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EPR INVESTIGATION OF TRANSITION METAL COMPLEXES
X. HYPERFINE COUPLING CONSTANTS AND LINEWIDTH FROM POORLY RESOLVED SPECTRA OF TITANIUM COMPLEXES*

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SUMMARY

Comparison with computer simulated spectra is used to determine hyperfine coupling constants and linewidths of poorly resolved EPR spectra of bridged Ti^{III}–Al complexes. The linewidth is found to depend strongly on the bridging atoms.

INTRODUCTION

In transition metal chemistry one frequently observes EPR solution spectra which are relatively simple, although they are poorly resolved due to broad lines. As examples see the signals of two Ti^{III}–Al complexes[1] in Fig. 1(a) and (b). Because of the interaction of the unpaired spin of the Ti^{III} with the nucleus of the Al (nuclear spin $I = \frac{5}{2}$) one would expect six equivalent, equidistant lines. The hyperfine coupling constants and linewidth data which are of interest not only for the purposes of identification and comparison with similar compounds, but sometimes also for an estimate of the electronic configuration, cannot be derived directly from such spectra with sufficient exactness.

Computor simulated spectra offer an easy route to these data.

RESULTS AND DISCUSSIONS

The Varian "Spectro System 100" and the Varian program for spectra simulation have been used for the present study. The hyperfine constant [in the present case a(Al)] and the linewidth T_2^{-1} have been varied until the best fit of the simulated with the experimental spectrum was obtained. If simulated spectra are to be compared with experimental ones measured with a different spectrometer equipment (as it was in the present case), only the ratio T_2^{-1}/a of the simulated spectrum is meaningful, and the absolute values of a and T_2^{-1} have to be determined by calibration. The peak-to-peak distance of the outer lines, ΔH, which can be obtained with high enough

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* For Part IX see ref. 3.

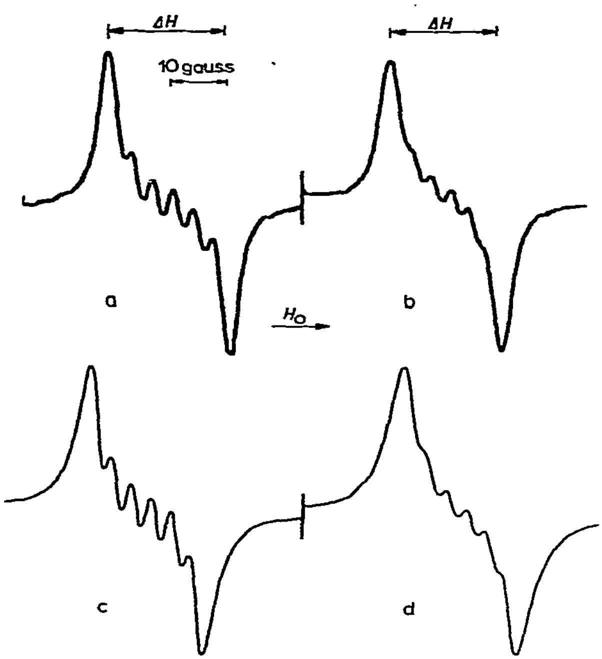


Fig. 1. EPR signals of the complexes $Cp_2TiCl_2Al(CH_3)Cl$ (a) and $Cp_2TiCl_2(C_2H_5)Cl$ (b), and their computer simulations, with $T_2^{-1}/a = 1.0$ (c) and $T_2^{-1}/a = 1.16$ (d). Cp = cyclopentadienyl. Temp. = 20°.

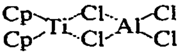
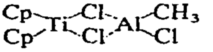
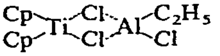
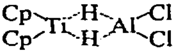
accuracy from the experimental spectrum (compare Fig. 1) is suitable for this purpose.

The best fitting simulated spectra for the experimental signals (a) and (b) are given in Fig. 1 (c) and (d), showing at the same time the sensitivity of the signal to the ratio T_2^{-1}/a.

For the complexes (a) and (b), as well as for two other complexes, the spectra of which have been published elsewhere[2,3], the results are summarized in Table 1. Such data are, of course, meaningful only if all external reasons for line broadening

TABLE 1

HYPERFINE COUPLING CONSTANTS AND LINEWIDTH DATA FOR SOME BINUCLEAR COMPLEXES OF Ti^{III} AND Al AT 20°

Complex	ΔH (gauss)	a(Al) (MHz)	T_2^{-1} (MHz)
 $Cp_2Ti(Cl)_2AlCl_2$	38.2	18.7	10.3
 $Cp_2Ti(Cl)_2Al(CH_3)Cl$	22.0	10.3	10.3
 $Cp_2Ti(Cl)_2Al(C_2H_5)Cl$	20.0	9.0	10.8
 $Cp_2Ti(H)_2AlCl_2$	[a]	30.2	1.4

[a] The spectrum of this complex[3] is well enough resolved not to require the computer simulation method.

(concentration broadening, overmodulation, saturation) have been avoided experimentally.

The first three complexes in the Table present very similar linewidths, which presumably are determined mainly by unresolved hyperfine structure from the bridge chlorine atoms and the protons of the π-bonded cyclopentadienyl rings. This assumption is supported by the results of the last complex in Table 1, where the chlorine in the bridges is replaced by hydrogen: in this case the hyperfine structure of the bridge hydrogens as well as of the aromatic hydrogens is resolved[3], and very narrow lines are observed (only the hyperfine coupling constant of the Al is included in Table 1, for further details see ref. 3.)

The small differences in the linewidth between the first two complexes and the third one in Table 1 are, however, believed to be significant. In cases of anisotropic g-values the linewidth in solution is, in first approximation, proportional to the rotational correlation time, and thus to the cube of the molecular radius[4]. The difference in T_2^{-1} might therefore be related to the presence of the somewhat more bulky substituent C_2H_5 in the case of the third complex.

The hyperfine coupling constants a, on the other hand, reflect the unpaired spin density at the aluminum nucleus which depends on the electron donor ability of the exocyclic substituents at the Al[5].

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REFERENCES

1 G. Henrici-Olivé and S. Olivé, *Angew. Chem.*, 80 (1968) 796; *Angew. Chem. Int. Ed. Engl.*, 7 (1968) 822.
2 G. Henrici-Olivé and S. Olivé, *Makromol. Chem.*, 121 (1969) 70.
3 G. Henrici-Olivé, *J. Organometal. Chem.*, 19 (1969) 309.
4 A. Hudson and G. R. Luckhurst, *Chem. Rev.*, 69 (1969) 191.
5 G. Henrici-Olivé and S. Olivé, *Advan. Polymer. Sci.*, 6 (1969) 421.