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Crystal Structure and EPR Studies of Bis[1,3-Di(*p-n*-Octylphenyl)Propane-1,3-Dionato]Oxovanadium(IV)

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We report here the synthesis, crystal structure and Electron Paramagnetic Resonance (EPR) studies of the compound bis[1,3-di(*p-n*-octylphenyl)propane-1,3-dionato]oxovanadium(IV) abbreviated as $C_8(VO)C_8$. The molecular crystalline properties of this compound are dealt with in this paper. The compound crystallizes in the triclinic, $P\bar{1}$ space group with a = 11.956(4), b = 15.802(5), c = 16.293(4) Å, α = 103.22(2), β = 110.61(2), and γ = 90.88(3); Z=2. The two vanadium centers are crystallographically equivalent and the shortest V-V bond distance is 9.5803 Å. The hyperfine splitting pattern in single crystal EPR spectrum clearly shows the presence of weak pair-wise magnetic interaction. The splitting originates in a combination of hyperfine and fine structure caused by dipolar and exchange coupling of nearest-neighboring molecules related by inversion through the unit cell origin. The sign and the value of the exchange coupling constant, J = + 30 G, was determined by simulation of EPR spectra. The principal g and A values obtained are $g_{\|}$ = 1.934 and $g_{\perp}$ = 1.982, $A_{\|}$ = 192 G and $A_{\perp}$ = 69 G.

Keywords: Exchange coupling; Dipolar interaction; Hyperfine splitting

Abbreviations: EPR, Electron Paramagnetic Resonance; $C_8(VO)C_8$, bis[1,3-di(*p-n*-octylphenyl)propane -1,3-dionato]oxovanadium(IV)

INTRODUCTION

Electron paramagnetic resonance has been extensively used in investigating the bonding[1] and interactions[2] of transition metal complexes. Among these complexes those of vanadium occupy a unique position due to extreme stability of

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the VO^{2+} oxo ion[3]. The oxovanadium(IV) species, VO^{2+}, is perhaps the most stable and persistent diatomic cation available for varied complex ion research[4]. Furthermore, the ground state configuration, [Ar] $3d^1$, of the tetravalent vanadium gives this species added attraction because of the expected similarities via the "hole" formalism to the Cu-d^9 system.

Vanadium chemistry has had an impressive advance[5–9] and considerable interest in terms of the chemistry of oxovanadium(IV) complexes. In particular, dinuclear oxovanadium(IV) complexes, has been increasing rapidly as reflected in the increasing number of reports in the literature[10,11]. EPR of several binuclear vanadium(IV)-tartrates and citrates have been studied[10, 12] since tartaric acid and citric acid, acting as a tetradentate ligand, readily form polynuclear complexes with oxovanadium(IV) ion, both in solid state[13] and in solution[14,15]. The unusual and complicated EPR spectral behavior of the oxovanadium(IV)-tartrate system has been discussed by Dunhill *et al.*[16] and James *et al.*[17] and was attributed to exchange coupled oxovanadium(IV) pairs in the triplet state.

Several EPR studies of paramagnetic metal-metal and metal-free radical interactions in metalloenzymes and model complexes have concerned systems where the apparent distance of the dipolar and exchange interactions is decidedly long range, i.e., 8–10 Å or longer. Since exchange interactions decrease exponentially with respect to r while the dipolar interactions decrease as a function of $\frac{1}{r^3}$ (r being the internuclear distance), it is evident that the dipolar anisotropy must be a prominent feature of long range spin-spin coupling.[18] It should therefore be possible to obtain information about the structure and magnitude of exchange and dipolar interactions from EPR studies.

This paper reports the crystal structure and EPR studies of single crystal of the title compound, $C_8(VO)C_8$, as an out growth of our interest in the coordination chemistry of oxovanadium (IV) and the use of EPR to study interelectronic coupling between neighboring sites. Often, EPR measurements on pure single crystal seldom yield much information due to magnetic concentration. This work is an example of the less common case of a neat paramagnetic sample which displays fine structure.

EXPERIMENTAL SECTION

Preparation of $C_8(VO)C_8$

To a stirred warm solution of bis[1,3-di(4-*n*-octylphenyl)propane-1,3-dione (0.232 g, 0.5 mmol) in ethyl alcohol (25 ml) was added a solution of vanadyl sulphate trihydrate (0.054 g, 0.25 mmol) in water (5 ml). To this greenish suspen-

sion, a solution of sodium acetate (0.082 g, 1.01 mmol) in water (3 ml) was added. The resulting mixture was stirred and refluxed for thirty minutes and then stirred at room temperature for two hours. The green precipitate formed was filtered off, washed with water, ethyl alcohol and dried. This was repeatedly crystallized from butan-2-one until the melting point was constant (yield = 0.22 g; m.pt. = 142.5°C).

Suitable single crystals were obtained by recrystallization from acetone or chloroform solution under a nitrogen gas atmosphere. Exposure to oxygen dissolved in solution decomposes the compound. Single crystals of the compound grew in about three days as shiny green colored long needles.

X-ray Structure Analysis

The structure $C_8(VO)C_8$ was determined from single-crystal X-ray diffraction data collected on an Enraf Nonius CAD-4 computer controlled diffractometer (graphite-monochromatized MoKα radiation: $\lambda = 0.7107$ Å). A green crystal ($0.4 \times 0.2 \times 0.1$ mm) of $C_8(VO)C_8$ was mounted on a glass fiber and centered. The orientation matrix and lattice parameters were optimized from a least squares calculation on 25 strong centered reflections in the range $2°<\theta<45°$. A total of 9774 unique reflections were measured out of which 5716 had intensity $I \geq 2\,\sigma(I)$ and were used for structure determination. The intensity data were corrected for Lorentz and polarization effects and then reduced to $|F_0|$ values. The structure was solved in triclinic space group by direct methods using SHELX-86 computer program[19] and refined by full matrix least-squares refinement and difference Fourier synthesis. At convergence, R1 equals to 0.06 and the goodness-of-fit on F^2 is 0.856. The structure refinement is done using SHELXL-93[20] computer program. Summaries of the crystal data and details concerning the intensity data collection and structure refinement are given in Table I; full details have been deposited in the Supporting Information.

