ELECTRON SPIN RESONANCE SPECTRAL STUDIES OF VANADYL COMPLEXES WITH SOME SCHIFF BASES

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Abstract—Vanadyl complexes with Schiff bases of 2-hydroxy-1-naphthalidene and aryl amines were prepared. The ESR spectra of all the complexes were recorded at room temperature and at liquid nitrogen temperature (177 K), by the method of Kneubuhl, Sands and German. A small polycrystalline sample of the tetracyanoethylene (TCNE) free radical was used as a "g" marker. The spectra were again analysed by the method of Kneubuhl, Sands and Garman. The values |g|, g_{\parallel} (parallel), g_{\perp} (perpendicular), |A|, A_{\parallel} , A_{\perp} were obtained. The expression $hv = g\beta H$ was used for evaluating the "g" values. Due to rapid tumbling of the molecules in solution at room temperature the anisotropy is not observed, but it is clearly visible at 177 K. "g" is a function indicating covalency and therefore an order of covalency in the vanadyl complexes has been reported.

The ESR spectra of metal complexes have been studied by various workers.¹⁻⁶ Such studies give information regarding the stereochemistry of metalions in their complexes and the nature of metal-ligand bonding. Detailed ESR studies of metal-oxygen, metal-nitrogen and metal-sulphur bonding have been reported.^{7,8} The spectra of vanadyl complexes have been reported by a few authors. The ESR spectra of vanadyl complexes with some Schiff bases have been studied and interpreted by the authors.

EXPERIMENTAL

The vanadyl complexes with Schiff bases of 2-hydroxy-1-naphthalidene-anil and some substituted 2-hydroxy-1-naphthalidene-anils were prepared by refluxing vanadyl sulphate and the corresponding Schiff base in a 1:2 ratio in ethanol for 2 h. The complexes were characterized by their electronic and IR spectra, magnetic studies and by conductivity measurements in solution. These properties suggest a square-pyramidal structure for the complexes. The ESR spectra of the vanadyl complexes were recorded on a Varian E-112 spectrometer (X-band) at room temperature (R.T.) and at 177 K in chloroform. A minute polycrystalline

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sample of the TCNE free radical was used as a "g" marker. All these spectra were run at RSIC, I.I.T., Powai, Bombay. The spectra are represented in Figs 1 and 2.

RESULTS AND DISCUSSION

The ESR spectra were analysed by the method of Kneubuhl,⁹ Sands¹⁰ and German *et al.*¹¹ The "g" values from ESR spectra obtained at R.T. are presented in Table 1. The hyperfine coupling (A) and "g" values at 177 K are presented in Table 2. The ESR spectra (Figs 1 and 2) of the complexes indicate square-pyramidal symmetry. These facts support the observation made on the basis of magnetic and spectral studies. Kivelson and Neiman³ showed that g_{\parallel} is a moderately sensitive function for indicating covalency. In view of this covalency of the metal-ligand bond in the

Table 1. Room temperature "g" values from ESR spectraof vanadyl complexes

Vanadyl complexes of	$g_{\scriptscriptstyle \ }$	g_{\perp}	<i>g</i>
HNA	1.973	2.008	1.996
HNPCA	1.971	2.001	1.990
HNOCA	1.972	2.000	1.990
HNMCA	1.960	2.005	1.990



 Table 2. Liquid nitrogen temperature "g" values and "A" values of vanadyl complexes

Vanadyl complexes of	<i>g</i> 1	g_{\perp}	<i>g</i>	A	A_{\perp}	 <i>A</i>
HNA	1.969	2.005	1.993	158.57	64.28	95.71
HNPCA	1.962	1.991	1.981	171.42	57.85	95.70
HNOCA	1.966	1.993	1.984	171.42	58.57	96.18
HNMCA	1.960	2.005	1. 990	174.28	57.14	96.18

present vanadyl complexes the following order is suggested: 2-hydroxy-1-naphthalidene-anil (HNA) > 2-hydroxy-1-naphthalidene-4'-chloro-anil (HNPCA) > 2-hydroxy-1-naphthalidene-2'-chloroanil (HNOCA) > 2-hydroxy-1-naphthalidene-3'chloro-anil (HNMCA).

Values for all of the complexes in the polycrystalline state are nearly the same as in chloroform. Therefore it is quite probable that the arrangement of the vanadyl ion in the polycrystalline state and in chloroform may be the same.⁸

There are eight lines in all the spectra taken at room temperature. This is due to hyperfine splitting of ⁵¹V whose nuclear spin number I = 7/2. This shows that a single vanadium is present in the molecule, i.e. it is a monomer. Since there is rapid tumbling of molecules in solution at room temperature, the anisotropy is not observed and single |g|and |A| values are obtained (Table 1).

The anisotropy is clearly visible in the spectra recorded at 177 K in chloroform. Eight bands each due to g_{\parallel} and g_{\perp} are observed separately, the former being fully resolved. g_{\parallel} , g_{\perp} , A_{\parallel} , A_{\perp} , values were measured from the spectra. The values are normal for a square-pyramidal structure.¹²⁻¹⁴ From these values, |A| and |g| were calculated using the expressions:

$$|g| = 1/3(g_{\parallel} + 2g_{\perp})$$
 and $|A| = 1/3(A_{\parallel} + 2A_{\perp})$.

The values thus evaluated are shown in Table 2. The values of |g| and |A| calculated from these formulae agree closely with the values measured from room temperature spectra, thus confirming the accuracy of the calculations. The "g" values are all very close to the spin-only value (the free electron value) of

2.0023, suggesting little spin-orbit coupling. The spin Hamiltonian is simple and can be written in terms of "g" and "A" only, as follows:

$$\begin{aligned} \mathscr{H} &= g_{\parallel}\beta H\xi S\xi + g_{\perp}\beta (HxSx + HySy) \\ &+ A_{\parallel}S\xi I\xi + A_{\perp}(SxIx + SyIy). \end{aligned}$$

The solution spectra thus agree with the squarepyramidal structure for the vanadyl complexes under study.

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