

Structure and Molecular Bonding Parameters from ESR Spectra of Some Schiff Bases Vanadyl Ion Complexes

Salih H.Abbass , Mouayed A.Hussein and Hayat H.Abbass
Department of Chemistry, College of science, University of Basrah
Basrah, Iraq

ISSN -1817 -2695

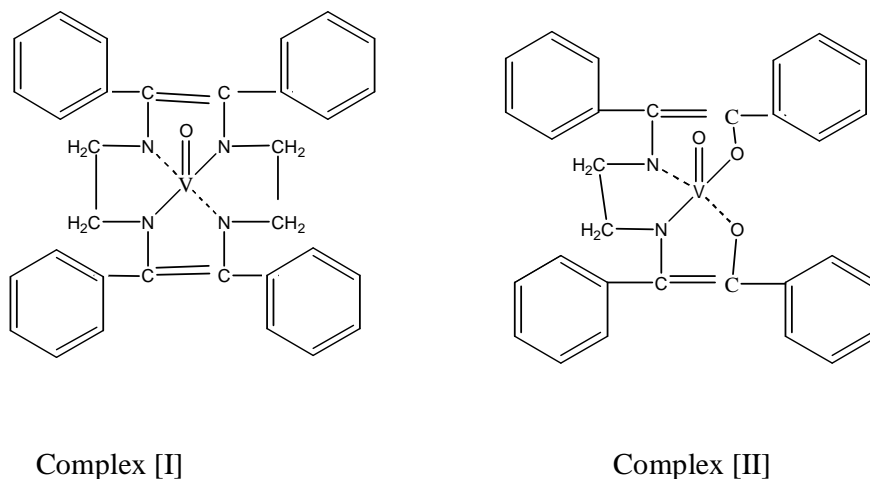
Received 8/12/2005, Revised 15/9/2006, Accepted 11/10/2006

ABSTRACT

The electron spin resonance spectra of vanadyl ion complexes of N,N',N'',N'''-Bis(benzil) azomethine Bis(1,2-ethylene diamine) and N,N-Bis(benzil) azomethine 1,2-ethylene diamine have been studied in solution at room temperature and frozen glasses. The spectra have been analyzed and the components of the g tensor and hyperfine tensors of complexes have been obtained. The unpaired electron is in the antibonding orbital (B_{2g}). The spin Hamiltonian parameters have been equated to atomic orbital coefficients in some of the molecular orbital involved in bonding in these complexes.

INTRODUCTION

The role of vanadium as a biometal is well established [1] and encompasses stimulating and regulatory as well as inhibitory [2,3]. Vanadium has also been recognized as an essential element in photosynthesis [4-6] and catalytically active center in some biosystem [7-11]. Most of studies of vanadium complexes focused on the spectroscopic and thermodynamic properties [12-14]. In the present paper, ESR spectra obtained from magnetically dilute glasses containing some Schiff bases complexes of vanadyl ion were described, which are analogues to the complexes and coordination environment of vanadyl ion with large biomolecules [15,16] in order to obtain detailed information about the structure and the nature of the bonding in these complexes. The structure of the studied complexes are shown in Scheme 1.



Scheme 1

EXPERIMENT

The Schiff bases of N,N',N'',N''' -Bis(benzil) azomethine Bis(1,2-ethylene diamine) and N,N' -Bis(benzil) azomethine 1,2-ethylene diamine were prepared as described by Khahawer and Memon [17]. The complexes of N,N',N'',N''' -Bis(benzil) azomethine Bis(ethylene diamine) [I] and N,N' -Bis(benzil) azomethine 1,2-ethylene diamine [II] with vanadyl ion were prepared by dissolving 6.3×10^{-6} mol of $VOSO_4$ in 10 ml H_2O and 5.3×10^{-6} mol of the ligand in 25 ml ethanol, the solutions then mixed at room temperature for 30 minutes. The precipitate was filtered, washed with ethanol and then collected by filtration.

The ESR spectra of the complexes were recorded with a varian E-109 spectrophotometer whose operating frequency is 9.305 GHz and field set is 3400 G at 298 and 77 K in about 10^{-3} M $CHCl_3$ solutions. Visible-absorption spectra were recorded on UVIDEC-650 double beam spectrophotometer. The wave numbers of the band maxima of these complexes are listed in Table 1.

