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ELECTRON PARAMAGNETIC RESONANCE OF TRANSITION METAL COMPLEXES

XVI*. INVESTIGATION OF A NEW VANADYL–TERTIARY STIBINE COMPLEX

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SUMMARY

The solution spectrum of the 1/1 complex of $VOCl_2$ and tributylstibine in toluene is reported. The hyperfine lines of ^{121}Sb and ^{123}Sb are well resolved in the outer parts of the signal, and the following data have been determined: $g=1.975$, $a(V)=279$ MHz, $a(^{121}Sb)=204$ MHz, $a(^{123}Sb)=110$ MHz.

We previously discussed the EPR spectrum of complexes of $VOCl_2$ with various organic phosphines[1,2] and with an arsine[3], we now describe the ^{121}Sb and ^{123}Sb hyperfine pattern obtained from a complex of $VOCl_2$ with tributylstibine.

A solution of $VOCl_2$ in tetrahydrofuran (THF), in the presence of an excess of Bu_3Sb, presents a pure VO^{2-} signal (8 lines, $g=1.968$, $a(V)=298$ MHz; no interaction with Sb nuclei). However, if the THF is distilled off, and replaced by toluene, the EPR spectrum shown in Fig. 1 is obtained. (Pretreatment with THF serves to solubilize the $VOCl_2$). The spectrum is composed of two superimposed sets of hyperfine lines corresponding to ^{121}Sb ($I=5/2$, $\mu=3.342$; 57.25%) and ^{123}Sb ($I=7/2$, $\mu=2.533$; 42.75%), respectively, and of a relatively weak signal of remaining VO^{2-} (lines marked ○, correspond to some 10–20% of the total vanadium). The Sb hyperfine lines may easily be discerned in the outer parts of the spectrum (● for ^{121}Sb, + for ^{123}Sb).

The general pattern of the hyperfine structure indicates that the unpaired electron of the vanadyl ion interacts with only one Sb nucleus (compare the stick diagram, below the spectrum, for the Sb-hyperfine structure corresponding to m_I(vanadium)$=\pm 7/2$; in the case of interaction with two Sb nuclei the outer lines should show a 1/2/3 ... intensity distribution). This is in contrast to the results from the phosphine and arsine complexes[1-3], where the interaction is with two nuclei. We designate $H_1, H_2, \ldots H_8$ as the field positions of the eight vanadium lines; H_{11}, $H_{12}, \ldots H_{16}$ as those of the six lines into which the first vanadium line is split due to the interaction with ^{121}Sb; $H_{81}, H_{82}, \ldots H_{86}$ as those of the six lines into which the last

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* For Part XV see ref. 1.

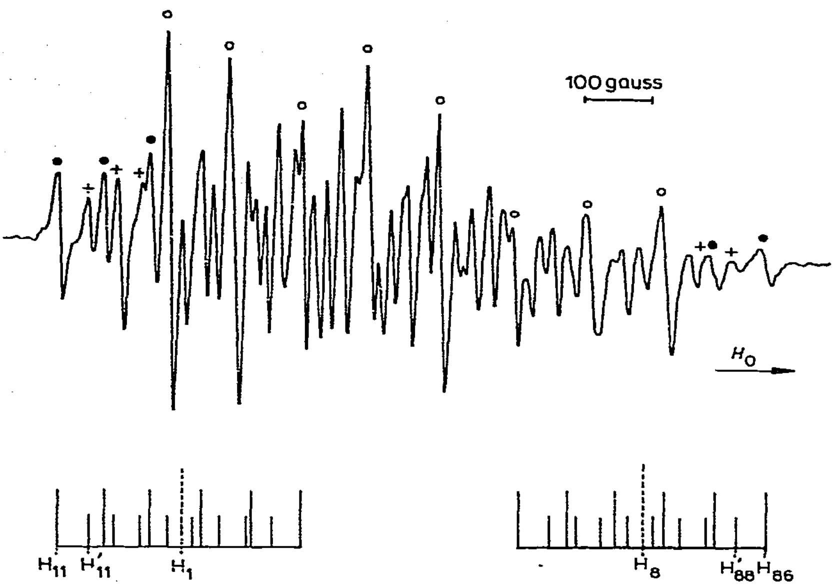

Fig. 1. ESR signal of the complex of $VOCl_2$ with tributylstibine, in toluene. $[VOCl_2] \simeq 5 \times 10^{-3}$ mol/l; Sb/V $\simeq$ 10; $T = 20°$.

vanadium line is split by ^{121}Sb; H'_{12}, ... H'_{18} those of the eight lines resulting from the first vanadium line through the interaction with ^{123}Sb; etc. For the evaluation of the spectrum we make use of the fact that the distance between the first and the last line of the spectrum is given by:

$$H_{86} - H_{11} = 7\,a(\mathrm{V}) + 5\,a(^{121}\mathrm{Sb}) \tag{1}$$

[a(V) and $a(^{121}$Sb) are the hyperfine splitting constants of vanadium and antimony-121]. On the other hand, the distance between the second and the penultimate lines in the spectrum is given by:

$$H'_{88} - H'_{11} = 7\,a(\mathrm{V}) + 7\,a(^{123}\mathrm{Sb}) \tag{2}$$

Using the theoretical relationship between the hyperfine splitting constants of the two antimony isotopes:

$$\frac{a(^{121}\mathrm{Sb})}{a(^{123}\mathrm{Sb})} = \frac{\mu(^{121}\mathrm{Sb}) \cdot I(^{123}\mathrm{Sb})}{\mu(^{123}\mathrm{Sb}) \cdot I(^{121}\mathrm{Sb})} = 1.85$$

and the experimental data $H_{86} - H_{11} = 1080$ gauss and $H'_{88} - H'_{11} = 990$ gauss, we can calculate the constants a(V), $a(^{121}$Sb) and $a(^{123}$Sb) with the aid of eqns. (1) and (2).

