

ELECTRON SPIN RESONANCE SUPER-HYPERFINE SPLITTING STUDY OF POLYCRYSTALLINE NIOBOCENE AND VANADOCENE DICHLORIDESJana HOLUBOVA¹, Zdenek CERNOSEK² and Ivan PAVLIK³*Department of General and Inorganic Chemistry, University of Pardubice, 532 10 Pardubice, Czech Republic; e-mail: ¹ holubova@hlb.upce.cz, ² cernosek@hlb.upce.cz, ³ pavlik@hlb.upce.cz*

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The electron spin resonance (ESR) spectra of niobocene and vanadocene dichlorides were studied on the title compounds prepared as magnetically diluted species in polycrystalline form. The resolved super-hyperfine splitting of anisotropic ESR spectra of both studied compounds was firstly observed. Computer simulation confirmed that this super-hyperfine splitting is due to interaction of unpaired electron with nuclear spin of two chlorine ligands. Average value of super-hyperfine coupling constant is 13.3 MHz for niobocene dichloride. For vanadocene dichloride, it is estimated to be in the range of 6–10 MHz. It corresponds approximately to 10% delocalization of metal unpaired electron spin density onto chlorine ligands in case of niobocene dichloride and to 4–7% delocalization in case of vanadocene dichloride.

Key words: Electron spin resonance; Organometallic compounds; Hyperfine interaction.

Electron spin resonance (ESR) has been widely used to obtain detailed information about distribution of unpaired electron in paramagnetic transition metal complexes.

The hyperfine splitting (HFS) of the ESR spectra of complexes bis(η^5 -cyclopentadienyl) niobium(IV) dichloride and bis(η^5 -cyclopentadienyl) vanadium(IV) dichloride (niobocene dichloride and vanadocene dichloride, hereafter NBC and VDC) have been the subject of some investigations, e.g. refs^{1–6}.

Because of nonzero nuclear spin of chlorine ligands the study of super-hyperfine splitting (S-HFS) of ESR spectra gives the possibility to estimate total magnitude of unpaired electron delocalization onto ligands. The nuclear spin of chlorine is $I = 3/2$ (natural abundance 100%) and it is possible to expect S-HFS in the ESR spectra of both dichlorides. The interaction of unpaired electron spin with two equivalent nuclei with $I = 3/2$ results in splitting of HFS transitions into septets with the 1 : 2 : 3 : 4 : 3 : 2 : 1, ratio of line intensities.

Another possible interaction of unpaired electron spin with ten equivalent protons of two cyclopentadienyl ligands should lead to eleven-line S-HFS multiplet with the 1 : 252 intensity ratio of outer and central lines and has to be taken into account.

Super-hyperfine splitting related to delocalization of unpaired electron onto Cl-ligands was studied for both complexes (NBC and VDC) in their diluted solutions indirectly by

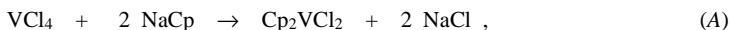
analysis of the thermal dependence of the ESR line-width⁷. The lineshape was assumed to be pure Lorentzian and the super-hyperfine interaction of unpaired electron with Cp-ring protons was neglected. Provided the value of spin-dipolar constant of electron interaction in p-orbital of Cl is 137 MHz, the unpaired electron was found to be delocalized on the chlorine ligands by about 4% and 3% in NBC and VDC, respectively.

The only known resolved S-HFS of chlorine ligands of related compounds was found in the bis(methylcyclopentadienyl) niobium(IV) dichloride in a single crystal of bis(methylcyclopentadienyl) zirconium(IV) dichloride for such an orientation that the magnetic field is parallel to the NbCl₂ plane and bisects the Cl–Nb–Cl angle⁸. The S-HFS coupling constant was found to be $|A'_{\text{Cl}}| = 20.7$ MHz.

