

band is considerably decreased in intensity. In the case of the second group the contribution of the C=S stretching and the NH₂ rocking motions to the 970 cm.⁻¹ band will be decreased, since this contribution is greater for the 1490 cm.⁻¹ band as is seen from the increased intensity of this band. Therefore, the intensity of the band at 970 cm.⁻¹ will also be decreased on complexing as in the case of the first group.

The band at 774 cm.⁻¹ of methylthiourea is considered to correspond to the band at 731 cm.⁻¹ of thiourea which arises from the motion consisting of C=S stretching and symmetric C-N stretching. This frequency corresponds to those of the bands observed in the spectra of the complexes in this region.

Finally the band observed at 718 cm.⁻¹ for methylthiourea may be explained as the out-of-plane NH₂ bending vibration. This band is shifted on deuteration, and no corresponding band was observed for symmetric dimethylthiourea. Bands of almost the same frequency are observed in the spectra of the complexes.

As explained above, the spectra of the metal complexes measured in this experiment can be divided into two groups. There is no doubt that the coördination of the first group takes place through sulfur. However, for the second group the spectral evidence for the coördination through nitrogen is not so conclusive as in the case of the urea complexes. This is due to the fact that the C=O stretching frequency in urea or methylurea lies well above the C-N stretching frequency, whereas the C=S frequency is not much different from the C-N frequency.

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The Effect of Coördination on Electron Withdrawal

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The electron withdrawing power of a group III metal is found to decrease when it is coördinated with diethyl ether. It is also confirmed that gallium has a greater electronegativity than aluminum.

Introduction

In trying to relate chemical shifts in proton magnetic resonance spectra, with the nature of the substituent attached to the proton, a relationship was developed between the separation of methyl and methylene protons of an ethyl group and the electron withdrawal power of the substituent attached to the ethyl group.¹ For the halogens this relationship could be expressed by: electronegativity = 0.695(ΔCH₃ - ΔCH₂) + 1.71. By changing the constant to 2.1 good agreement was found with the metal alkyls and hydrogen itself.² Since there is a large magnetic anisotropy associated with the unshared pairs of electrons of the halogens, this will affect the shielding of protons adjacent to them. Therefore a different constant term is required when this additional shielding is absent. This equation predicts a reversal in the positions of the resonance lines due to the methyl group and the methylene group for a substituent of low electronegativity, and this has been shown for AlCl(C₂H₅)₂.³ A similar type of equation, based on rather limited data, has been developed to relate spin coupling between the protons with the electronegativity of the substituent.⁴

It was thought that since electron withdrawal tendencies can be obtained for individual elements in their ethyl compounds by this method, it would also be useful in studying the change in electron withdrawal upon coördination of an element.

Experimental

The proton resonance spectra were obtained at 40 Mc. in a manner described previously.⁵ Triethylgallium, originally prepared in this Laboratory⁶ and stored in a sealed ampoule, was distilled before use. Triethylgallium etherate was prepared from triethylgallium and diethyl ether and excess ether was removed by pumping at -40°. Triethylaluminum was obtained from U. S. Industrial Chemicals Co., and the etherate was prepared in the same way as the gallium compound. Conventional vacuum techniques were employed throughout. Triethylxonium fluoroborate was kindly supplied by A. M. Eastham of the National Research Council. Solutions in spectroscopic grade methylene chloride and acetonitrile were prepared in an inert atmosphere.

Results

The proton magnetic resonance spectra obtained from a series of compounds are shown in Table I.

In all cases except gallium triethyl and aluminum triethyl J/δ was small enough so that the values of J and δ were obtained by direct measurement of the separation of the lines in a multiplet and between the centers of the two multiplets, respectively. This approximation might cause a slight error for the ethyl groups attached to gallium in gallium triethyl etherate. However, a more refined method of calculation could not be

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TABLE I

Compound	J , cycles/ sec.	δ' , p.p.m. ^a	J/δ at 40 Mc. ^b	E
$O(CH_2CH_3)_2$	7.1	+2.50	0.071	3.8
$(CH_3CH_2)_3Al$	7.9	-0.71	.276	1.6
$(CH_3CH_2)_3Al-$	6.0	-1.02	.143	1.4
$-O(CH_2CH_3)_2$	5.8	+2.25	.065	3.7
$(CH_3CH_2)_3Ga$	7.9	-0.50	.391	1.75
$(CH_3CH_2)_3Ga-$	5.4	-0.58	.234	1.7
$-O(CH_2CH_3)_2$	5.0	+2.12	.059	3.6
$(CH_3CH_2)_3O^+BF_4^-$	4.7	+3.12	.038	4.3

^a A positive δ' means that the signal appears at higher field, that is, the protons are more shielded. ^b δ is expressed in cycles per second since J is field independent and is normally expressed in cycles per second. Thus J/δ becomes dimensionless.

used here because of the almost complete overlap of the methyl resonances from the ethyl groups attached to gallium and to oxygen. The true value of the chemical shift could only be greater, and not less, than that reported. Such a difference would not affect the arguments to be presented.