For the calculation of the g-factor, the true centre of the spectrum, H_0, was found by correcting the apparent centre, $(H_8 + H_1)/2$, to second order[4]:

$$H_0 = \frac{H_8 + H_1}{2} + \frac{7\,a(\mathrm{V})^2}{4\,H_0}$$

The field positions H_1 and H_8, which cannot be taken directly from the spectrum, were evaluated, taking into account second order effects[4], according to:

$$H_1 = H_{11} + 5\,a(^{121}\mathrm{Sb})/2 + 5\,a(^{121}\mathrm{Sb})^2/4\,H_1 = 2987 \text{ gauss}$$

and:

$$H_8 = H_{86} - 5\,a(^{121}\mathrm{Sb})/2 + 5\,a(^{121}\mathrm{Sb})^2/4\,H_8 = 3697 \text{ gauss}$$

The results of the computations are: $g = 1.975$; $a(\mathrm{V}) = 279$ MHz; $a(^{121}\mathrm{Sb}) = 204$ MHz and $a(^{123}\mathrm{Sb}) = 110$ MHz.

Finally the stick diagram for the antimony hyperfine structure corresponding to m_I(vanadium)$= \pm 7/2$ was drawn to scale, making use of the calculated parameters and correcting the second order according to:

$$\begin{aligned} H_{11} &= H_1 - 5\,a(^{121}\mathrm{Sb})/2 - 5\,a(^{121}\mathrm{Sb})^2/4\,H_1 \\ H_{12} &= H_1 - 3\,a(^{121}\mathrm{Sb})/2 - 13\,a(^{121}\mathrm{Sb})^2/4\,H_1 \\ &\vdots \\ H_{16} &= H_1 + 5\,a(^{121}\mathrm{Sb})/2 - 5\,a(^{121}\mathrm{Sb})^2/4\,H_1, \text{ etc.} \end{aligned}$$

Table 1 shows a comparison of some spectroscopic parameters of complexes of $\mathrm{VOCl_2}$ with trialkylated P, As and Sb derivatives. The penultimate column contains the spin density at the nucleus of the Group V element (E) calculated from the measured splitting constant, a_E, and the isotropic coupling constant a_{iso}[5].

TABLE 1

SOME SPECTROSCOPIC PARAMETERS OF COMPLEXES OF $\mathrm{VOCl_2}$ WITH $\mathrm{R_3E}$

E	a_E *(gauss)*	a_{iso} *(gauss)*	*Spin density at E (%)*	*Reference*
^{31}P	26	3676	0.71	2
^{75}As	29	3431	0.85	3
^{121}Sb	74	6089	1.22	This paper
^{123}Sb	40	3297	1.21	This paper

Although it is obvious that only complexes having the same symmetry should strictly be compared, a trend appears. On going from P to Sb the spin density on these nuclei increases. In other words, the unpaired electron is moving in a molecular orbital containing s-orbital contributions from *E*, increasing in the series P < As < Sb. If this sequence is regarded as an expression of an "acceptor ability", increasing in the series P < As < Sb, consistency is evident with results reported by Chatt *et al.*[6], who found that the donor ability, and thus the coordination affinity decreases in the series P > As > Sb.

The fact that only one stibine molecule is coordinated to the vanadium, whereas two arsine and two phosphine ligands were so coordinated in the previously studied complexes[1-3], is probably due to the same lower coordination affinity and to the known lower stability of Sb complexes as compared with those of P and As[7]. In agreement with this explanation, efforts to obtain complexes of $\mathrm{VOCl_2}$ with tributylbismuth failed.

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REFERENCES

1 G. Henrici-Olivé and S. Olivé, *J. Amer. Chem. Soc.*, 93 (1971) 4154.
2 G. Henrici-Olivé and S. Olivé, *Angew. Chem.*, 82 (1970) 955; *Angew. Chem. Int. Ed. Engl.*, 9 (1970) 957.
3 G. Henrici-Olivé and S. Olivé, *Chem. Commun.*, (1969) 596.
4 See, e.g. K. Scheffler and H. B. Stegman, *Elektronenspinresonanz*, Springer-Verlag, 1970.
5 B. A. Goodman and J. B. Raynor, *Advan. Inorg. Chem.*, 13 (1970) 135.
6 S. Ahrland, J. Chatt and N. R. Davies, *Quart. Rev.*, 12 (1958) 265.
7 J. Chatt, *J. Chem. Soc.*, (1951) 652.