum of zirconium(III) trichloride shows a sharp strong single band at 333 cm^{-1}. In the 3,5-L adduct, this band appears at 340 cm^{-1} indicating that the metal-halogen bonds remain essentially equivalent, while in the 2,4-L adduct the shift is to lower frequency, 321 cm^{-1}, accompanied by the appearance of shoulders both above and below this value indicating the existence of a more complex structure. Reflectance spectra (Figure 1) were the only source of electronic spectra owing to the insolubility of the lutidine adducts. The spectra of the adducts can only be interpreted in light of the reflectance spectrum of powdered zirconium(III) chloride diluted with magnesium sulfate. This spectrum (a) is dominated by the strong broad absorption at 17.4 kK. The shoulder at 27.8 kK and the low-intensity absorption at 9.0 kK are intense absorptions in the spectrum of pure zirconium(III) chloride[22] which diminish in intensity upon reduction of particle size. From this we conclude that these transitions are related to surface and bulk structural features of the pure solid phase. Upon introduction of the lutidines into the zirconium(III) chloride structure, the intense absorption at 17.4 kK shifts to 20.4 and 21.1 kK for the 2,4- (b) and 3,5- (c) luti-

(21) F. R. Gamble, J. H. Osieck, and F. J. DiSalvo, *J. Chem. Phys.*, 55, 3525 (1971).

(22) E. M. Larsen, J. W. Moyer, F. Gil-Arnao, and M. J. Camp, *Inorg. Chem.*, 13, 574 (1974).

dine adducts, respectively. This is consistent with the introduction of a strong field ligand into the metal ion environment. The breadth of these absorptions makes it difficult to determine whether this should be attributed to a single transition. If the absorption spectrum of powdered zirconium trichloride can be interpreted in terms of the D_{3h} site symmetry of the metal ion,[23] then two transitions should be seen, A_{1g} to each of the two sets of two degenerate orbitals of E_g symmetry. The introduction of the lutidine ligand should lower the site symmetry, probably split degenerate levels, change the magnitudes of the energy separation between levels, and thus result in a more complex spectrum. Thus, the appearance of the moderately intense absorption at 11.1 kK could be rationalized although the difference in intensity of the 20 and 11.1 kK peaks, and their shifts with respect to the 17.4 peak in zirconium(III) chloride require further explanation. It is possible of course that the simple ligand field model is not applicable in light of the probable metal ion interaction occurring in the solid phase.

The magnetic behavior (Figure 2) of the lutidine adducts is similar to that of the zirconium trihalides investigated in detail by Camp.[24] The plot of susceptibility *vs.* temperature shows the same kind of broad maximum seen in the trihalides, although the magnitude of the susceptibility of the 2,4 adduct is an order of magnitude smaller than that of the 3,5 adduct. Although we have no quantitative explanation of the magnetic behavior, we can say that some features of the trihalide solid state structure must be retained upon adduct formation.

We have already noted that the nature of the products recovered from the solution phase of these syntheses requires a second reaction in addition to adduct formation. The green solution of the 3,5-lutidine system and the ruby red solution of the 2,4-lutidine system cannot simply reflect a ligand field effect in the light of the similarity of the reflectance spectra of the two adducts (unless the solution species were of considerably different compositions). The most convincing evidence for alternate reaction comes from the fact that the products recovered from solution, although black and paramagnetic, have X-ray powder patterns of the $ZrCl_4 \cdot 2L$ adducts; thus, an oxidation-reduction reaction must be occurring. This oxidation of the zirconium must occur either by disproportionation of the zirconium(III) in the presence of the lutidine or by a reaction in which zirconium(III) reduces the lutidine to a radical anion which then reacts further to give organic products. We have not separated or characterized any specific organic compounds, although their presence is consistent with the analytical data. These products are black and must contain some reduced state of zirconium as shown by their paramagnetism. However, the zirconium(IV) must be the major component of the mixture. The product recovered from the soluble fraction of the 3,5 system has an X-ray pattern which contains no extraneous lines although the X-ray powder pattern from the 2,4 system does contain some lines in addition to the zirconium(IV) adduct. A disproportionation reaction would require the zirconium(IV) and zirconium(II) to be present in equimolar quantitites. The X-ray powder patterns would suggest that this is not the case. It is possible that any zirconium(II) produced would be used up in a further reaction, but a direct reaction with zirconium(III) and lutidine in a fashion similar to that of alkali metals with pyridine derivatives[25] seems more reasonable. This oxidation-reduction reaction does not occur at room temperature in the solid state, although the adducts undergo irreversible decomposition of some sort at about 150°.

