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ELECTRON PROTON RESONANCE OF TRANSITION METAL COMPLEXES
VII*. EPR-APPROACH TO LEWIS ACIDITY OF GROUP III HALIDES

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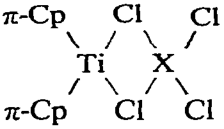
SUMMARY

Complexes of di-π-cyclopentadienyltitanium chloride (Cp_2TiCl) with the trichlorides of Group III elements, having the bridged structure



X = B, Al, Ga, In

show EPR hyperfine interaction of the unpaired electron of the Ti^{III} with the magnetic nuclei of the Group III elements. The hyperfine pattern of ^{115}In ($I = 9/2$) is reported for the first time.

From the isotropic coupling with ^{11}B, ^{27}Al, ^{69}Ga, ^{71}Ga, ^{115}In, the unpaired spin density in the relevant *s*-orbitals of the Group III elements is estimated. The following series is deduced for the Lewis acidity (electron acceptor ability) of the halides: $GaCl_3 > BCl_3 > AlCl_3 > InCl_3$. The results are considered in the light of published information, and chemical evidence is advanced for the strong acid character of $GaCl_3$.

The hyperfine interaction of unpaired electrons with magnetic nuclei allows, with certain assumptions, an estimate of the density of the unpaired spin in the orbitals of the atoms involved (see *e.g.* ref. 1).

In EPR experiments carried out in solution only the Fermi contact interaction has to be taken into account, *i.e.* only the spin density in *s*-orbitals of atoms with magnetic nuclei has to be considered.

If a complex molecule, containing a paramagnetic ion and an atom X with a magnetic nucleus, produces in solution an EPR signal showing hyperfine interaction, the unpaired electron of the paramagnetic ion may be described as occupying a molecular orbital of the form

$$\psi = c_{s,X} \cdot \varphi_{s,X} + \Sigma\, c_i \cdot \varphi_i \qquad (1)$$

where $\varphi_{s,X}$ is the *ns*-orbital of X, and the φ_i are the other orbitals of which the MO is made up, including also the metal orbital containing the unpaired electron in the

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[*] For Part VI see ref. 4.

free ionic species. The square of the coefficients of the orbital $\varphi_{s,X}$ (*i.e.* the density of the unpaired spin at the nucleus X) can be determined as[1]:

$$c_{s,X}^2 = a(X)/A(X) \tag{2}$$

where $a(X)$ is the experimental hyperfine splitting, and $A(X)$ is the isotropic splitting which would be observed if the unpaired electron were entirely localised in the relevant *s*-orbital of the atom considered ("isotropic coupling constant for the free atom X"). Free atom values $A(X)$ are generally not known from experiment, but they may be calculated with moderate accuracy from self-consistent field wave functions, and are tabulated for numerous atoms[1,2].

As has been pointed out by Symons[1], eqn. 2 presupposes several assumptions which, however, may be discarded if trends of population of the *s*-orbitals along a series of *similar species* are to be considered.

The elements of Group III of the Periodic Table possess magnetic nuclei; their halides are strong electron acceptors which easily form stable complexes with suitable donors. If the same paramagnetic donor molecule is reacted with the series of the trichlorides BCl_3, $AlCl_3$, $GaCl_3$, $InCl_3$, one may expect complexes of similar structure. The EPR spectra of these complexes will then allow us to estimate and compare the unpaired spin density at the magnetic nuclei of the respective halides.

Di-π-cyclopentadienyltitanium chloride (Cp_2TiCl) is a suitable donor molecule; its complexes with the halides under consideration show well resolved EPR signals in toluene. The spectra of the complexes with BCl_3, $AlCl_3$ and $GaCl_3$ have already been reported[3,4]. The measurements have now been extended to the Ti^{III}–In complex. (For experimental details see ref. 3.)

The EPR spectrum of the Ti^{III}–In complex in toluene is given in Fig. 1. The ten equivalent lines are due to the interaction of the unpaired electron of the Ti^{III} with the nucleus of one indium atom (^{115}In, natural abundance 95.85%, $I=9/2$). The spectroscopic parameters are $a(^{115}In)=41$ MHz and $g=1.972$. The $^{47,49}Ti$ satellite lines could not be observed in this spectrum due to the relatively low signal to noise ratio.

Table 1 compares the EPR spectroscopic data of all Group III halides so far investigated. The very similar g-values and $^{47,49}Ti$ splittings suggest that the complexes have the same structure. In the case of the Ti^{III}–Al complex the structure has

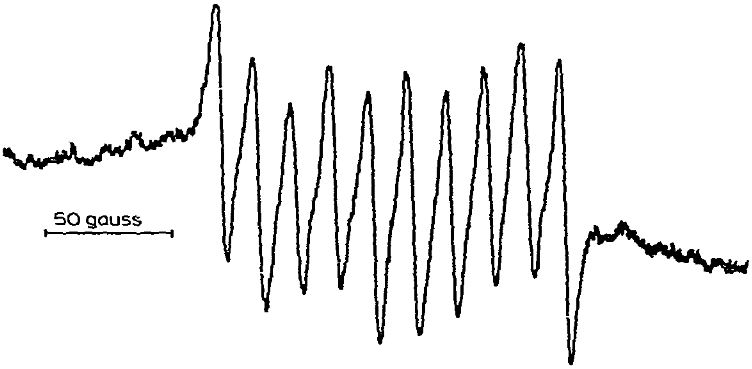


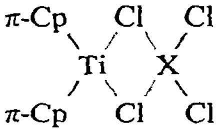
Fig. 1. EPR signal of the Ti^{III}–In complex in toluene solution, at 20°.