TABLE I Crystallographic Data for $C_8(VO)C_8$

Empirical formula: $C_{62}H_{86}O_5V$	Fw: 962.25
a = 11.956(4) Å	Space group: $P\bar{1}$
b= 15.802(5) Å	T = 293(2)K
c= 16.293(4) Å	λ = 0.71073Å
α = 103.22(2)°	$\rho_{(calcd)} = 1.146$ g/cm^3
β= 110.61(2)°	$\mu = 2.24$ cm^{-1}
γ= 90.88(3)°	R= 0.06
V = 2789.4(14) Å^3	R_w= 0.1444
Z = 2	

$\mathbf{R1} = \Sigma[|F_0|-|F_c|]/\Sigma|F_0|$
$R_w = [\Sigma\{w(F_0^2-F_c^2)\}/\Sigma(wF_0^4)]^{1/2}$

Electron Paramagnetic Resonance (EPR)

EPR of single crystals were recorded at both X-band (~9.5GHz) and Q-band (~34.5 GHz) frequencies using a Varian E-112 spectrometer at 100 kHz modulation. DPPH was used as an internal g-marker. A single crystal of approximate dimension 0.25 × 0.5 × 0.3 mm was selected for EPR studies by examining it under polarizing microscope. The morphology of the crystal, determined using X-ray diffractometer is shown in Figure 1. The flat face is found to be $(01\bar{1})$ plane and the long axis is a-axis. The measurements were made by fixing the flat face on a KCl crystal. The laboratory axes X, Y, Z were taken along the orthogonal edges of the KCl crystal such that X-axis is perpendicular to $(01\bar{1})$, Z axis is along a-axis and Y axis is orthogonal to X and Z. The first derivative EPR spectra of single crystals of $C_8(VO)C_8$ were recorded at Q-band by rotating about three orthogonal axes (laboratory frame). Computational analysis employed a digital DEC ALPHA 3000 computer.

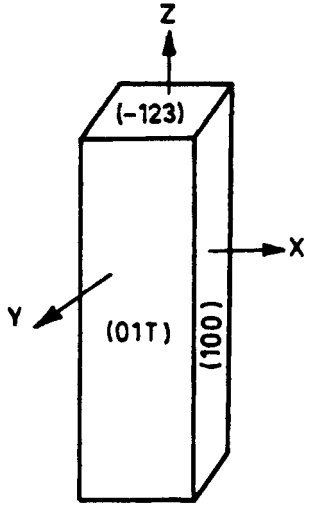

FIGURE 1 Morphology of the single crystal of $C_8(VO)C_8$ used for EPR measurements

RESULTS AND DISCUSSION

Crystal Structure

The ORTEP representation of the molecular structure is shown in Figure 2 and the perspective view of the molecules with respect to the unit cell diagram is pre-

sented in Figure 3. The central metal atom, vanadium, exhibits a square pyramidal geometry and is displaced from the VO_4 plane by 0.59 Å. The O-V-O angles are O1-V-O2 = 86.26°, O3-V-O4 = 85.83°, O1-V-O4 = 84.08°, O2-V-O3 = 82.90°. The important bond angles and bond length are given in Table II. The vanadium atom is coordinated to five oxygen atoms. The V-O5 double bond length is found to be 1.593(3) Å, which is in the range usually found for vanadyl monomeric complexes. Both the octyl chains are fully extended in an all-*trans* conformation.

TABLE II Bond Lengths and Angles for $C_8(VO)C_8$[a]

Bond lengths (Å)	
V-O5	1.593(3)
V-O4	1.956(2)
V-O1	1.957(2)
V-O3	1.958(2)
V-O2	1.959(2)
Bond Angles (deg.)	
O5-V-O4	106.99(14)
O5-V-O1	107.27(13)
O4-V-O1	84.08(10)
O5-V-O3	107.63(13)
O4-V-O3	85.83(10)
O1-V-O3	145.10(11)
O5-V-O2	108.43(13)
O4-V-O2	144.58(11)
O1-V-O2	86.26(10)
O3-V-O2	82.90(10)

a. Symmetry transformations used to generate equivalent atoms: -x, -y, -z.

The shortest V-V distance is 9.5803 Å and the two vanadium atoms are related by the symmetry (1-x, 1-y, -z). The molecules are associated as inversion pairs as shown in Figure 3. The phenyl rings of the two nearest molecules are approximately parallel and are on the top of each other. The short contact distances are between these phenyl rings and those between C17 of one phenyl with C19 and C20 of the other (C17-C19 = 3.51Å and C17-C20 = 3.59 Å). The axial oxygen O5 is also close to the phenyl carbon atoms of the neighboring molecules related by (1-x, 1-y, -z) and the distance O5-C20 is 3.55 Å. The long octyl chains interpenetrate each other into the neighboring molecule. The overlapping geometry between phenyl rings of the neighboring molecules can facilitate a strong π-π^* interaction. The packing diagram and the intermolecular distances show that the long octyl chains of neighboring molecules interpenetrates forming an imbricate arrangement.

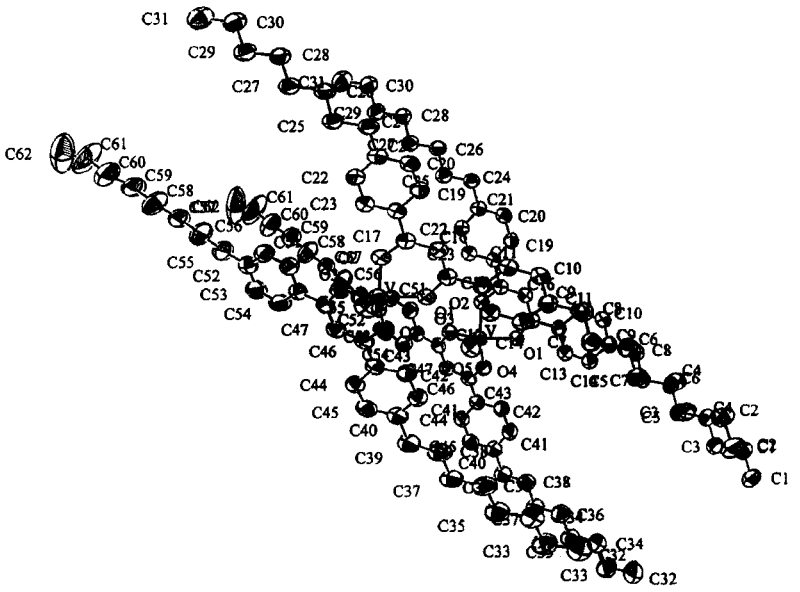

FIGURE 2 ORTEP representation and atom numbering scheme of $C_8(VO)C_8$ molecule using 50% thermal ellipsoids