Table (1): Band maxima (cm^{-1}) in the vis. absorption of N,N',N'',N''' -Bis(benzil) azomethine Bis(1,2-ethylene diamine) and N,N' -Bis(benzil) azomethine 1,2-ethylene diamine vanadyl ion complexes in $CHCl_3$.

complex	ΔE_{xz}	Log (C)	$\Delta E_{x^2-y^2}$	Log(C)
[I]	16700	3.92	17000	3.81
[II]	16100	3.88	17500	3.85

RESULTS & DISCUSSION

As shown in Fig. 1 the ESR spectrum of the complexes recorded at room temperature is characteristic for VO^{+2} in which the unpaired electron interacts with ^{51}V giving eight major peaks according to the rule $(2I+1)$ which I is the spin quantum number, its value $7/2$, with relative intensities 1:7:21:35:35:21:7:1 according to Pascals triangle which is refers to the delocalization of electron about the nucleus [18]. Table 2 lists the isotropic g_0 and A_0 obtained from the analysis of the ESR spectra for these complexes. Upon freezing the solutions at 77K, the recorded ESR spectrum revealed axially symmetric pattern as shown in Fig. 2.

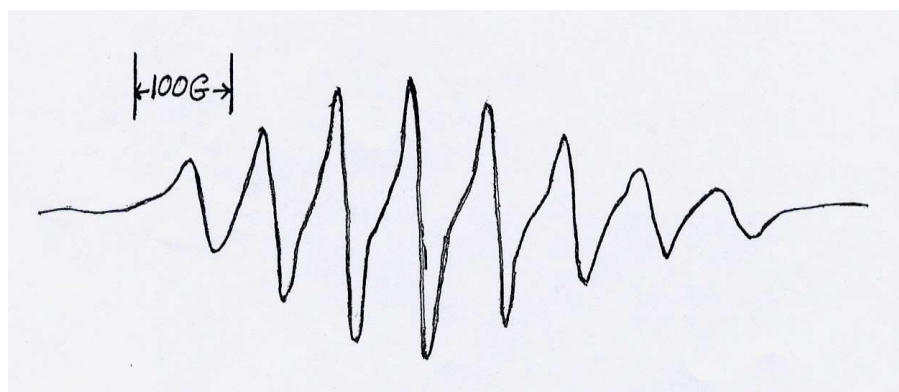


Figure (1): ESR spectrum of complex [I] at 298 K.

Table(2): Spin-Hamiltonian parameters for VO^{+2} complexes in $CHCl_3$. All hyperfine tensor components are in units of cm^{-1} , limits of g_{\parallel} and g_{\perp} are ± 0.0004 , for A_{\parallel} are ± 0.00005

complex	g_{\parallel}	g_{\perp}	A_{\parallel}	A_{\perp}	g_{\perp}	A_0
[I]	1.9891	1.9720	0.00604	0.00277	1.9784	0.00386
[II]	1.9891	1.9718	0.00607	0.00278	1.9783	0.00387

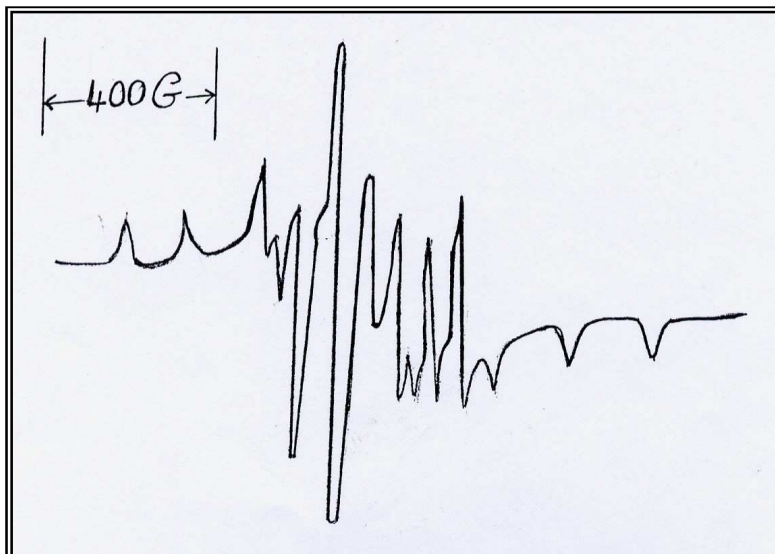
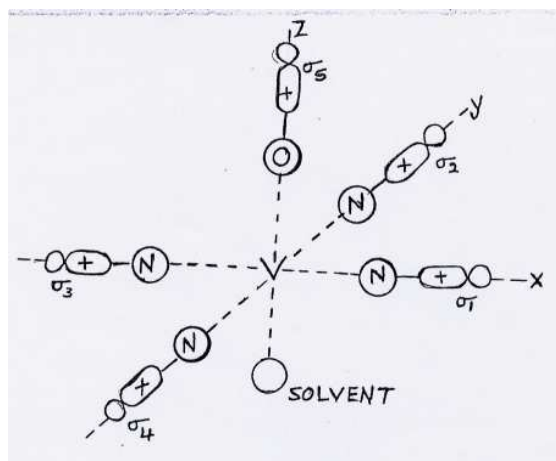