The data for aluminum triethyl were obtained at 60 Mc. where J/δ is 0.185 and then converted to results at 40 Mc.⁷

J and δ for gallium triethyl were calculated by the moment method.⁸ The proton resonance spectrum of gallium triethyl is shown in Fig. 1 and

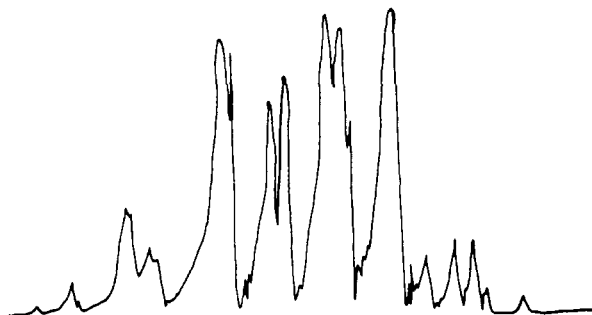


Fig. 1.—Proton resonance spectrum of gallium triethyl.

the relative positions and intensities of the lines listed in Table II. The moment method yields the chemical shift with greater accuracy than the spin coupling constant since only second moments are required in calculating chemical shift but fourth

TABLE II

PROTON RESONANCE SPECTRUM OF GALLIUM TRIETHYL			
Line	Intensity	Line	Intensity
0.0	1.5	33.4	163
4.1	6.0	34.7	72
5.0	1.5	35.4	16
10.4	48	40.5	178
13.2	15	44.4	12
14.0	8.0	47.5	19
21.2	150	49.6	17
22.2	38	51.1	4.0
26.8	72	55.5	3.0
28.5	68		

(7) This spectrum was kindly supplied by Varian Associates.

(8) W. Anderson and H. M. McConnell, *J. Chem. Phys.*, **26**, 1496 (1957).

moments are required in calculating spin coupling. However the large number of adequately separated lines in the spectrum of gallium triethyl makes it likely that the calculations are quite reliable.

A good example of the reversal in order of appearance of the resonance absorption of the ethyl protons is triethyl aluminum etherate, Fig. 2.

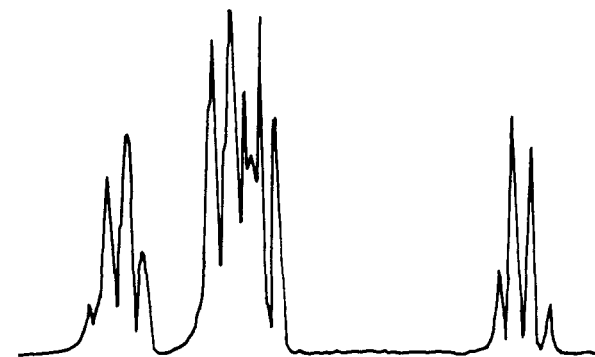


Fig. 2.—Proton resonance spectrum of aluminum triethyl etherate.

Here two completely separate ethyl groups are apparent, with their arrangements opposite to each other. One can assign the triplet on the left to the ethyl groups on the aluminum since its intensity is somewhat greater. This should be the case since it arises from three ethyl groups rather than two. When there is interaction between the chemical shift and spin coupling of two groups of protons those peaks of one group which are closest to those of the other group are enhanced in intensity and *vice versa*. Similarly the peaks which are furthest away have their intensity decreased. These changes in intensity are clearly apparent in each spin-spin multiplet in Fig. 2 and further confirm the assignment of the peaks.

Discussion

It is confirmed that the electronegativity of gallium is greater than that of aluminum. This is contrary to the usual situation where electronegativity decreases down the periodic table but has been shown to be the case for some group III and group IV elements.^{9,10}

The electron withdrawal power of aluminum and gallium are seen to decrease on coordination with ether, since their apparent electronegativities decrease. This is to be expected since donation of electrons from the oxygen would increase the electron density about the metal and therefore decrease its tendency to share the electrons of the carbon-metal bond. Contrary to expectation the apparent electronegativity of the oxygen also decreases upon coordination. Since the number of unshared pairs of electrons is reduced from two to one upon coordination, this can introduce a significant change in the magnetic anisotropy and therefore the shielding of the methylene group. This effect could easily overshadow the change in shielding due to a change in electron withdrawing power. This is shown to be the case since the apparent

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electronegativity of the oxygen in triethyloxonium fluoroborate is much larger than in the etherate, as would be expected.