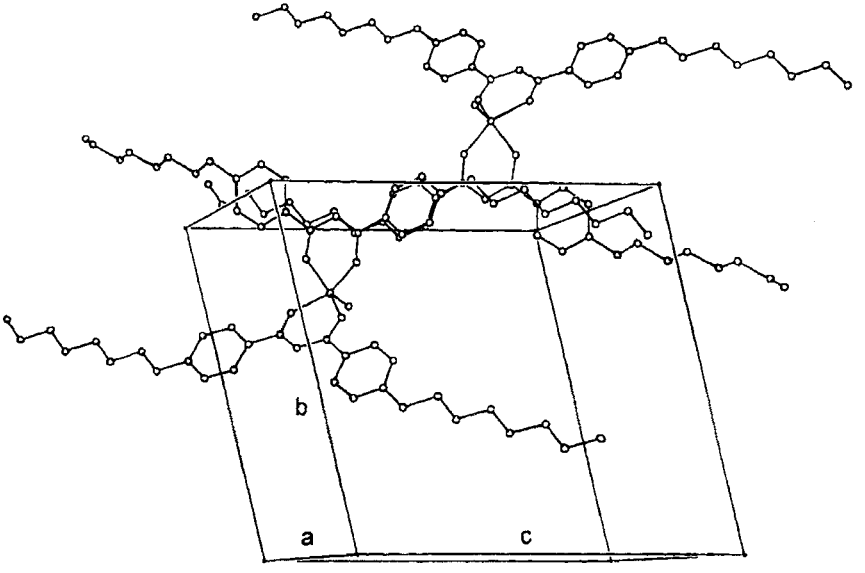

FIGURE 3 Perspective view of $C_8(VO)C_8$ molecules w.r.t. the unit cell showing the overlap of phenyl rings of the neighboring molecules

EPR measurements

Single crystal measurements were made by rotating the magnetic field in three orthogonal planes at RT. The spectra recorded at 77 K showed no significant variation in resolution compared to that at RT. The principal g and A values obtained from the diagonalization are $g_{\|} = 1.934$ and $g_{\perp} = 1.982$, $A_{\|} = 192$ G and $A_{\perp} = 69$ G. The orientational dependence of the experimental spectra in the XY plane is shown in Figure 4. In this plane, at $\theta = 0°$ where g is maximum, nine well resolved lines are observed. In dilute vanadyl system (I = 7/2) only 8 lines are expected[21]. The nine-line pattern suggests the presence of magnetic interaction from at least two equivalent vanadium nuclei. Also, in this plane, there are a maximum of 16 lines at $\theta = 90°$ and a minimum of 8 lines at $\theta = 40°$. This indicates that the dinuclear species is not perfectly isolated in the lattice and intermolecular magnetic interactions are operative which cause merging of the signals.

The spectra were simulated using the FORTRAN program GNDIMER[22].

The spin Hamiltonian used for spectral simulation was

$$\hat{H} = \sum_{i=1}^{2}[\beta(g_{\|}S_{iz}B_z + g_{\perp}(S_{ix}B_x + S_{iy}B_y))] + AS_{iz}I_{iz} + B(S_{ix}I_{ix} + S_{iy}I_{iy}) + \hat{H}_{dip} - JS_1, S_2 \quad (1)$$

This Hamiltonian consisting of the g-tensor (g), hyperfine tensor (A), dipole dipole interaction (D) and the isotropic exchange interaction (J) was solved using second order perturbation theory. The input parameters for simulation are the values of coincidence of g and A, along with the values of D and J.

Examination of the fine structure in the spectra indicates strongly that dipolar and /or spin exchange interaction is definitely present in the system. The X-ray crystal structure indicates that there could be an exchange interaction between two vanadyl ions, related by inversion, placed at a distance of 9.58 Å from each other, through phenyl rings. The intermolecular contacts between the carbon atoms of the phenyl rings of the $C_8(VO)C_8$moiety are about 3.51 Å related by (1-x, 1-y, -z). This shows that there is a good probability of both through space dipolar interaction and a weak exchange coupling through a possible superexchange pathway between two units.

The first step in the analysis is the estimation of D, J and A values. The dipolar coupling is estimated using the equation

$$D_{\text{dip}}(\text{in gauss}) = \frac{\frac{3}{4}g\beta(1 - 3\cos^2\theta)}{r^3} \quad (2)$$

where g is the g factor, β is the Bohr magneton. When r, the internuclear distance is 9.58Å, D_{dip} calculated is ≈ 32 G. The hyperfine coupling, A measured from