Figure (2): ESR spectrum of complex [I] at 77 K.

The complexes considered here have C_{4v} symmetry with unpaired electron are in the $3d_{xy}$ (b_2) (β_2) orbital form coplanar bonds between the vanadium ion and the ligands, the vanadyl oxygen is attached axially above the vanadium as shown in Fig. 3 [19] and the vanadium atom lies slightly above the plane formed by the four singly-bonded atoms.



Figure(3): The structure of complex[I](σ orbital)

The relevant antibonding molecular orbitals for these complexes can be written :

$$\psi(B_{2g}) = \beta_2 d_{xy} + \frac{1}{2} \beta_2' (P_y^{(1)} + P_x^{(2)} - P_y^{(3)} - P_x^{(4)}) \quad \dots\dots(1)$$

$$\psi(B_{1g}) = \beta_1 d_{x^2-y^2} + \frac{1}{2} \beta_1' (\sigma_x^{(1)} - \sigma_y^{(2)} + \sigma_x^{(3)} - \sigma_y^{(4)}) \quad \dots\dots(2)$$

$$\psi(E_g) = \delta d_{xz} + \delta' P_x^{(5)} + \sqrt{\frac{1}{2}} \delta'' (P_z^{(1)} - P_z^{(2)}) \quad \dots\dots\dots(3)$$

$$\psi(a_1) = \alpha_1 (d_z^2 + S_0) + \alpha_1' \sigma^{(s)} \quad \dots\dots\dots(4)$$

$$\psi(a_{11}) = \alpha_{11} (d_z^2 - S_0) - \frac{1}{2} \alpha_{11}' (\sigma_x^{(1)} + \sigma_y^{(2)} + \sigma_x^{(3)} + \sigma_y^{(4)}) \quad \dots\dots\dots(5)$$

The d's represent vanadium 3d orbitals , S₀ the vanadium 4s orbital, σ refers to an sp² ligand orbital directed towards the vanadium nucleus, the p's are ligand 2p orbitals directed along the molecular axis, and the subscript 5 indicates the vanadyl oxygen. The β', α', δ', δ'' are coefficients of the ligand wave functions [20].

The appropriate spin Hamiltonian for this system has the form [18].

$$\begin{aligned} \bar{H} = & \mu_0 [g_{\parallel} S_z H_z + g_{\perp} (S_x H_x + S_y H_y) + A_{\parallel}^{(v)} S_z^{(v)} I_z^{(v)} + \\ & A_{\perp}^{(v)} (S_x I_x^{(v)} + S_y I_y^{(v)})] + \sum_N [A_{\parallel}^{(N)} S_z I_z^{(N)} + A_{\perp}^{(N)} (S_x I_x^{(N)} + S_y I_y^{(N)})] \end{aligned} \quad \dots\dots\dots(6)$$

Where (z , _{||}) and (x,y,_⊥) refer to the directions parallel and perpendicular, respectively to the vanadyl V-O bonds, (S , I^(v), I^(N)) refer to the electron spin, the vanadium nuclear spin and the ligand (nitrogen for complex [I] and also oxygen for complex [II]) nuclear spins respectively , H is the applied magnetic field and μ₀ is the Bohr magniton. The spin Hamiltonian parameters extracted from the analysis of the spectra recorded at 77 K are listed in Table 2 .From equations (1-5) and by using the second order perturbation procedure ,it is possible to derive equations for the spin-Hamiltonian parameters [20].

