was found at a position intermediate between the corresponding bands of the 4+ and 6+ complexes. An NH₃ "rocking" frequency (ρNH₃) of 800 cm⁻¹ was found for the 5+ complex; the corresponding frequencies for the 4+ and 6+ complexes were 750 and 840 cm⁻¹ respectively. Similarly, a stretching frequency (νRu–NH₃) attributed qualitatively to a metal–NH₃ stretching mode was found at 449 cm⁻¹ for the 5+ ion, while the corresponding frequencies for the 4+ and 6+ ions were 438 and 461 cm⁻¹, respectively. Taube et al.[6] also measured some ir bands of some simple salts of I; they noted that bands obtained for the 5+ complex were "rather intermediate" between those of 4+ and 6+ ions and found no evidence of superposition of 4+ and 6+ bands in the 5+ spectra.

The simplest conclusion from these results is that the ion I has a delocalized, symmetrical ground state. This agrees with the interpretation of the near-infrared "mixed-valence" band.

(iii) X-Ray Photoelectron Spectra. The XP spectra of the tosylate salts of I and of the corresponding 4+ and 6+ ions have been reported by Citrin.[13] Although the Ru 3d spectrum is partially obscured by the strong C 1s ionization, the XP spectrum of I is analyzed as showing two 3d₅/₂ bands separated by 2.7 eV, at positions roughly corresponding to those in the Ru(II)–Ru(II) and Ru(III)–Ru(III) complexes, respectively. This was interpreted[13] as providing direct evidence that the ion I contains two different Ru centers (i.e., Ru(II) and Ru(III)) in the ground state. It has generally been assumed that a mixed-valence complex would show only one XPS band at a position intermediate between those of the (II) and (III) ions if it possessed a delocalized ground state. However, it has recently been shown[9] that for a delocalized complex of the type of I, with $J \simeq 0.4$ eV, two 3d₅/₂ bands would be expected at energies very close to those of the (II) and (III) ions. The reason for this somewhat surprising result is that such complexes are highly polarizable, and the photoionized valence states are split owing to electron relaxation in the strong field of the core vacancy. We may conclude from this that the XPS measurements, at least at their present level of resolution, provide no evidence against the assignment of a delocalized ground state to I. Quantitative predictions have been made[9] of the rather small departures expected in frequency and intensity from localized behavior, and very accurate future XPS measurements may possibly further test the assignment.

Although the assignment of a delocalized ground state to the ion I runs counter to the generally accepted view, we believe that it is the one in best accord with the available physical measurements.[14] It should be mentioned finally that Mayoh and Day[15] have argued in favor of the opposite interpretation (trapped-valence ground state) by proposing a criterion for delocalization based on perturbation theory. This assumes that J should be less than $\chi/4$, in our terminology, for the lower potential surface to contain only one minimum. As pointed out elsewhere,[9] this criterion for the existence of a single minimum is incorrect (it should be $J < \chi/2$), but in any case the use of perturbation theory to obtain the ground-state electronic wave function is also incorrect when the electronic coupling is large. The interpretation of the wave function of mixed-valence complexes proposed by Mayoh and Day has no physical basis. Their further perturbation calculations[16] on the metal–ligand charge-transfer band of I, based on the assumption of a trapped-valence ground state, are not relevant to a delocalized complex.

Further details of the measurements and calculations reported above, and discussion of the factors influencing electron delocalization, will be published shortly.

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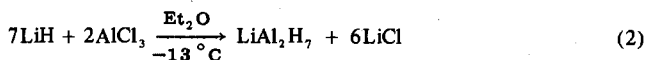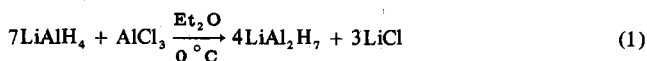University of Sydney   P. R. Taylor[1c]
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Further Investigations Concerning the Existence of Complexes of Lithium Aluminum Hydride and Aluminum Hydride in Diethyl Ether and in the Solid State

AIC50847Y

Sir:

Recently[1] we reported a study of the reaction of LiAlH₄ and AlH₃ in several mole ratios in diethyl ether and THF in an attempt to prepare the previously reported compounds LiAl₂H₇, LiAl₃H₁₀, and LiAl₄H₁₃. Contrary to previous reports no evidence was found to indicate the existence of any of the above compounds or any complex between LiAlH₄ and AlH₃. However, while the above report was in press, we found what could be interpreted as some evidence[7] possibly indicating the existence of LiAl₂H₇ when prepared according to eq 1 and 2. We have now studied the reaction of LiAlH₄ and LiH with

$$7\text{LiAlH}_4 + \text{AlCl}_3 \xrightarrow[\text{0 °C}]{\text{Et}_2\text{O}} 4\text{LiAl}_2\text{H}_7 + 3\text{LiCl} \qquad (1)$$

$$7\text{LiH} + 2\text{AlCl}_3 \xrightarrow[-13\,°\text{C}]{\text{Et}_2\text{O}} \text{LiAl}_2\text{H}_7 + 6\text{LiCl} \qquad (2)$$

AlCl₃ in detail as possible routes to LiAl₂H₇ as well as LiAl₃H₁₀ and LiAl₄H₁₃.

The reaction of LiAlH₄ and AlCl₃ in 7:1 molar ratio in diethyl ether at 0 °C (eq 1) yields a white precipitate of lithium chloride and a clear solution containing LiAlH₄ and AlH₃ in equimolar portions. The presence of LiAlH₄ and AlH₃ in solution is confirmed by the occurrence of characteristic strong bands at 1785 cm⁻¹ (Al–H stretching vibration in AlH₃) and 1760 cm⁻¹ (Al–H stretching vibration in LiAlH₄). The elemental analysis of the white solid isolated after complete removal of the ether solvent showed a Li:Al:H ratio of 0.571:1.00:3.33. Anal. Calcd for "LiAl₂H₇"·0.29Et₂O:[8] Li,

Table I. X-Ray Powder Diffraction Patterns of "$LiAl_2H_7$" and "$LiAl_4H_{13}$"

"$LiAl_2H_7$"[a]		"$LiAl_2H_7$"[b]		"$LiAl_2H_7$"[c]		"$LiAl_4H_{13}$"[d]		"$LiAl_4H_{13}$"[e]		$LiAlH_4$		AlH_3		"$LiAl_3H_{10}$"[f]	
d, Å	I/I₀	d, Å	I/I₀	d, Å	I/I₀	d, Å	I/I₀	d, Å	I/I₀	d, Å	I/I₀	d, Å	I/I₀	d, Å	I/I₀
		11.6	mw	11.6	mw							11.6	vs	11.5	s
11.4	m	5.15	m	6.70	vvw	11.6	s	11.6	s					6.8	vvw
5.31	w	4.45	ms	5.15	mw	5.33	w	6.6	vw	5.36	w			5.4	vvw
4.61	mw	3.85	s	4.45	ms	4.62	m	5.58	w	4.48	m	4.59	s	4.6	s
4.45	m	3.65	ms	3.85	s	4.44	w	4.6	ms	4.00	vw				
3.85	s	3.32	s	3.65	ms	3.85	s	3.85	s	3.89	s			3.85	s
3.67	m	3.25	s	3.32	s	3.66	w	3.65	m	3.68	m			3.65	m
3.41	m	2.98	m	3.25	s	3.45	w	3.50	ms	3.53	vw			3.52	m
3.31	m	2.92	m	2.98	ms	3.33	m	3.24	s	3.43	w				
3.22	mw	2.67	m	2.92	m	3.24	s	2.85	w	3.32	m				
3.00	w	2.57	w	2.67	m	3.01	w	2.78	w	3.24	m	3.24	m	3.25	s
2.92	w	2.45	mw	2.58	w	2.95	w	2.65	vvw	3.03	m				
2.85	mw	2.325	mw	2.45	mw	2.85	m	2.55	vvw	3.00	w				
2.67	w	2.18	m	2.30	w	2.65	w	2.30	w	2.95	m			2.96	s
2.45	w	2.10	w	2.18	w	2.45	vw	2.12	vvw			2.89	ms		
2.16	w	2.05	mw	2.10	w	2.39	vw	1.96	vw	2.68	m			2.65	w
2.01	w	1.970	vvw	2.08	mw	2.12	vw			2.54	vw			2.56	w
1.78	w	1.78	vw	1.97	vvw					2.45	w				
		1.62	w	1.78	vw					2.42	m			2.35	vvw
		1.52	w	1.64	w					2.24	w				
		1.48	vvw							2.15	w			2.15	w
										2.05	w			2.08	w
										2.01	vw			2.025	w
										1.98	w				
										1.92	vw				
										1.89	vw				
										1.80	vw				
										1.78	w				
										1.76	w				
										1.74	w				