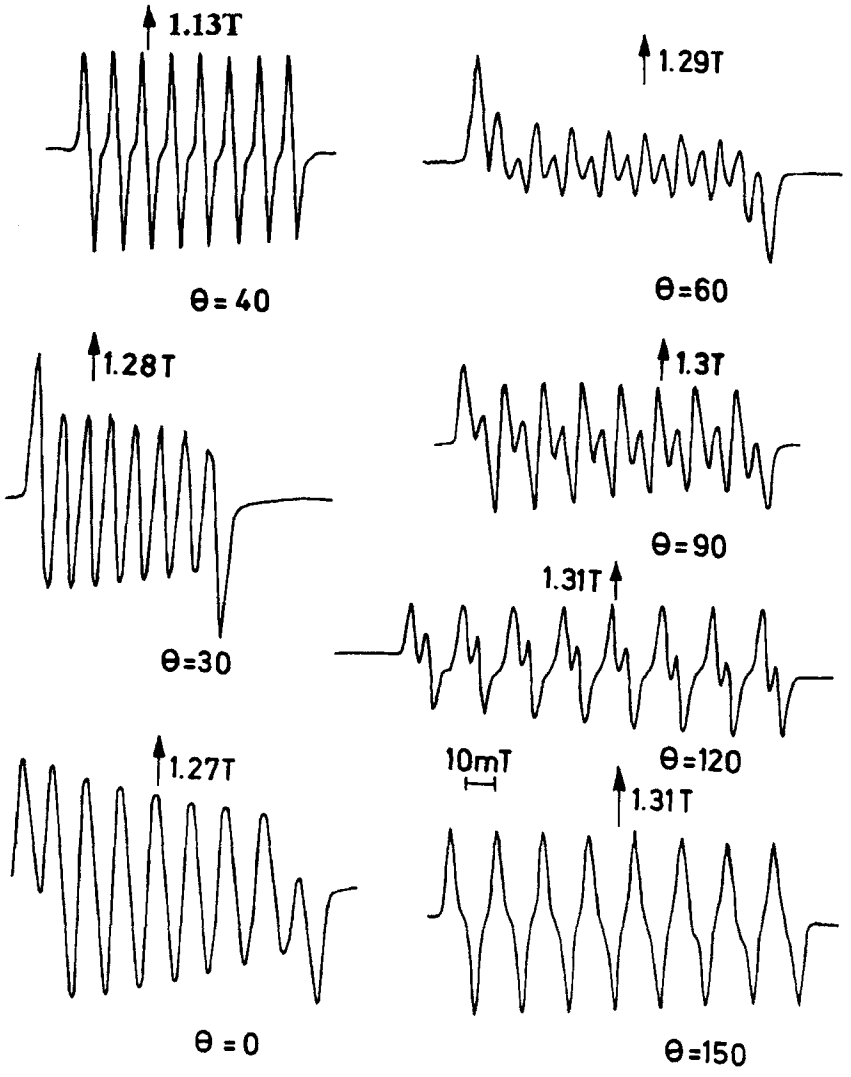

FIGURE 4 Q-band EPR spectra of single crystals of $C_8(VO)C_8$ at RT for certain orientations of magnetic field scanning the XY plane

the separation between hyperfine lines of polycrystalline spectrum agrees well with that obtained from dilute solution spectrum. The value of J could not be measured directly from the spectrum at all orientations.

In the YZ plane, at $\theta = 30°$, a 16 line pattern is seen. As θ varies, it reduces to an 8 line pattern. Unlike in the XY plane where a 9 line pattern is seen, here there were no 9 line pattern and only 16 and 8 line patterns are observed. In XZ plane, at all orientations only an 8 line pattern is seen for the title compound.

The angular variation causes D and A values to change depending upon the orientation of B vector with the respective tensors. J, the isotropic exchange, is constant at all angles. The direction cosines of D_{zz} (Figure 5) with respect to g_x, g_y and g_z frame are calculated using the crystal structure data and are

$$[0.0365 \quad 0.8960 \quad -0.44245]$$

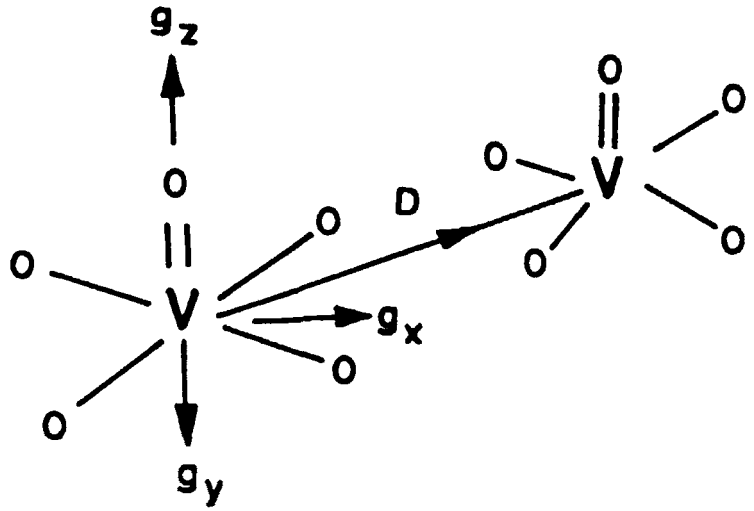

FIGURE 5 Orientation of V-V vector (Dzz) with respect to the g-tensor frame in $C_8(VO)C_8$ system

A few selected single crystal spectra in the XY plane were simulated and are shown in Figure 6. The spin Hamiltonian parameters used for simulation of these spectra are given in Table III. In this plane, the dipolar effect is clearly seen because the V=O ions are closely stacked along this plane and the dipolar interaction between the neighbors are expected to be more along the stacking axis. At $\theta = 0$, where D is maximum (32 G) and J is (30 G), 9 lines are seen and the separation between the last line and the last but one is found to be 60 G. Attempts to simulate the spectra only with D could not reproduce the experimental spectrum. Thus the combination of D and J of same sign and almost equal magnitude could account for the appearance of the spectrum. In the other two planes, namely, YZ