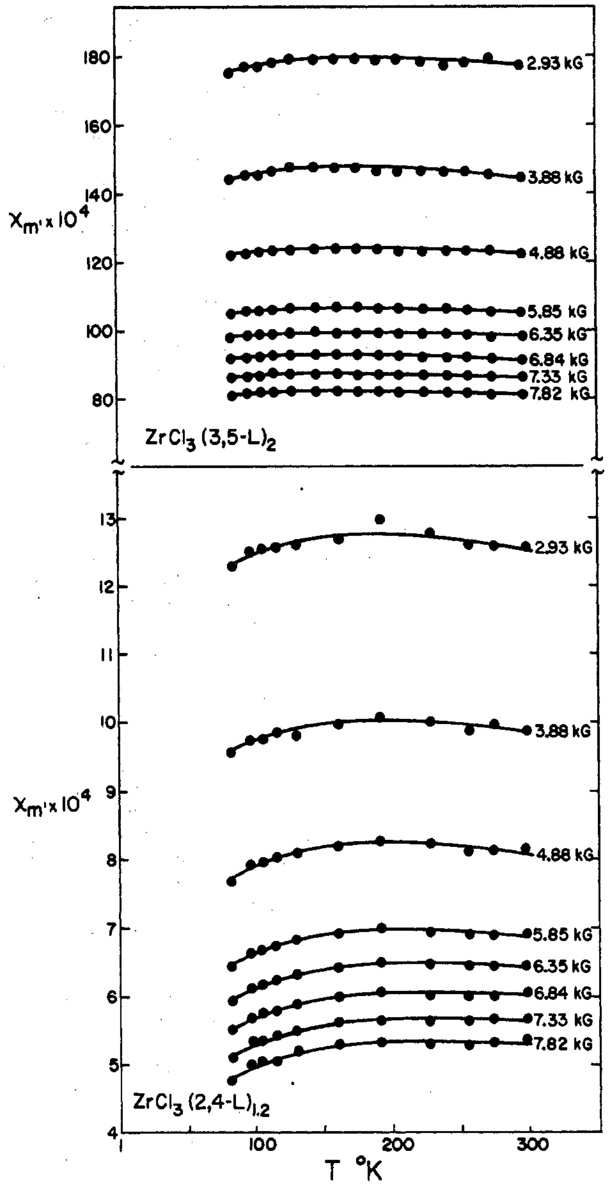


Figure 2. Magnetic susceptibility temperature and field dependence for the 2,4-L and 3,5-L adducts of zirconium(III) chloride.

The oxidation-reduction reaction is enhanced under conditions of excess lutidine. Therefore, syntheses carried out in ampules in which the product is recovered as the residue remaining after the solvent, and excess ligand are removed by vacuum distillation rather than filtration, are subject to contamination by products of the oxidation-reduction reaction. Fowles[3] acknowledged the possible presence of zirconium(IV) in his products but did not consider it a likely possibility. In the light of our observations this conclusion should be reviewed.

These observations also lead to the conclusion that the organic reducing agents used for the reduction of niobium(V) and molybdenum(V) will be incapable of reducing zirconium(IV) to zirconium(III) under similar conditions.

Experimental Section

Reagents. Zirconium tetrachloride was obtained from Titanium Alloys Division of National Lead Co. and Alfra Inorganics, Inc. Zirconium tetrabromide and tetraiodide was synthesized from the elements. All of the tetrahalides were purified by repeated sublimation[22]

---

(23) L. F. Dahl, T. I. Chiang, P. W. Seabaugh, and E. M. Larsen, *Inorg. Chem.*, 3, 1236 (1964).

(24) M. J. Camp and E. M. Larsen, *Inorg. Chem.*, in press.