[a] Solid from $LiAlH_4$ + AlH_3 in 1:1 molar ratio. [b] Solid from $LiAlH_4$ + $AlCl_3$ in 7:1 molar ratio. [c] Solid from LiH + $AlCl_3$ in 7:2 molar ratio. [d] Solid from $LiAlH_4$ + AlH_3 in 1:3 molar ratio. [e] Solid from $LiAlH_4$ + $AlCl_3$ in 13:3 molar ratio. [f] Solid from $LiAlH_4$ + $AlCl_3$ in 5:1 molar ratio.

7.75; Al, 60.32; H, 7.88. Found: Li, 7.90; Al, 60.32; H, 7.42. The x-ray powder diffraction pattern for "$LiAl_2H_7$" is shown in Table I. It is readily seen that the so-called complex corresponds to a mixture of $LiAlH_4$ and AlH_3. However, the weak line at 11.6 Å is not as well defined as in the physical mixture of $LiAlH_4$ and AlH_3 (1:1 molar ratio). The dta–tga of "$LiAl_2H_7$" under static argon atmosphere is shown in Figure 1. The thermogram shows gas evolution at 95 and 170 °C with simultaneous weight losses of 11.0 mg (13.2%) and 3.7 mg (4.4%), respectively. The first gas evolution corresponds to a large weight loss and is undoubtedly due to loss of both solvent and decomposition of AlH_3. The second gas evolution is probably due to decomposition of $LiAlH_4$. It is important to note that the thermogram (Figure 1) is quite similar to the thermogram of the solid obtained after mixing ether solutions of AlH_3 and $LiAlH_4$ in 1:1 molar ratio followed by removal of solvent under vacuum. We have already reported[1] that the solid obtained by this method is indeed a physical mixture of $LiAlH_4$ and AlH_3 and not the complex "$LiAl_2H_7$". We have also shown that the thermogram (Figure 1) is almost identical with the thermogram obtained for a physical mixture of solid $LiAlH_4$ and solid AlH_3 mixed in 1:1 ratio. Thus, the reaction of $LiAlH_4$ and $AlCl_3$ in 7:1 molar ratio in diethyl ether yields a mixture of $LiAlH_4$ and AlH_3.

The reaction of LiH and $AlCl_3$ in 7:2 molar ratio in diethyl ether at 0 °C also yields a mixture of $LiAlH_4$ and AlH_3 in solution as determined by infrared spectroscopy. The x-ray powder diffraction data (Table I) of the solid obtained after complete removal of solvent show it to be a physical mixture of $LiAlH_4$ and AlH_3. The dta–tga of the solid is similar to the thermogram (Figure 1) of the solid obtained by the reaction of $LiAlH_4$ and $AlCl_3$ in 7:1 molar ratio. Thus, both methods yield the same compound.