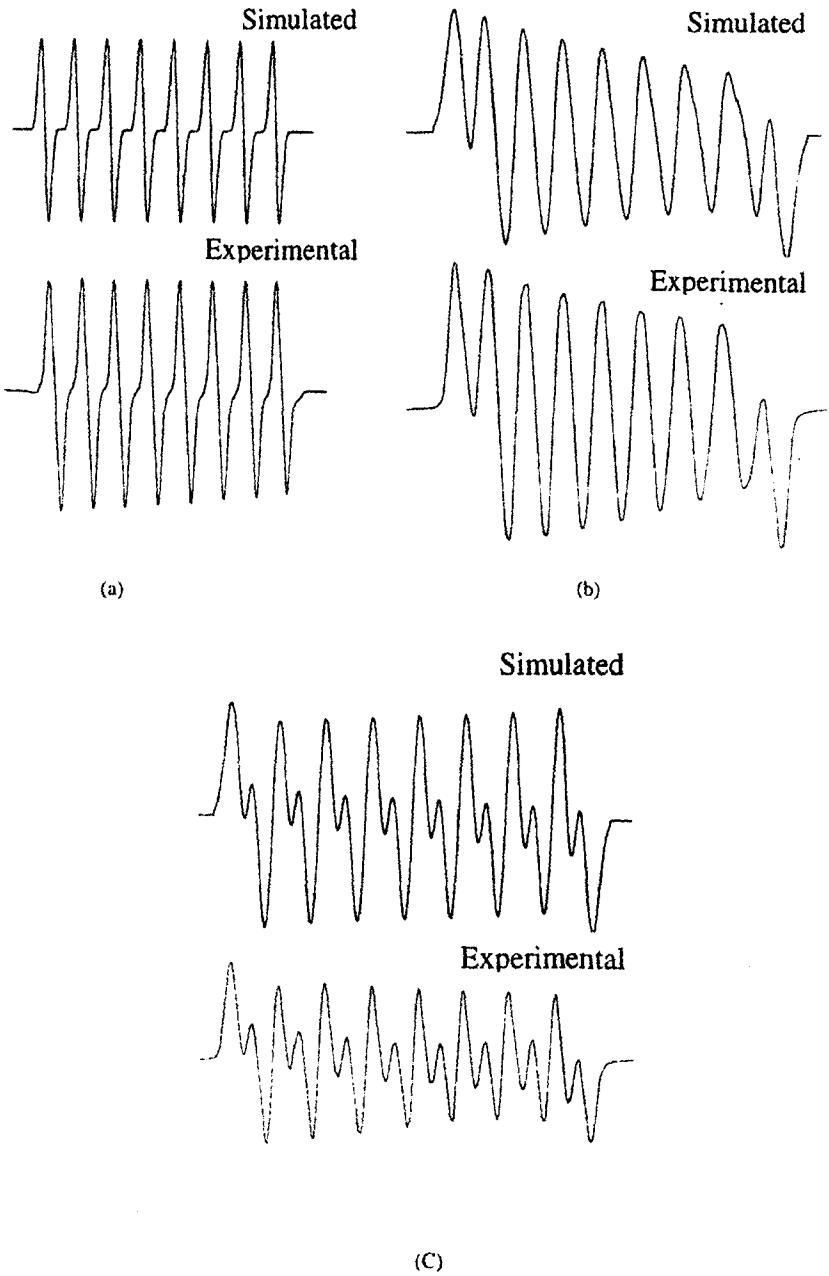

FIGURE 6 Comparison of experimental and simulated single crystal EPR spectrum of $C_8(VO)C_8$ (a) at $\theta = 0°$ (b) at $\theta = 40$ (c) at $\theta = 90°$ in the XY plane

and XZ, though J is constant as in XY plane, D is very small. So its effect is not clearly seen in the spectra. The possibility that the appearance of 16 lines could be due to two magnetically inequivalent sites is ruled out from the fact that the two molecules in the unit cell are related by center of inversion, and the fact that the spectra are not very different in the X- and Q- band frequencies Also, the same g and A values could simulate the observed spectrum at both frequencies.

TABLE III Spin Hamiltonian parameters for $C_8(VO)C_8$at some orientations in the XY plane for simulated spectra

θ	*g-value*	*A-value (Gauss)*	D_{zz} *(Gauss)*	*J (Gauss)*	*See Figure 6*
0	1.976	75	32	30	a
40	1.94	190	18	30	b
90	1.96	110	10	30	c

In this system, there is a weak magnetic interaction between two $C_8(VO)C_8$ molecules in the lattice. It is difficult to precisely predict the exact mechanism of the exchange coupling in the absence of information on the MO energy levels of the complex, as well as variable temperature magnetic susceptibility data. However, from published literature on exchange coupled neat (undiluted) vanadyl systems some speculative remarks can be made. Belford and coworkers[23]in their EPR study of intermolecular exchange interaction in pure crystals of cis-bis (1-phenyl-1,3-butanedionato)oxovandium(IV) accounted for the very low magnitude of J in terms of either direct metal-metal orbital overlap or weak super-exchange pathway involving π orbitals of neighboring ligand benzene moieties. They also mention that, unlike in neat Cu (II) complexes where exchange coupling is through the antibonding $d_x2\text{-}_y2$ or d_z2 orbitals, in vanadyl complexes, the orbital of the unpaired electron occupies a non-bonding orbital which tend to be localized on the metal leading to very poor overlap and low magnitude of J. In the present case also, from the crystal structure data and the local coordination geometry, we believe that the unpaired electron formally occupies a d_{xy} orbital and exchange coupling is more likely to involve a super exchange pathway involving intermolecular overlap between the π orbitals of phenyl rings on neighboring molecules which are at a distance of 3.51 Å. From the close agreement between the simulated and experimental spectra at several orientations, which was possible only by employing the same sign for D and J, it is clear that they are in fact of the same sign and, incidentally, of almost same magnitude as well.

SUPPORTING INFORMATION AVAILABLE

Detailed crystal data and structure refinement (Table I), Fractional Coordinates of non-hydrogen atoms (Table II), Fractional Coordinates of hydrogen atoms (Table III), and Anisotropic displacement parameters (Table IV) for $C_8(VO)C_8$.

Supplementary materials

TABLE I Crystal Data and Structure Refinement for C_8VOC_8

Systematic name	: Bis(1,3-di(*p*-*n*-octylphenyl)propane – 1,3dionato)oxovanadium(IV)	
Structural formula	: $(C_3HO_2)_2VO(C_6H_4)_4(C_8H_{17})_4$	
Empirical formula	: $C_{62}H_{86}O_5V$	
Formula weight	: 962.25	
Temperature	: 293(2) K	
Crystal system	: Triclinic	
Space group	: $P\bar{1}$	
Unit cell dimensions	: a- 11.956(4) Å	α = 103 22(2)°
	: b= 15.802(5) Å	β= 110.61(2)°
	: c= 16.293(4) Å	γ= 90.88(3)°
Volume	: 2789.4(14) $Å^3$	
Z	: 2	
No. reflns. used for unit cell determination	: 25	
Cell measurement theta min/max	: 10/15	
Crystal shape	: Needle	
Crystal colour	: Green	
Density (calculated)	: 1.146 g/cm^3	
Absorption coefficient	: 2.24cm^{-1}	
F(000)	: 1038	
Crystal size	: 0.4 × 0.2 × 0.1mm	
Data collection		
Diffractometer	: Enraf Nonius CAD-4	
Radiation type	: Mo-Kα	
Wavelength	: 0.71073Å	
Radiation source	: Fine focus sealed tube	
Monochromator	: Graphite	