A more subtle indication that this method applies to triply attached oxygen, as well as doubly attached, comes from the difference in apparent electronegativity of the oxygen in aluminum and gallium triethyl etherates. Since the aluminum is less electronegative, it would coordinate more strongly with the oxygen of the ether which would in turn have a higher apparent electronegativity than in triethylgallium etherate. It is indeed found that the apparent electronegativity of the oxygen in triethylaluminum etherate is greater.

No agreement was found between the spin cou-

pling of the methyl and methylene protons and the electronegativity of the substituent attached to the ethyl group. This makes the validity of the equation relating them rather doubtful.⁴

Conclusion

Proton magnetic resonance spectra show that the electron withdrawing power of an element is reduced when it coordinates with an electron donor. It is also confirmed that the electronegativity of gallium is greater than that of aluminum.

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ITHACA, NEW YORK

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Interaction of Tetraisopropyl Titanate and Monoethylamine in *n*-Decane Solution

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The interaction of tetraisopropyl titanate (TPT) and monoethylamine has been studied at 25 and 35° in *n*-decane solution and has been found to be weaker than previously-reported interactions between amines and titanium chlorides.

Stable donor-acceptor bonds can be formed between basic nitrogen compounds and titanium(IV) and titanium(III) chlorides. Antler and Laubengayer¹ have shown that trimethylamine reacts with TiCl₄ and TiCl₃ to form the addition compounds TiCl₄·(Me)₃N and TiCl₃·2(Me)₃N. These compounds, in which the titanium shows an apparent coordination number of five, are crystalline solids which can be sublimed *in vacuo* without decomposition. Emel us and Rao² have recently reported the six-coordinated addition compounds TiCl₄·2Py, TiCl₄·2CH₃CN and TiCl₄·2(C₆H₅)CN. The enthalpy of formation of the solid TiCl₄·2Py complex from TiCl₄ and pyridine was reported to be -28 kcal./mole.

Molecular association, presumably resulting from formation of Ti-O(R)·Ti coordinate oxygen bridges, has been observed for the *n*-alkyl titanates up to *n*-hexyl³⁻⁵. With the *sec*-alkyl and *t*-alkyl titanates, on the other hand, molecular association is blocked by the steric effects of the groups adjacent to the bridging oxygens, and these titanium esters have been found to be essentially monomeric.^{6,7}

Little has been published about the existence or stability of complexes between nitrogen com-

pounds and titanium alkoxides. Schmitz-DuMont⁸ has reported that the compound K₂[Ti(OMe)₄(NH₂)₂] is obtained by reaction of tetramethyl titanate with potassium amide. Reaction between tetraisopropyl titanate (TPT) and monoethylamine to yield a solid 1:1 addition compound has been observed by Gulledge,⁹ who crystallized the compound TPT·EtNH₂ at room temperatures from concentrated mixtures of the titanium ester and excess amine in cyclohexane. A preliminary X-ray study by Gulledge of the TPT·EtNH₂ crystals indicated a hexagonal structure with four molecules in a unit cell of dimension *a*₀ = 10.41 Å., *c*₀ = 22.25 Å. At room temperature in the absence of excess monoethylamine TPT·EtNH₂ underwent slow dissociation with evolution of the volatile amine.

Experimental

Materials.—Tetraisopropyl titanate was distilled at reduced pressure through a 16" Vigreux column. The center cut (b.p. 79.0° at 2.50 mm.) was stored in the dark under nitrogen.

Monoethylamine was fractionated in a 1 × 30" vacuum jacketed column packed with 3/16" Fenske helices and was subsequently sealed under vacuum in Pyrex ampoules one end of which had been drawn out to form a capillary break-off tip. As a test of purity, four ampoules chosen at random were broken under standard HCl and the neutralization equivalent was measured. The observed neutralization equivalent was 45.05 ± 0.4; calcd. for EtNH₂, 45.08.

n-Decane was dried by refluxing over sodium metal and fractionated through the previously-described one inch diameter column. The distillate boiling between 174.2-174.6° at 767 mm. was retained and stored under nitrogen. Samples were periodically analyzed for water by the Karl Fischer procedure. Found: 0-0.05 g. H₂O/l.

Benzene (reagent grade) was dried over sodium and used without further purification.

Cryoscopic Measurements.—Measurements of the freezing point depression of benzene by TPT were made under a

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