Because single crystals of both NBC and VDC have not yet been prepared all previous studies were made using diluted frozen solutions, see e.g. refs^{1,4}. The ESR spectra were not, however, sufficiently resolved to observe S-HFS. In this work, S-HFS in NBC and VDC has been studied using magnetically diluted compounds in a diamagnetic polycrystalline matrix of Cp₂TiCl₂. In this way the broadening of ESR line due to intermolecular interaction was suppressed and the well-resolved ESR spectra were obtained.

EXPERIMENTAL

Niobocene dichloride (NBC) used in our study was commercial specimen (Fluka) with guaranteed purity better than 97%. Vanadocene dichloride (VDC) was synthesized according reaction scheme⁹:



under dried argon atmosphere. The obtained product was purified by vacuum sublimation and its composition was confirmed by elementary analysis. Its purity also was checked by IR spectroscopy. Polycrystalline samples were prepared by crystallisation of a mixture of NBC or VDC with diamagnetic titanocene dichloride (TDC) in mass concentration ratio 1 : 50 from dichloromethane solution under low pressure at room temperature.

ESR spectra of samples obtained were measured in the X-band of the ERS-221 spectrometer (ZWG Berlin) at liquid nitrogen temperature. Microwave power was 10 mW, sufficiently low to avoid saturation; modulation frequency of magnetic field was 100 kHz. Modulation amplitude used for the measurement of overall spectra was $10 \cdot 10^{-4}$ T and super-hyperfine splitting was studied with modulation amplitude $1 \cdot 10^{-4}$ T. Microwave frequency used for NBC was 9.283 GHz and 9.520 GHz for VDC.

Spectra obtained were computer simulated using ESR simulation software SimFonia v.1.2 (Bruker). Second-order perturbation theory for interaction of unpaired electronic spin with niobium or vanadium nuclear spin and first-order perturbation theory for interaction with nuclear spins of chlorine ligands, anisotropic linewidths and mixed Lorentzian/Gaussian lineshape were used.

RESULTS AND DISCUSSION

The ESR spectrum of NBC in TDC matrix and its computer simulation are presented in Fig. 1 and Table I.

It is apparent that both the spectra correspond well each other. A similar agreement was also obtained for the observed and simulated ESR spectra of VDC, (Fig. 2, Table I). This allowed us to conclude that the matrix of diamagnetic titanocene dichloride had no measurable effect on the ESR spectra of NBC and VDC.

The regions of ESR spectra having no bands overlap and relatively high intensities were used to study the delocalization of unpaired electron over the chlorine ligands. These regions of the spectrum of NBC in Fig. 1 are denoted by arrows. The parts of spectrum corresponding to values of nuclear spin number $m_I = +5/2$ in x -direction and $m_I = +9/2$ in the y - and z -directions were used for further study.

Whether coincidence of the **g**- and **A**-tensor axes occurs or not can be determined from powder spectra by computer simulation¹. Our spectra were accurately simulated assuming coincident **g**- and **A**-tensor axes. Orientation of axis corresponds with molecule orientation according to ref.⁸.

It follows from Figs 3 and 4 it is evident that well resolved S-HFS due to ligands are observed in the x - and z -directions of the Cp_2NbCl_2 coordinate system⁸.

The ESR spectrum of VDC showed resolved HFS in x - and y -direction while z -component of the ESR spectrum was not resolved due to very small value of HFS constant

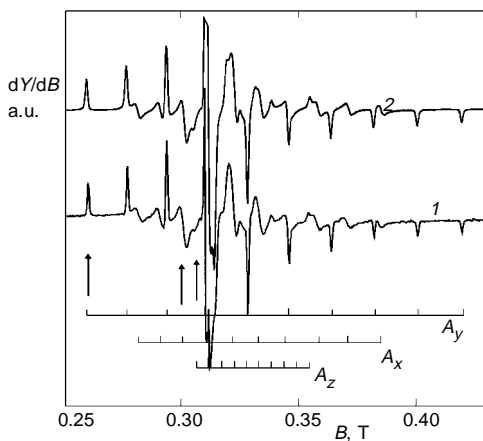


FIG. 1

Niobocene dichloride ESR spectrum measured in magnetically diluted polycrystalline sample (1) and its computer simulation (2). The components marked by arrows were used for super-hyperfine splitting study. A_i ($i = x, y, z$) are the components of hyperfine splitting tensor