Measurement method	: $\omega - 2\theta$
Standard reflns.	: 2 measured every 1 hour
Theta range for data collection	: 2.14 to 25.06°
Index ranges	: $-14 \leq h \leq 13, -18 \leq k \leq 18, 0 \leq l \leq 19$
Reflections collected	: 9774
Independent reflections	: 9774 [R(int) = 0.0]
No. reflns., I >2 sigma(I)	: 5716
Absorption correction	: PSISCAN
Max. and min. transmission	: 0.96 and 0.85
Solution and refinement:	
Atom sites soln. – primary	: Direct
Atom sites soln. – secondary	: Difference Fourier
Atom size soln. – hydrogens	: Geometrical
Treatment of hydrogen atoms	: Riding model
Refinement method F^2	: Full-matrix-block least-squares on
Data / restraints / parameters	: 9774 / 3 / 410
Goodness-of-fit(S)[I>2sigma(I)]	: 0.849
Goodness-of-fit(S) (all data)	: 0.856
Final R indices [I>2sigma(I)]	: R=0.06, R_w=0.1444
R indices (all data)	: R=0.113, R_w=0.1932
Maximum shift/esd	: 0.996
Mean shift/esd	: 0.032
Largest diff. peak and hole	: 0.257 and −0.0355 e.Å^{-3}
Computer programs:	
Data collection	: CAD-4 system
Cell refinement	: CAD-4 system
Data reduction	: CAD-4 system
Structure solution	: SHELXS-86
Structure refinement	: SHELXL-93
Molecular graphics	: ORTEP
Publication material	: SHELXL-93

R1	$=\Sigma\|F_0\|-\|F_c\|/\Sigma\|F_0\|$
R_w	$= [\Sigma\{w(F_0^2-F_c^2)\}/\Sigma(wF_0^4)]^{1/2} = [\sigma^2 (F_0^2) + (0.0883P)^2 + 2.6765\ P$
w^{-1}	$= (F_0^2 + 2F_c^2)/3$
where P	$= [\Sigma\{w(F_0^2-F_c^2)^2\}/(n-p)]^{1/2}$
S	

TABLE II Fractional Coordinates of Non-hydrogen Atoms ($\times 10^4$)

Atom	*x*	*y*	*z*
V	4733(1)	7519(1)	2183(1)
O(1)	3360(2)	6683(2)	1939(2)
O(2)	4681(2)	6934(2)	970(2)
O(3)	5268(2)	8551(2)	1891(2)
O(4)	3947(2)	8322(2)	2858(2)
O(5)	5867(2)	7251(2)	2910(2)
C(1)	4465(5)	2865(3)	5408(3)
C(2)	4130(4)	2624(3)	4576(3)
C(3)	3250(4)	3297(3)	4541(3)
C(4)	2935(4)	3075(3)	3698(3)
C(5)	2086(4)	3757(3)	3635(3)
C(6)	1790(3)	3513(3)	2788(3)
C(7)	−932(3)	4174(2)	2709(3)
C(8)	−671(3)	3888(3)	1853(3)
C(9)	215(3)	4468(2)	1708(3)
C(10)	515(4)	4209(3)	951(3)
C(11)	1342(4)	4693(3)	795(3)
C(12)	1911(3)	5478(2)	1397(2)
C(13)	1597(4)	5753(2)	2140(3)
C(14)	772(4)	5253(2)	2296(3)
C(15)	2848(3)	6013(2)	1275(2)
C(16)	3143(3)	5793(2)	509(2)
C(17)	4038(3)	6251(2)	379(2)
C(18)	4334(3)	5998(2)	−446(2)
C(19)	3866(3)	5215(2)	1102(2)
C(20)	4186(3)	5006(2)	1849(2)
C(21)	4982(3)	5552(2)	1984(2)
C(22)	5452(3)	6327(2)	1330(2)
C(23)	5134(3)	6541(2)	−579(2)
C(24)	5311(3)	5287(2)	2816(2)
C(25)	6195(3)	5924(3)	2904(2)
C(26)	6478(4)	5634(3)	3759(2)
C(27)	7329(4)	6307(3)	3840(3)
C(28)	7659(4)	6044(3)	4672(3)

Atom	*x*	*y*	*z*
C(29)	8440(4)	6742(3)	4774(3)
C(30)	8820(4)	6481(3)	5574(3)
C(31)	9629(5)	7173(4)	5658(4)
C(32)	2539(6)	8334(4)	8436(4)
C(33)	1771(5)	9054(4)	8372(4)
C(34)	1171(5)	8786(3)	7705(3)
C(35)	−413(4)	9500(3)	7616(3)
C(36)	194(5)	9224(3)	6950(3)
C(37)	844(4)	9954(3)	6781(3)
C(38)	1401(4)	9646(3)	6078(3)
C(39)	1924(4)	10358(3)	5806(3)
C(40)	2453(3)	10067(2)	5088(2)
C(41)	2175(4)	9226(3)	4529(3)
C(42)	2691(3)	8953(2)	3892(3)
C(43)	3489(3)	9516(2)	3776(2)
C(44)	3747(4)	10361(2)	4316(3)
C(45)	3226(4)	10622(2)	4949(3)
C(46)	4073(3)	9161(2)	3121(2)
C(47)	4662(3)	9690(2)	2801(2)
C(48)	5201(3)	9373(2)	2179(2)
C(49)	5689(3)	9944(2)	1755(2)
C(50)	6181(4)	9573(2)	1121(3)
C(51)	6603(4)	10077(3)	686(3)
C(52)	6542(3)	10978(2)	854(3)
C(53)	6078(4)	11334(3)	1495(3)
C(54)	5653(4)	10847(2)	1938(3)
C(55)	6931(4)	11530(3)	346(3)
C(56)	8024(4)	11335(3)	156(4)
C(57)	8319(4)	11842(3)	−428(3)
C(58)	9475(6)	11715(3)	−543(4)
C(59)	9767(6)	12182(3)	−1151(4)
C(60)	10976(7)	12135(5)	−1187(5)
C(61)	11233(10)	12609(8)	−1806(7)
C(62)	12037(9)	12917(9)	−1788(7)