TABLE 1

EPR SPECTROSCOPIC DATA OF THE COMPLEXES (I)–(V)

Complex	X	g-value	$a(^{47,49}Ti)$ MHz	a(X) MHz	A(X) MHz
(I)	^{11}B	1.975	32	16.3 (ref. 3)	2020 (ref. 1)
(II)	^{27}Al	1.975	30	19 (ref. 3)	2746 (ref. 1)
(III)	^{69}Ga	1.974	32	91 (ref. 4)	7470 (ref. 1)
(IV)	^{71}Ga	1.974	32	116 (ref. 4)	9500 (ref. 1)
(V)	^{115}In	1.972		41	9530 (ref. 6)

been determined by Natta *et al.*[5] by X-ray structure analysis: Ti and Al, each in approximately tetrahedral environment, are linked together by two three-center bridge bonds, with chlorine as bridging atoms. Thus the complexes may be represented as



(I), X = ^{11}B
(II), X = ^{27}Al
(III), X = ^{69}Ga
(IV), X = ^{71}Ga
(V), X = ^{115}In

The squares of the coefficients $c_{s,X}$ of eqn. (1), as calculated from eqn. (2), are given in Table 2, indicating by far the highest unpaired spin density at the nucleus in the case of gallium.

The results obtained may be interpreted in terms of the electron acceptor ability of the halides. Although the original concept of Lewis acidity was related to the ability of a compound to accept a pair of electrons (lone pair) from a suitable donor, it appears adequate to extend the concept to paramagnetic one-electron donors such as the Ti^{III} species. Relative Lewis acidities for the halides obtained in this way, are included in Table 2. The series has been referred to an arbitrary value of 100 for the relative Lewis acidity of BCl_3, in order to make it comparable with a series $BCl_3 > AlCl_3 > InCl_3$ obtained recently by Deters *et al.*[7], measuring the NMR shifts of the α-protons of ethers on complex formation with the halides. In spite of the different magnitudes measured, the agreement is quite satisfactory.

The higher acidity of BCl_3 as compared with that of $AlCl_3$ is in agreement with

TABLE 2

UNPAIRED SPIN DENSITY AT NUCLEUS X IN COMPLEXES $Cp_2TiCl_2XCl_2$

X	$c^2_{s,X} \times 10^2$	Relative Lewis acidity of XCl_3	
		from EPR	from NMR[7]
^{69}Ga	1.22	150	
^{71}Ga	1.22	150	
^{11}B	0.81	100	100
^{27}Al	0.70	86	81
^{115}In	0.43	53	64

the qualitative information accumulated for a long time from the behavior of these compounds in Friedel–Crafts, polymerization or isomerization reactions. The strong Lewis acid character of $GaCl_3$, on the other hand, is somewhat unexpected. But also with respect to ketones as donors, the acceptor series $GaCl_3 \simeq GaBr_3 > BF_3$ was recently reported by Mohammed and Satchell[8].

The strong acidic character of $GaCl_3$, deduced in the present work from EPR data, is also supported by chemical evidence. The complex of $GaCl_3$ with the Ti^{III} compound is not very stable in solution. The EPR signal of this complex consists of two nicely resolved quadruplets (for the two $I = 3/2$ isotopes ^{69}Ga and ^{71}Ga)[4]. This signal changes with time, and especially if a greater excess of $GaCl_3$ is present. The final many line signal is identical with the EPR spectrum of the complex formed from the *mono*cyclopentadienyltitanium(III) halide and $GaCl_3$. Obviously $GaCl_3$ is able to induce the removal of a Cp ring from the Cp_2 compound. Such behavior was found for $AlCl_3$ only in the presence of moisture or in halogenated aliphatic solvents, and was ascribed there to the action of $H[AlCl_4]$ or a similar ionic species[9]. Presumably the $GaCl_3$ is able to form such species even in extremely dry toluene.

Considering the electron acceptor ability of the elements along a group of the periodic table, one has to take into account that mainly two parameters of opposite influence are operative to define this property: increasing size which tends to diminish the acceptor capacity, and the effective nuclear charge[10] Z^*. The latter depends on the shielding of the surrounding electrons, and experiences a considerable increase from Al to Ga, due to the presence of the first transition series between these two elements. From Ga to In it remains then unchanged. ($Z^* = 3.15$, 4.65 and 4.65 for Al, Ga and In respectively, in the approximation of Slater's rules[10]). This would qualitatively explain the increase of acidity for $GaCl_3$, whereas between B and Al, and between Ga and In the expected decrease due to size is observed. An additional influence may, however, come from a *d–d* overlap between Ga and Ti (as it has been suggested for Ti–Ti in $Cp_2TiCl_2TiCp_2$[11]), which would bring the two metals closer together.

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