Although we have already reported on the work of Bousquet and co-workers in our previous paper, we decided to attempt
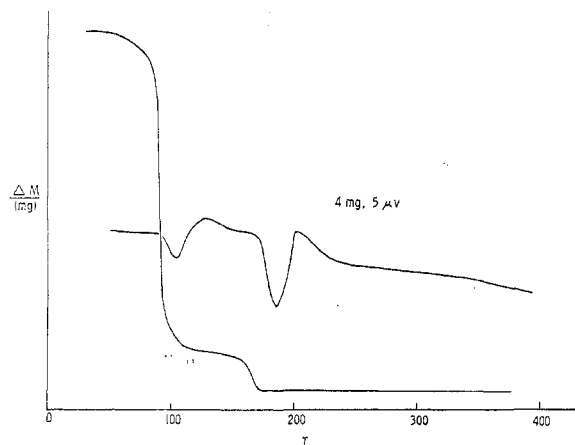
Figure 1. Dta–tga of "$LiAl_2H_7$" ($7LiAlH_4$ + $AlCl_3$ → $3LiCl$ + $4LiAl_2H_7$) under static argon atmosphere.

to prepare $LiAl_4H_{13}$ by the reaction of $LiAlH_4$ and $AlCl_3$ in 13:3 mole ratio in an attempt to determine if $AlCl_3$ plays any role in the formation of the so-called complexes of $LiAlH_4$ and AlH_3. The reaction of $LiAlH_4$ and $AlCl_3$ in 13:3 molar ratio in diethyl ether at 0 °C yields a mixture of $LiAlH_4$ and AlH_3 in solution confirmed by infrared spectroscopy. The elemental analysis of the white solid obtained after complete removal of solvent corresponds to an empirical formula $LiAl_4H_{13}$·$0.96Et_2O$.[8] The x-ray powder diffraction data are given in Table I. The dta–tga of the solid is similar to that shown in Figure 1. The x-ray powder diffraction data as well as dta–tga of the solid show it to be a physical mixture of $LiAlH_4$ and AlH_3 rather than a complex.

Similarly, in an attempt to prepare $LiAl_3H_{10}$ by the reaction of $LiAlH_4$ and $AlCl_3$ in 5:1 molar ratio in diethyl ether at 0 °C, no evidence was found to indicate the presence of $LiAl_3H_{10}$

complex. The infrared spectrum of the clear solution obtained after the complete reaction of $LiAlH_4$ and $AlCl_3$ showed the presence of $LiAlH_4$ and AlH_3 in solution. Elemental analysis of the white solid obtained after complete removal of the solvent corresponds to an empirical formula $LiAl_3H_{10}$· $0.81Et_2O$.[8] The x-ray powder diffraction data (Table I) as well as the dta–tga of the solid under static argon atmosphere (Figure 1) indicate that actually it is a physical mixture of $LiAlH_4$ and AlH_3 and not a complex.

In conclusion, we have repeated the work of previous workers[2-6] in exactly the same manner described in the literature. However, we do not find convincing evidence to indicate the existence of $LiAl_2H_7$, $LiAl_3H_{10}$, and $LiAl_4H_{13}$. The difference in x-ray powder diffraction data and dta–tga of the so-called "$LiAlH_4$–AlH_3" complexes reported by previous workers may be due to the isolation of solids with different degrees of solvation than the $LiAlH_4$ and AlH_3 to which they were compared. In addition we now know that ether cleavage of AlH_3·OEt_2 occurs during the dta–tga heating process resulting in the formation of hydridoaluminum alkoxides. These alkoxides decompose at temperatures different from those of $LiAlH_4$ and AlH_3, possibly giving misleading information that complexes are present.

Our work is not to be interpreted to mean that complexes of $LiAlH_4$ and AlH_3 do not exist or that they have not been prepared by previous workers in this area. Our report is only that *we* have not been able to find evidence of such complexes after considerable effort to do so.

Registry No. $LiAlH_4$, 16853-85-3; AlH_3, 7784-21-6; LiH, 7580-67-8; $AlCl_3$, 7446-70-0; $LiAl_2H_7$, 12258-28-5; $LiAl_3H_{10}$, 23065-75-0; $LiAl_4H_{13}$, 12330-41-5.