TABLE III Fractional Coordinates of Hydrogen Atoms ($\times 10^4$) for $C_8(VO)C_8$

Atom	*x*	*y*	*z*
H(1A)	−5024(5)	2410(3)	5386(3)
H(1B)	−4827(5)	3404(3)	5424(3)
H(1C)	−3755(5)	2934(3)	5942(3)
H(2A)	−3786(4)	2072(3)	4558(3)
H(2B)	−4856(4)	2541(3)	4041(3)
H(3A)	−2517(4)	3368(3)	5068(3)
H(3B)	−3585(4)	3854(3)	4578(3)
H(4A)	−2576(4)	2528(3)	3674(3)
H(4B)	−3673(4)	2982(3)	3172(3)
H(5A)	−2444(4)	4304(3)	3655(3)
H(5B)	−1346(4)	3850(3)	4160(3)
H(6A)	−1446(3)	2960(3)	2766(3)
H(6B)	−2532(3)	3424(3)	2266(3)
H(7A)	−1274(3)	4727(2)	2721(3)
H(7B)	−185(3)	4265(2)	3227(3)
H(8A)	−381(3)	3317(3)	1835(3)
H(8B)	−1425(3)	3817(3)	1344(3)
H(10)	142(4)	3686(3)	532(3)
H(11)	1524(4)	4492(3)	278(3)
H(13)	1947(4)	6287(2)	2546(3)
H(14)	590(4)	5454(2)	2813(3)
H(16)	2713(3)	5306(2)	53(2)
H(19)	3330(3)	4829(2)	−1033(2)
H(20)	3856(3)	4480(2)	−2277(2)
H(22)	5991(3)	6710(2)	−1398(2)
H(23)	5469(3)	7066(2)	−150(2)
H(24A)	4579(3)	5195(2)	−3347(2)
H(24B)	5644(3)	4731(2)	−2820(2)
H(25A)	6937(3)	6008(3)	−2383(2)
H(25B)	5872(3)	6484(3)	−2895(2)
H(26A)	5735(4)	5529(3)	−4283(2)
H(26B)	6836(4)	5087(3)	−3759(2)
H(27A)	6961(4)	6849(3)	−3846(3)
H(27B)	8060(4)	6419(3)	−3306(3)

Atom	*x*	*y*	*z*
H(28A)	8077(4)	5524(3)	−4646(3)
H(28B)	6927(4)	5895(3)	−5205(3)
H(29A)	8007(4)	7253(3)	−4824(3)
H(29B)	9155(4)	6909(3)	−4229(3)
H(30A)	8106(4)	6331(3)	−6121(3)
H(30B)	9233(4)	5961(3)	−5533(3)
H(31A)	9829(5)	6956(4)	−6184(4)
H(31B)	10350(5)	7315(4)	−5128(4)
H(31C)	9221(5)	7687(4)	−5716(4)
H(32A)	−2890(6)	8560(4)	8878(4)
H(32B)	−2055(6)	7880(4)	8614(4)
H(32C)	−3165(6)	8099(4)	7857(4)
H(33A)	−2266(5)	9515(4)	8210(4)
H(33B)	−1158(5)	9296(4)	8965(4)
H(34A)	−1786(5)	8533(3)	7116(3)
H(34B)	−668(5)	8332(3)	7875(3)
H(35A)	−917(4)	9952(3)	7440(3)
H(35B)	198(4)	9757(3)	8206(3)
H(36A)	−406(5)	8906(3)	6378(3)
H(36B)	767(5)	8823(3)	7165(3)
H(37A)	1471(4)	10258(3)	7346(3)
H(37B)	281(4)	10368(3)	6585(3)
H(38A)	2031(4)	9288(3)	6310(3)
H(38B)	793(4)	9276(3)	5541(3)
H(39A)	2546(4)	10717(3)	6342(3)
H(39B)	1298(4)	10726(3)	5593(3)
H(41)	1630(4)	8838(3)	4586(3)
H(42)	2500(3)	8382(2)	3535(3)
H(44)	4275(4)	10755(2)	4250(3)
H(45)	3404(4)	11196(2)	5297(3)
H(47)	4701(3)	10292(2)	3014(2)
H(50)	6227(4)	8973(2)	988(3)
H(51)	6937(4)	9811(3)	269(3)
H(53)	6049(4)	11936(3)	1637(3)
H(54)	5338(4)	11121(2)	2365(3)

Atom	*x*	*y*	*z*
H(55A)	6277(4)	11480(3)	−227(3)
H(55B)	7047(4)	12135(3)	688(3)
H(56A)	7944(4)	10717(3)	−135(4)
H(56B)	8697(4)	11444(3)	728(4)
H(57A)	7685(4)	11684(3)	−1023(3)
H(57B)	8312(4)	12458(3)	−172(3)
H(58A)	9493(6)	11095(3)	−772(4)
H(58B)	10108(6)	11896(3)	50(4)
H(59A)	9187(6)	11951(3)	−1760(4)
H(59B)	9657(6)	12793(3)	−965(4)
H(60A)	11091(7)	11524(5)	−1375(5)
H(60B)	11560(7)	12369(5)	−580(5)
H(61A)	10924(10)	12194(8)	−2395(7)
H(61B)	10692(10)	13062(8)	−1844(7)
H(62A)	11856(9)	13203(9)	−2274(7)
H(62B)	12577(9)	12487(9)	−1856(7)
H(62C)	12406(9)	13341(9)	−1220(7)

TABLE IV Anisotropic Displacement Parameters ($A^2 \times 10^3$) for $C_8(VO)C_8$ The Anisotropic Displacement Factor Exponent Takes the Form: $-2\pi^2[h^2a^{*2}U11 + \ldots + 2hka^*b^*U12]$