(25) V. Kalyanaraman, C. N. R. Rao, and M. V. George, *J. Chem. Soc. B*, 2406 (1971).

under vacuum in sealed glass tubes. Zirconium trichloride was prepared in a sealed tube from purified zirconium tetrachloride and zirconium or aluminum metal using pure aluminum trichloride solvent as previously described.[22] 2,6-Lutidine, 2,4-lutidine, and 3,5-lutidine from Aldrich Chemical Co., were refluxed 12 to 24 hr over freshly dried barium oxide and distilled under dry nitrogen. The dry lutidine was degassed and either used immediately or stored at −10° under vacuum in sealed glass ampules fitted with break seals. The uncorrected distillation temperatures were 142-143° for 2,6-lutidine, 156-157° for 2,4-lutidine, and 168-170° for 3,5-lutidine. Benzene, Mallinckrodt analytical reagent grade, thiophene free, was stirred over sodium-potassium alloy, degassed, and vacuum distilled into the reaction vessel.

Analyses. Elemental analyses (Table I) were performed by Galbraith Laboratories, Knoxville, Tenn. Owing to water and oxygen sensitivity of the products, samples of each compound were submitted in three parts, each sealed in a glass ampule under vacuum; one sample for zirconium analysis, one sample for halide analysis, and one sample for carbon, hydrogen, and nitrogen analysis. This allowed the analyst to delay opening the ampule until just before the analysis was performed.

Characterization Techniques. The nmr spectrum of $ZrCl_4 \cdot 2,6\text{-L}$ in dry benzene-d_6 was obtained on a Varian XL-100 instrument, in a sealed 5-mm tube.

Infrared spectra of solids (Table II) were obtained as Fluorolube or Nujol mulls on sodium chloride and cesium iodide plates. Beckman IR-10 (4000-300 cm^{-1}) and Perkin-Elmer 457 (4000-250 cm^{-1}) spectrometers were used. Mulls were prepared in the drybox by grinding the compound and mulling agent in an agate mortar and pestle. The film of mulling agent and close contact of the plates gave adequate protection from the atmosphere; no change was observed in the spectrum after an hour. However, as a precaution the mulls in their holders were put in screw cap bottles and removed only seconds before the spectrum was recorded.

X-Ray powder patterns (Table III and Table IV; see paragraph at end of paper regarding supplementary material) were obtained in 0.3-mm Lindemann capillaries loaded in the drybox, temporarily protected with a plug of stopcock grease and sealed in a match flame outside the drybox. A 114.6-mm Debye-Scherrer camera and nickel filtered copper Kα radiation was used. The intensities were estimated visually and are relative to the strongest lines in each film.

The magnetic measurements were determined as described for the zirconium(III) halides[24] (Table V).

Melting point tubes were filled in the drybox. The end of the tube was plugged with stopcock grease, removed from the drybox, and sealed in a cool gas-oxygen flame. Melting points were determined using a Thomas Unimelt apparatus.

Syntheses. Manipulation of reactants and products was either done on the vacuum line (1 μ pressure) or carried out in a stainless steel drybox in an atmosphere of nitrogen maintained at or below 50 ppm oxygen and 10 ppm water. Materials with appreciable vapor pressure at 20° were not handled in the drybox; this includes all of the ligands and solvents used in this research.

The reactions between zirconium tetrahalides and the lutidines were carried out similarly for all combinations of tetrahalide and lutidine, with a few variations, by the reaction of the lutidine with a suspension of zirconium tetrahalide in benzene at room temperature. All reactions ran 3 days or more to ensure completion, although it is likely that the reactions were essentially complete in less than 1 day.