$$g_{\parallel} = 2.0023 - \frac{8\lambda\beta_1^2\beta_2^2}{\Delta E_{x^2-y^2}} \left[1 - \frac{1}{2} \left(\frac{\beta_1'\beta_2'}{\beta_1\beta_2} \right) T(n) - \left(\frac{\beta_1'}{\beta_1} \right) S - \left(\frac{\beta_2'}{\beta_2} \right) \pi \right] \quad \dots\dots\dots(7)$$

$$g_{\perp} = 2.0023 - \frac{8\lambda\beta_2^2\delta^2}{\Delta E_{xz}} \left[1 - \frac{1}{2} \left(\frac{\delta''\beta_2'}{\delta\beta_2} \right) \left(\frac{1}{2} \right)^2 - \left(\frac{\beta_2'}{\beta_2} \right) \pi - \left(\frac{\delta''}{\delta} \right) \pi_0 \right] \quad \dots\dots\dots(8)$$

$$A_{\parallel} = P \left[-\beta_2^2 \left(\frac{4}{7} + k \right) - \frac{8\lambda\beta_1^2\beta_2^2}{\Delta E_{x^2-y^2}} - \frac{6\lambda\beta_2^2\delta^2}{7\Delta E_{xz}} \right] \quad \dots\dots\dots(9)$$

$$A_{\perp} = P \left[\beta_2^2 \left(\frac{2}{7} - k \right) - \frac{11\lambda\beta_2^2\delta^2}{7\Delta E_{xz}} \right] \quad \dots\dots\dots(10)$$

Or

$$A_{\parallel} = P \left[-\beta_2^2 \left(\frac{4}{7} + k \right) + (g_{\parallel} - 2.0023) + \frac{3}{7} (g_{\perp} - 2.0023) + D_{\parallel} + \frac{3}{7} D_{\perp} \right] \quad \dots(11)$$

$$A_{\perp} = P \left[\beta_2^2 \left(\frac{2}{7} - k \right) + \frac{11}{14} (g_{\perp} - 2.0023) + \frac{11}{14} D_{\perp} \right] \quad \dots(12)$$

$$A_0 = -PK - (2.0023 - g_0)P \quad \dots(13)$$

Where λ is the spin-orbit coupling constant for the vanadium ion in the appropriate valence state its value has been shown to be 135 cm^{-1} [20], K is the isotropic Fermi contact parameter, $\Delta E_{x^2-y^2}$ and ΔE_{xz} are the transition from the B_{2g} state to the B_{1g} and E_g states respectively, these values are listed in Table 1, and P is :

$$P = 2 \gamma_i \mu_0 \mu_n \langle C_i | r^{-3} | C_i \rangle$$

Where γ_i is the gyromagnetic ratio of the V or ligand N, O nucleus, μ_n is the nuclear magneton, r is the distance from nucleus to the unpaired electron and C_i represents to the vanadium 3d or the ligand 2p wave functions, its value has been reported to be 1.22 cm^{-1} , and S and π are the overlap integrals :

$$S = -2 \langle d_{x^2-y^2} | \sigma_1 \rangle$$

$$\pi = 2 \langle d_{xy} | p_y \rangle = 2 \langle d_{xz} | p_z \rangle$$

$$\pi_0 = \langle d_{xz} | p_x \rangle^{(5)}$$

$T(n)$ is :

$$T(n) = n - \sqrt{\frac{1}{3}} (1 - n^2)^2 R \int_0^{\infty} r^2 R_p(r) \frac{d}{dr} [R_s(r)] dr$$

Where R is the vanadium-ligand distance and $R_p(r)$ and $R_s(r)$ are normalized radial 2p and 2s functions respectively. The evaluation of $T(n)$ is well discussed in ref. [20]. D_{\parallel} and D_{\perp} are small corrections which can readily be determined from equations (11) and (12), A rough estimate sets $D_{\parallel} = 0.005$ to 0.020 and $D_{\perp} = 0.0005$ to 0.0018 [20].

The assignment of the electronic transition listed in table 1 together with the values of λ , p , s , π , π_0 and $T(n)$ now allow us to calculate the values of the bonding parameters β_1 , β_2 and δ from equations (7-13). The parameters obtained in this way are in Table 3.

Table (3): Molecular orbital coefficients of vanadyl complexes.