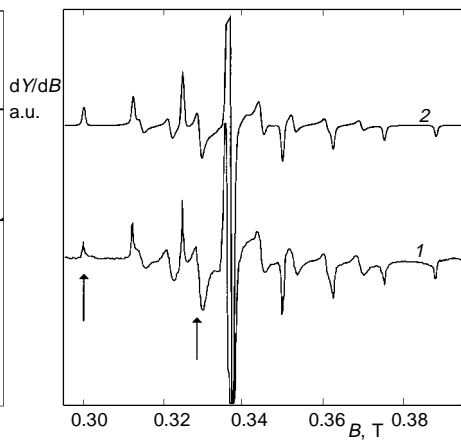


FIG. 2

Vanadocene dichloride ESR spectrum measured in magnetically diluted polycrystalline sample (1) and its computer simulation (2). The components marked by arrows were used for super-hyperfine splitting study

TABLE I

Spin hamiltonian and lineshape^a parameters of $\text{Cp}_2 \cdot \text{NbCl}_2$ and $\text{Cp}_2 \cdot \text{VCl}_2$: g principal values of \mathbf{g} -tensor; $|A|$ principal values of \mathbf{A} -tensor of central atom; $|A'|$ principal values of \mathbf{A} -tensor of chlorine atoms; ΔH_{pp} linewidth of derivative spectrum

Direction	x	y	z
Cp_2NbCl_2			
g	1.983	1.950	2.010
$ A $, MHz (Nb, $I = 9/2$)	320.7	485.7	166.4
$ A' $, MHz (Cl = $3/2$)	19.5	6.0	14.4
ΔH_{pp} , 10^4 T	4.2	4.5	3.0
Cp_2VCl_2			
g	1.983	1.971	1.997
$ A $, MHz (V, $I = 7/2$)	218.2	347.2	56.1
$ A' $, MHz (Cl = $3/2$)	12.0	6.0	0.01
ΔH_{pp} , 10^4 T	3.5	7.0	10.0

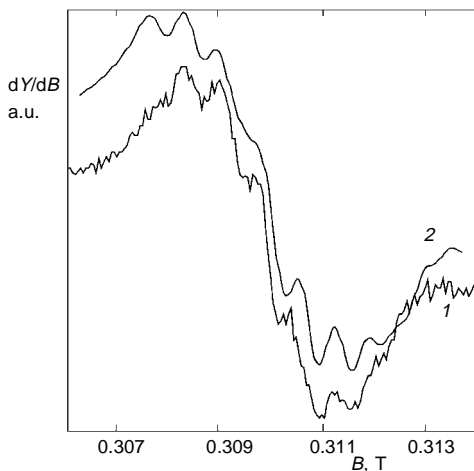
^a 50% of Lorentzian and 50% of Gaussian lineshape was used for both ESR spectra simulation.

FIG. 3

Super-hyperfine splitting of the x -component with $m_I = +5/2$ of niobocene dichloride anisotropic ESR spectrum (1) and its computer simulation (2)

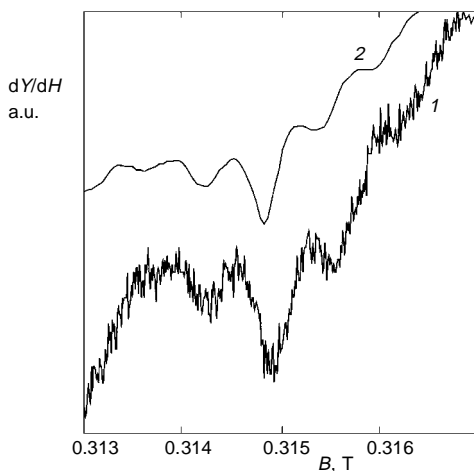


FIG. 4

Super-hyperfine splitting of the z -component with $m_I = +9/2$ of niobocene dichloride anisotropic ESR spectrum (1) and its computer simulation (2)

$|A_z| = 56.1$ MHz (Table I). A poorly resolved S-HFS was observed only in the x -direction (Fig. 5).