The reaction of zirconium tetrachloride with 3,5-lutidine is typical. The reaction vessel consists of a 30-mm tube 150 mm long sealed at one end. The other end is furnished with an axial 9 mm medium wall tube about 75 mm long terminating in a standard taper 14/35 male joint and a second tube 10 mm i.d. at about 30° to the first containing a break seal and terminating in a standard taper 14/35 female joint. The male joint is fitted with a stopcock adapter, evacuated, gently flamed, and taken into the inert atmosphere box along with any other necessary glassware which had been dried in a 110° oven and put in the entry port hot. Five millimoles (1.17 g) of zirconium tetrachloride was introduced into the reaction vessel through a long stemmed Pyrex funnel. The stopcock adapter was replaced, the reaction vessel removed from the drybox, attached to the vacuum line, and evacuated. Lutidine was vacuum distilled into a "U" trap, warmed, and measured in a short length of pipet attached to the bottom of the trap. The measured lutidine was distilled into the reaction vessel followed by 35 ml of dried, degassed benzene. The reaction vessel was sealed off with a torch, warmed to room temperature, and then shaken for 3 days or more.

To recover the product, the reaction vessel was fitted with a stopcock adapter and reattached to a vacuum manifold equipped with a pump-through trap as well as a 100-ml reservoir flask. The manifold was evacuated for 30 min and then closed off from the vacuum line and the break seal of the reaction vessel broken. An ice-water bath was placed around the 100-ml flask and most of the benzene distilled into the flask. The last 25-50% of the solvent was collected in the pump-through trap. When the solid product appeared dry, the stopcock was closed, and the reaction vessel was removed and reattached directly to the vacuum line and pumped on for more than 30 min before taking it into the inert atmosphere box. The reaction vessel was opened and the product removed and ground gently in a porcelain mortar. At this point all the samples necessary for characterization were taken and the remainder of the sample was loaded into storage ampules which were evacuated and sealed.

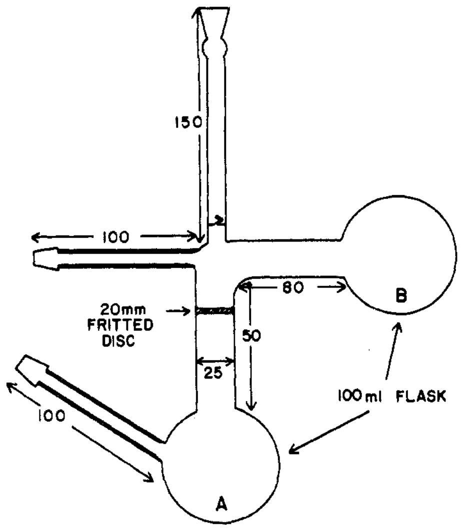


Figure 3. Filtering reaction vessel (all dimensions in millimeters).

Two useful modifications of the above procedure were used. The reaction tube may be designed as a linear two-section ampule, the first section of which contains a medium frit through which the tetrahalide is sublimed into the second section. The first section is then sealed off and removed and the reaction ampule handled as described. This additional procedure reduces hydrolytic and glass chip impurities to a minimum. A second modification is shown in Figure 3. In this case the tetrahalide is loaded into the bulb containing the fritted disk. The benzene and lutidine are distilled into the second bulb and frozen and both loading arms sealed. Some benzene is then transferred onto the metal tetrahalide to form a slurry. Then the remaining benzene-lutidine solution is poured through the filter onto the slurry. After the reaction is considered complete, the tube is tilted to filter after which some of the benzene is distilled back into the reaction ampule for washing purposes. In the case when the reaction product is soluble it can be isolated from the solution ampule by vacuum transfer of the solvent.

Purification of certain of the adducts by sublimation was carried out in a sealed glass ampule 7-12 mm in diameter and 7.5 to 15 cm long containing up to 1.0 g of product. The ampules were loaded in the drybox, evacuated, and sealed. During the sealing operation a small glass hook was fashioned on the end of the ampule so that it could be suspended from a wire in a tube furnace. The ampule was suspended almost completely within the furnace with its top at room temperature.

Zirconium Trichloride and Lutidines. The zirconium trihalide is loaded *via* a long stemmed funnel into reaction flask A (Figure 3). After removal from the inert atmosphere box and reattachment to the vacuum line, benzene and lutidine were distilled into the ampule as previously described. The loading arms were sealed off while the reaction mixture was frozen and then warmed to room temperature. The course of reaction differed with each lutidine as noted in the following paragraphs.