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Formation Constant of $Pd(CN)_4^{2-}$

AIC505747

Sir:

Two potentiometric studies of $Pd(CN)_4^{2-}$ using palladium metal electrodes are reported in the literature,[1,2] which give log β_4 for this complex as 51.6[1] and 42.4.[2] In addition, log K_5 has been reported as 2.9,[2] and a value of $\Delta H_{\beta_4} = -92.3$ kcal mol^{-1} was determined[2] calorimetrically. Apart from the disparity between them, these log β_4 values seem rather low. For example, combining the reported enthalpy change on complex formation with the two formation constants gives entropies of −74[1] and −116 gibbs mol^{-1},[2] which is very much

more unfavorable than could be expected from the entropy change on complex formation of other similar cyanide complexes, e.g., $Hg(CN)_4^{2-}$ with $\Delta S_{\beta_4} = -34$ gibbs mol^{-1} and $Ni(CN)_4^{2-}$ with $\Delta S_{\beta_4} = -7$ gibbs mol^{-1}.

In order to resolve the above disparity, we decided to carry out a potentiometric study using a palladium metal electrode. As discussed below, the potentials measured were meaningless in relation to the formation constant of $Pd(CN)_4^{2-}$. An indication that log β_4 was very large, larger than 60, was, however, obtained. All techniques for measuring stability constants involve a competition reaction of some kind. A stability constant such as that for $Pd(CN)_4^{2-}$ presents a rather unusual problem, since the complex is not easily broken down. Thus, a glass-electrode study could not be used, since, with log β_4 greater than 60, the proton will not be able to remove cyanide from the complex to any great extent. However, if the equilibrium is studied in the presence of a second ligand, such as chloride, the cyanide ion is competing with chloride rather than with water for coordination to the palladium(II) ion. Since chloride has very little affinity for the proton, the presence of the chloride ion will enable the proton to compete with the palladium(II) ion more effectively for the available cyanide. In this type of competition reaction one measures the reaction constant for

$$PdCl_4{}^{2-} + 4HCN \rightleftharpoons Pd(CN)_4{}^{2-} + 4H^+ + 4Cl^-$$
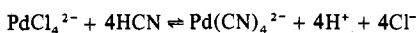
This reaction constant is then combined with the formation constant of $PdCl_4^{2-}$, which we have measured to be 11.0 using a palladium metal electrode, to give the formation constant of $Pd(CN)_4^{2-}$. We decided to use uv spectroscopy to monitor the equilibrium concentrations of $PdCl_4^{2-}$ and $Pd(CN)_4^{2-}$ as functions of pH and HCN and Cl$^-$ concentrations and thereby to calculate the formation constant of $Pd(CN)_4^{2-}$.

Experimental Work. All reagents used were of reagent grade. The concentration of palladium in the solutions was checked analytically. The cell and accompanying equipment for making the potentiometric study are described elsewhere.[3] Uv spectra were recorded using a Beckmann Acta CIII recording spectrophotometer. Kinetic runs were carried out at 25 °C.

Results and Discussion. **(a) Potentiometry.** Potentials, which were not very reproducible, were obtained with different CN$^-$ to $Pd(CN)_4^{2-}$ ratios. The potentials were sensitive to stirring speed, indicating that they were not equilibrium potentials but were mixed potentials resulting from some reaction taking place at the electrode. The uv spectra of the solutions indicated a slow increase of $Pd(CN)_4^{2-}$ concentration with time, showing that the reaction was the dissolution of palladium by cyanide. Tests using an oxygen electrode showed that the initial concentration of oxygen was less than 0.01 ppm, which could not account for the quantity of palladium dissolved. It therefore seemed likely that the dissolution of palladium was taking place with hydrogen evolution

$$Pd(s) + 2H^+ + 4CN^- \rightarrow Pd(CN)_4{}^{2-} + H_2(g)$$
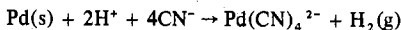
This reaction should be sensitive to pH, so that, in order to minimize its contribution, the pH was taken up from 9, the natural pH of the solutions, to 12. Even here sensitivity to stirring speed was observed, although a much slower dissolution rate was found. With prolonged exposure to these solutions, the palladium wire became pH sensitive, indicating that it had absorbed sufficient hydrogen to act as a hydrogen electrode. Therefore, it would seem that the potentials observed by previous workers[1,2] were also not equilibrium potentials and that the stability constants reported by them are in error. The fact that the evolution of hydrogen took place in the solutions which we studied puts a lower limit on log β_4 for $Pd(CN)_4^{2-}$