With respect to the orientation of molecule in a coordinate system⁸, where the z -axis is defined as being normal to the plane that bisects the Cl–M–Cl bond angle (M = Nb, V), we assume that S-HFS of the x -axis component of ESR spectra corresponds to the interaction of unpaired electron with nuclear spin of two chlorine nucleus. This assumption is in agreement with seven observed components of S-HFS multiplet (Figs 3 and 5), and it is confirmed by computer simulation as well. The mean value of S-HFS constant found experimentally for NBC is $|A'_x| = 19.5$ MHz and $|A'_x| = 12$ MHz for VDC. The super-hyperfine splitting was also observed in the z -component of ESR spectrum of niobocene dichloride (Fig. 4). The mean value of this S-HFS component of NBC is $|A'_z| = 14.4$ MHz.

We suppose that the z -component of anisotropic S-HFS of NBC is due to interaction of the unpaired electron with nuclear spins of two chlorine ligands, however, the dipolar interaction of the unpaired electron with ten equivalent nuclei of cyclopentadienyl rings or combination of both these effects have to be considered.

The computer simulation of this fracture proved that observed S-HFS results from anisotropic interaction of unpaired electron with two equivalent chlorine nuclei (Table I, Fig. 4).

In the y -direction any resolved S-HFS was not observed but the computer simulation confirmed that broadening of this ESR line was caused by unresolved super-hyperfine splitting of unpaired electron spin with nuclear spin of two equivalent chlorine ligands (Table I).

Thus in case of NBC the averaged S-HFS constant is 13.3 MHz and comparing with this one for free ion ($|A'_{\text{Cl}}^{\text{free}}| = 137$ MHz, ref.¹⁰) we can estimate that about 10% of unpaired electron spin density is delocalized onto chlorine ligands.

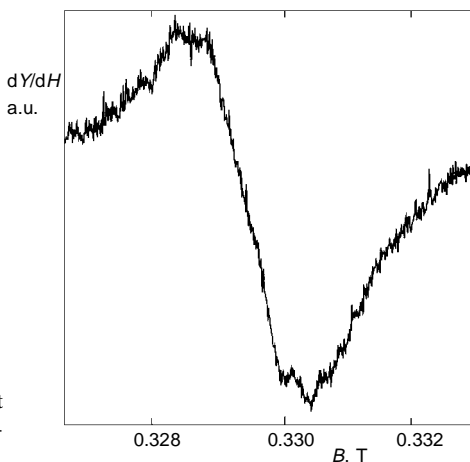


FIG. 5
Super-hyperfine splitting of the x -component with $m_I = +3/2$ of vanadocene dichloride anisotropic ESR spectrum

In case of VDC calculation of averaged S-HFS constant is more complicated because of unresolved z -component of hyperfine splitting. Thus the possible value of z -component of S-HFS constant can be only roughly estimated under assumption that its value can be either negligible on the one hand or maximally 12 MHz on the other hand (we supposed that maximum value could reach the value of x -component of S-HFS constant). Than the averaged S-HFS constant lies in range 6–10 MHz and it corresponds to delocalization of about 4–7% of electron spin density onto chlorine ligands.

Magnitudes of delocalization of unpaired electron density onto Cl-ligands, which we have found, are greater than those based on the study of thermally dependent ESR spectra of solutions (4 and 3%, for NBC and VDC, respectively)⁷. In contrast to our direct observation of S-HFS constants, the estimates from thermal dependence of ESR spectra linewidths in diluted solution are based on some simplified presumptions, especially the presumption of pure Lorentzian lineshape. This simplification can reduce the accuracy of estimation of S-HFS constant, especially in case of low electron density of delocalized electron.

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