2,6-Lutidine (5.6 mmol) and zirconium trichloride (0.96 mmol) in 50 ml of benzene remained unchanged during the course of 4 days. There was no evidence for trichloride solubility and all the trichloride was recovered unchanged after filtration of the benzene-lutidine solution into flask B and removal by vacuum distillation.

3,5-Lutidine (4.7 mmol) and zirconium trichloride (0.76 mmol) in 75 ml of benzene gradually yielded a green solution which increased in intensity to the point it appeared to be opaque. At the same time the green crystals gradually were converted to maroon crystals with the same apparent form as the original trichloride crystals. The product was separated from the solution by filtration and then all of the liquid phase was transferred *via* the vapor phase back onto the maroon solid. This cycle of filtration and distillation was repeated ten times after which the supernatant liquid above the maroon crystals remained colorless. The filtered product was washed by distilling about one-third of the liquid (mostly benzene) back and filtering a final time. The benzene and excess ligand were removed by opening the break seal and pumping. The maroon product constituted 96% of the yield and the dark residue obtained from the soluble portion the remaining 4%. The maroon product analyzed for $ZrCl_3 \cdot 2(C_7H_9N)$. *Anal.* Calcd for $ZrCl_3 \cdot 2(C_7H_9N)$: Zr, 22.15; Cl, 25.82; C, 40.83; H, 4.40; N, 6.80. Found: Zr, 22.31; Cl, 25.80; C, 40.63; H, 4.51; N, 6.71.

2,4-Lutidine (4.86 mmol) and zirconium trichloride (1.62 mmol) in 50 ml of benzene very slowly yielded a faint red colored solution which deepened to a burgundy red. Decantation of the solution through the filter revealed that substantially all the zirconium trichloride remained. The benzene and 2,4-lutidine were distilled back onto the trichloride leaving a red-brown solid in flask B. The solution above the trihalide again became red although less intense. The recycling process was repeated six more times (7 days) by which time the solid in flask A was an orange powder and the solid recovered from the soluble portion of the reaction system was now a black powder. The yield of orange powder was 0.31 g (28% of the zirconium), and the yield of the black powder was 0.18 g. The orange product analyzed for $ZrCl_3 \cdot 1.2(C_7H_9N)$. *Anal.* Calcd for $ZrCl_3 \cdot 1.2(C_7H_9N)$: Zr, 27.97; Cl, 32.61; C, 30.93; H, 3.34; N, 5.15. Found: Zr, 29.86; Cl, 32.69; C, 31.39; H, 3.42; N, 5.03. In a second synthesis run over a period of 30 days the product analyzed for $ZrCl_3 \cdot {}^4/_3(C_7H_9N)$. *Anal.* Calcd for $ZrCl_3 \cdot {}^4/_3(C_7H_9N)$: Zr, 26.82; Cl, 31.27; C, 32.95; H, 3.56; N, 5.48. Found: Zr, 26.65; Cl, 30.90; C, 33.28; H, 3.69; N, 5.44.

Acknowledgment. This work was supported in part by National Science Foundation Grant No. GP-9300. We also acknowledge the contributions of R. Clemmer for the reflectance spectra, D. Hillenbrand for the nmr spectra, and J. Kleppinger for the magnetic measurements. This work was initiated in the laboratories of the Inorganic Institute of the Technical University of Vienna at the time the senior author was Fulbright Lecturer there. He is indebted to the Director, Professor Viktor Gutmann, for making the facilities of the laboratory available, and the American-Austrian Commission, for their financial support.

Supplementary Material Available. Tables III and IV, X-ray powder pattern data, and Table V, magnetic susceptibility data, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-581.

Registry No. $ZrCl_4 \cdot 2(3,5\text{-L})$, 43158-20-9; $ZrBr_4 \cdot 2(3,5\text{-L})$, 43158-21-0; $ZrI_4 \cdot 2(3,5\text{-L})$, 43158-22-1; $ZrCl_4 \cdot 2(2,4\text{-L})$, 43158-23-2; $ZrBr_4 \cdot 2(2,4\text{-L})$, 43158-24-3; $ZrI_4 \cdot 2(2,4\text{-L})$, 43158-25-4; $ZrCl_4 \cdot (2,6\text{-L})$, 43158-26-5; $ZrBr_4 \cdot (2,6\text{-L})$, 43209-03-6; $ZrI_4 \cdot (2,6\text{-L})$, 43158-27-6; $ZrCl_3 \cdot 2(3,5\text{-L})$, 43162-25-0; $ZrCl_3 \cdot x(2,4\text{-L})$, 43207-71-2.