Atom	*U11*	*U22*	*U33*	*U23*	*U13*	*U12*
V	68(1)	54(1)	60(1)	13(1)	24(1)	2(1)
O(1)	76(2)	58(1)	66(2)	5(1)	33(1)	−4(1)
O(2)	67(2)	59(1)	61(2)	8(1)	27(1)	−1(1)
O(3)	72(2)	58(1)	64(2)	14(1)	26(1)	0(1)
O(4)	78(2)	57(1)	76(2)	13(1)	38(2)	5(1)
O(5)	74(2)	86(2)	71(2)	30(1)	7(1)	19(2)
C(1)	108(4)	112(4)	90(3)	38(3)	50(3)	9(3)
C(2)	91(3)	82(3)	81(3)	30(2)	41(3)	11(2)
C(3)	75(3)	84(3)	74(3)	23(2)	31(2)	7(2)
C(4)	67(3)	75(2)	79(3)	23(2)	33(2)	8(2)
C(5)	61(3)	80(3)	79(3)	20(2)	29(2)	4(2)
C(6)	52(2)	75(2)	79(3)	23(2)	25(2)	5(2)
C(7)	47(2)	76(2)	70(2)	21(2)	17(2)	5(2)
C(8)	53(2)	74(2)	78(3)	18(2)	22(2)	1(2)

Atom	*U11*	*U22*	*U33*	*U23*	*U13*	*U12*
C(9)	50(2)	62(2)	69(2)	18(2)	19(2)	4(2)
C(10)	97(3)	82(3)	73(3)	−5(2)	37(3)	−30(2)
C(11)	94(3)	79(3)	67(2)	1(2)	38(2)	−19(2)
C(12)	51(2)	56(2)	59(2)	17(2)	18(2)	5(2)
C(13)	73(3)	64(2)	73(3)	6(2)	34(2)	−2(2)
C(14)	74(3)	67(2)	78(3)	7(2)	39(2)	2(2)
C(15)	55(2)	56(2)	58(2)	20(2)	16(2)	6(2)
C(16)	59(2)	58(2)	55(2)	8(2)	20(2)	1(2)
C(17)	55(2)	53(2)	55(2)	18(2)	18(2)	12(2)
C(18)	50(2)	53(2)	50(2)	14(2)	14(2)	11(2)
C(19)	56(2)	56(2)	66(2)	15(2)	24(2)	7(2)
C(20)	59(2)	56(2)	59(2)	8(2)	18(2)	8(2)
C(21)	53(2)	59(2)	54(2)	15(2)	17(2)	17(2)
C(22)	63(2)	71(2)	60(2)	11(2)	24(2)	−4(2)
C(23)	64(2)	62(2)	61(2)	6(2)	25(2)	−1(2)
C(24)	59(2)	75(2)	59(2)	10(2)	22(2)	9(2)
C(25)	57(2)	80(2)	56(2)	13(2)	19(2)	13(2)
C(26)	62(2)	84(3)	59(2)	10(2)	23(2)	10(2)
C(27)	62(3)	86(3)	65(2)	10(2)	26(2)	13(2)
C(28)	65(3)	98(3)	64(2)	7(2)	25(2)	0(2)
C(29)	77(3)	91(3)	78(3)	18(2)	34(2)	14(2)
C(30)	85(3)	112(4)	78(3)	20(3)	35(3)	4(3)
C(31)	124(5)	120(4)	120(4)	43(3)	62(4)	14(4)
C(32)	129(5)	140(5)	150(6)	8(4)	71(5)	−17(4)
C(33)	105(4)	112(4)	123(4)	19(3)	61(4)	15(3)
C(34)	95(4)	105(4)	98(4)	17(3)	38(3)	3(3)
C(35)	83(3)	102(3)	90(3)	18(3)	38(3)	20(3)
C(36)	103(4)	98(3)	104(4)	17(3)	54(3)	18(3)
C(37)	65(3)	99(3)	76(3)	15(2)	27(2)	21(2)
C(38)	74(3)	97(3)	78(3)	15(2)	32(2)	19(2)
C(39)	57(3)	89(3)	83(3)	11(2)	29(2)	21(2)
C(40)	52(2)	68(2)	67(2)	12(2)	19(2)	20(2)
C(41)	64(3)	75(3)	81(3)	13(2)	32(2)	2(2)
C(42)	69(3)	62(2)	79(3)	11(2)	34(2)	6(2)
C(43)	52(2)	58(2)	56(2)	13(2)	14(2)	9(2)

Atom	*U11*	*U22*	*U33*	*U23*	*U13*	*U12*
C(44)	67(3)	63(2)	74(3)	8(2)	28(2)	2(2)
C(45)	70(3)	60(2)	75(3)	6(2)	23(2)	9(2)
C(46)	58(2)	56(2)	53(2)	13(2)	11(2)	9(2)
C(47)	68(3)	53(2)	62(2)	13(2)	20(2)	2(2)
C(48)	50(2)	57(2)	59(2)	13(2)	11(2)	2(2)
C(49)	53(2)	57(2)	58(2)	18(2)	12(2)	4(2)
C(50)	79(3)	54(2)	85(3)	19(2)	37(2)	6(2)
C(51)	79(3)	71(2)	77(3)	18(2)	36(2)	5(2)
C(52)	63(3)	65(2)	69(2)	21(2)	17(2)	1(2)
C(53)	97(3)	54(2)	87(3)	14(2)	36(3)	2(2)
C(54)	94(3)	58(2)	74(3)	14(2)	38(2)	5(2)
C(55)	88(3)	80(3)	92(3)	34(2)	36(3)	7(2)
C(56)	95(4)	94(3)	130(4)	56(3)	57(3)	23(3)
C(57)	104(4)	81(3)	75(3)	25(2)	38(3)	1(3)
C(58)	146(5)	99(4)	163(5)	59(4)	100(5)	27(3)
C(59)	152(5)	103(4)	100(4)	33(3)	65(4)	−6(3)
C(60)	196(8)	168(7)	190(7)	38(5)	129(7)	−29(6)
C(61)	269(13)	377(16)	247(11)	136(11)	169(11)	−66(11)
C(62)	188(10)	482(20)	203(10)	199(12)	−14(7)	−152(11)

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