Complex	β_1	β_2	δ
[I]	0.86	0.87	0.81
[II]	0.88	0.85	0.81

The values of β_1 in Table 3 indicate the extent of in plane σ -bonding between the metal $4d_{x^2-y^2}$ orbital and the ligand σ -orbital showing a considerable degree of covalency in the metal-ligand bonds. The high β_1 of complex [II] refers to the high delocalize atom of the unpaired electron on oxygen more than nitrogen donor ligand. This is predicted to be reduced the dipole-dipole interaction between magnetic moment of the electron and the nucleus.

The values of β_2 in Table 3 which indicate the extent of in-plane π -bonding between the metal $4d_{xy}$ orbital and the ligand π -orbital show that in each complex the unpaired electron

lies in the metal $4d_{xy}$ orbital and is strongly delocalized onto ligands. The decrease of β_2 value for complex [II] can be attributed to the presence in the basal plane of the complex of oxygen ligand known to be a good π -bonding ligand.

The values of δ explain the extent of the out of plane π -bonding between the metal $4d_{xz}$ and $4d_{yz}$ orbitals and the ligand π -orbitals. These values show an appreciable degree of covalency in both complexes.

REFERENCES

1. N.D.Chasteen, Struct. Bonding, 53, 105 (1983).
2. A.Green, Biochem. J., 238, 663 (1986).
3. U.J. Pick, Biol. Chem., 257, 611 (1982).
4. H.U.Meisch, H.Bielig, Arch. Microbio., 114, 67 (1977).
5. S.G.Brand, C.J.Hawkins, D.L.Parry, Inorg. Chem. 136, 33 (1987).
6. M.Asri Nawi, T.L.Riechel, Inorg. Chem. Acta, 136, 33 (1987).
7. J.M.Arber, B.R.Dobson, R.R.Eady, P.Stevens, S.S.Hasnain, C.D.Garne, B.E.Smith, Nature (London), 325, 372 (1987).
8. H.Vilter, photochemistry, 23, 1387 (1984).
9. E.deBoer, Y.VanKooyk, M.G.Tromp, H.Plat, R.Weaver, Biochim. Biophys. Acta, 48, 869 (1986).
10. N.D.Chasteen, J.K.Grady, C.E.Hooway, Inorg. Chem., 25, 2754 (1986).
11. D.Rutler, N.Danzitz, J. Am. Chem. Soc., 109, 1864 (1987).
12. D.Rehder, Magn. Reson. Rev., 9, 125 (1984).
13. B.Borah, C.Chen, W.Egan, M.Miller, A.Wlodawer, J.Cohen, Biochemist, 24, 2058 (1985).
14. H.Vilter, D.Rehder, Inorg. Chem. Acta, 136, L7 (1987).
15. A.S.Tracy, M.J.Gresser, K.M.Parkinson, Inorg. Chem. 26, 629 (1987).
16. M.J.Gresser, A.S.Tracy, J. Am. Chem. Soc. 108, 1935 (1986).
17. M.Y.Khahawar and Z.P.Memon, J. Chem. Soc., Pak., 4, 10 (1988).
18. C.J.Ballhausen and H.B.Gray, Inorg. Chem. 1, 111 (1961).
19. A. H.Al-Mowali and A.L.Parte, Iraqi J. Chem., 16, 146 (1991).
20. D.Kivelson and R.Neimon, J. Chem. Phys., 35, 149 (1961).

الخلاصة

يتضمن البحث تحضير ودراسة طبيعة التآصر والبناء الألكتروني للمعقد ن، ن، ن، ن- بن (بنزيل) أزوميثين بس (2،1- أثيلين داي أمين) والمعقد (ن، ن- بس (بنزيل) أزوميثين (2،1- أثيلين داي أمين) مع أيون الفناديل باستخدام تقنية الرنين الألكتروني البرمي في درجة حرارة 298 كلفن و 77 كلفن. أستخدمت معادلات الهاملتون لهذه المعقدات وأستنبطت العلاقات التي تربط المعاملات الأيزوتروبية مع معاملات المدارات الذرية للأوربيبتال الجزئي لإستخراج معاملات الأوربيبتال الجزئي (δ ، β_2 ، β_1) والتي تبين طبيعة التآصر لهذه المعقدات وبحسب ما أظهرته الدراسة على وجود الألكترون المفرد في المدار اللاتآصري $\Psi(B_{2g})$.