Contribution from the Department of Chemistry,
Case Western Reserve University, Cleveland, Ohio 44106

Stereochemistry and Electronic Structure of Oxovanadium(IV) Chelates with Tetradentate Schiff Base Ligands Derived from 1,3-Diamines

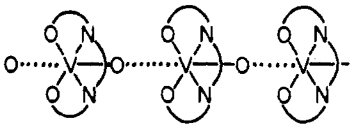
RICHARD L. FARMER and F. L. URBACH*

Received April 24, 1973

Oxovanadium(IV) chelates containing the tetradentate Schiff base ligands *N,N'*-bis(salicylidene)propane-1,3-diamine, *N,N'*-bis(7-methylsalicylidene)propane-1,3-diamine, *N,N'*-bis(3-isopropylsalicylidene)propane-1,3-diamine, and *N,N'*-bis(salicylidene)-(*S*)-(+)-butane-1,3-diamine have been prepared and their properties in the solid state and in donor and nondonor solvents have been characterized. These chelates have a polymeric structure (V–O–V bridging) in the solid state but dissociate to give monomeric five-coordinate species in nondonor solvents and monomeric six-coordinate species in donor solvents such as pyridine or dimethylformamide. The two lowest energy absorption bands are assigned to the $^2B_2 \rightarrow {}^2E(I)$ and $^2B_2 \rightarrow {}^2B_1$ (C_{4v} symmetry) transitions on the basis of solvent dependent spectral shifts in the electronic and infrared band maxima. The circular dichroism spectrum of [*N,N'*-bis(salicylidene)-(*S*)-(+)-butane-1,3-diamino]oxovanadium(IV) exhibits exciton components corresponding to the $\pi \rightarrow \pi^*$ transitions of the coupled azomethine chromophores. On the basis of the relative signs of the exciton components, the Schiff base ligand donor atoms are proposed to have a slight pseudotetrahedral distortion of Δ configuration about the V=O moiety.

Introduction

Oxovanadium(IV) chelates containing tetradentate Schiff base ligands derived from 1,2-diamines have been the subject of several recent reports.[1-5] These square-pyramidal complexes[6] exhibit a strong tendency to remain five-coordinate in both donor and nondonor solvents.[1,3-5,7] Expansion of the central chelate ring in the tetradentate complexes often leads to an increased ability for adduct formation.[8] For example, X-ray crystallographic data[9] have revealed that [*N,N'*-bis(salicylidene)propane-1,3-diamino]oxovanadium(IV), $VO(sal)_2tn$, exhibits a structure containing an infinite chain of square-pyramidal molecules connected by V--O--V bonds, 1.



1

---

[1] L. J. Boucher, E. C. Tynan, and T. F. Yen, *Inorg. Chem.*, 7, 731 (1968).

[2] L. J. Boucher and T. F. Yen, *Inorg. Chem.*, 7, 2665 (1968).

[3] L. J. Boucher and T. F. Yen, *Inorg. Chem.*, 8, 689 (1969).

[4] D. L. Daughdrill, D. F. Martin, and J. S. Binford, Jr., *J. Inorg. Nucl. Chem.*, 32, 2885 (1970).

[5] (a) R. L. Farmer and F. L. Urbach, *Inorg. Chem.*, 9, 2562 (1970); (b) R. L. Farmer and F. L. Urbach, *Chem. Commun.*, 1515 (1970).

[6] D. Bruins and D. L. Weaver, *Inorg. Chem.*, 9, 130 (1970).

[7] R. G. Garvey and R. O. Ragsdale, *Inorg. Chim. Acta*, 2, 191 (1968).

[8] S. Yamada, *Coord. Chem. Rev.*, 1, 415 (1966).

[9] M. Mathew, A. J. Carty, and G. J. Palenik, *J. Amer. Chem. Soc.*, 92, 3197 (1970).