NIOBOCENE DICHLORIDE AND NIOBOCENE DIIODIDE: ELECTRONIC ABSORPTION SPECTRA AND ELECTRON SPIN RESONANCE

Jana HOLUBOVA[1], Zdenek CERNOSEK[2] and Ivan PAVLIK[3]

Department of General and Inorganic Chemistry, Faculty of Chemical Technology,
University of Pardubice, 532 10 Pardubice, Czech Republic; e-mail: [1] jana.holubova@upce.cz,
[2] zdenek.cernosek@upce.cz, [3] ivan.pavlik@upce.cz

Received August 26, 1997
Accepted November 3, 1997

The effect of the halide ligand on the bonding of niobium in niobocene dichloride and niobocene diiodide was investigated. The electronic absorption spectra of the two compounds in the range of d–d transitions were resolved into four bands corresponding to transitions of the d^1 electron between five frontier orbitals in a molecule of symmetry point group C_{2v}. The energies of the frontier molecular orbitals were determined relatively to the energy of the orbitals in the spherically symmetric ligand field formed by the appropriate halide ligands. The effect of the halide ligands on the spin-orbital interaction of the HOMO orbital is discussed qualitatively on the basis the ESR spectra.

Key words: Sandwich complexes; Metallocenes; Niobocene dihalides; Electronic structure; d–d Spectra; ESR; EPR spectroscopy.

Bent metallocenes are a class of organometallic compounds which are studied from the theoretical point of view as well as for their catalytic and potential cytostatic properties. The electronic structure of bent metallocenes has been the subject of a number of theoretical and experimental studies[1–3]. A concept of the electronic structure of metallocenes of the Cp_2ML_n type (n = 1–3) based on qualitative MO calculations has been proposed by Lauher and Hoffmann[1]. Steward and Porte[3] studied UV-VIS spectra of bent metallocenes of the Cp_2MX_2 type. On the basis of analysis of ESR spectra of frozen solutions, they proposed an electronic structure of the compounds. For the region of d–d transitions (transitions of the unpaired electron between five frontier orbitals of the $1a_1$, b_1, b_2, $2a_1$, and a_2 symmetry) they suggested the order of the orbitals and, using Hückel MO LCAO calculations, they found the theoretical energies of the transitions. The authors, however, did not analyze the experimental spectra obtained.

One of metallocenes, which are of theoretical as well as practical interest, is the cytostatically active[4] niobocene dichloride (NBC), which can serve as a suitable d^1 model for studying the bonding at the central atom. The present paper describes a study of electronic absorption and ESR spectra of niobocene dichloride and niobocene diiodide (NBI) to assess the effect of the halide ligands on the bonding relations at the niobium atom.

EXPERIMENTAL

Polycrystalline niobocene dichloride was a commercial product of Fluka, of purity better than 96%. Polycrystalline niobocene diiodide was prepared from the dichloride by a published procedure[5].

Electronic absorption spectra were measured in the region of 8 000–45 000 cm^{-1} on a Hewlett–Packard HP-8435 UV-VIS-NIR spectrometer. The samples were dissolved under dry argon in freshly redistilled dichloromethane (dried with calcium chloride and 4Å molecular sieve and subsequently redistilled under argon). An OPUS software (Bruker) was employed for computer processing of the spectra.

EPR spectra were run on an ERS 221 instrument (ZWG Berlin) in the X-band (≈9.5 GHz). Magnetically diluted niobocene dichloride was measured in the solid state at liquid nitrogen temperature. A sample for such measurements was prepared[6] by crystallizing a mixture of niobocene dichloride and titanocene dichloride from a dichloromethane solution at a reduced pressure to get the concentration of the former in the resulting polycrystalline sample 2% (w/w). The EPR spectrum of niobocene diiodide was measured in a frozen dichloromethane solution at a concentration of 0.075 mol dm^{-3} at liquid nitrogen temperature. A SimFonia v.1.2 (Bruker) software was used for ESR spectra simulation.

RESULTS AND DISCUSSION

The experimental results were analyzed using the usual assumption that the compounds belong to symmetry point group C_{2v} (ref.[2]) and that the orientation of molecules in the coordinate system is as shown in Fig. 1.

Electronic Spectra

The electronic spectra of the d^1 complexes Cp_2NbCl_2 and Cp_2NbI_2 are shown in Figs 2 and 3, respectively. The spectra consist of two parts exhibiting different absorption intensities. The region with intensities not exceeding approximately 4 mol^{-1} m^2, 11 000–25 000 cm^{-1} for niobocene dichloride and 9 000–17 500 cm^{-1} for niobocene diiodide, corresponds to the d–d transitions. The intense absorptions at energies above 25 000 cm^{-1} for NBC and 17 000 cm^{-1} for NBI are due to ligand-to-metal charge transfer transitions (LMCT) which have not any major importance in the context of this work.

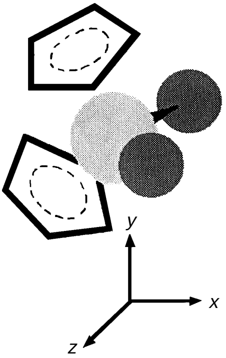

FIG. 1
Orientation of the metallocene molecule in the coordinate system

In agreement with the assumption of five frontier orbitals[1], the spectra in the d–d transition region can be resolved into four absorption bands, as shown in Figs 2 and 3 and Table I. On the basis of the theoretical results[3] and with regard to the orientation of the molecule in the Cartesian coordinate system (Fig. 1), an assignment of the absorption bands is suggested as given in Table I. The highest excitation energy band, exhibiting the lowest integral intensity, is attributed to the ${}^2A_1 \rightarrow {}^2A_2$ transition, which is forbidden in C_{2v} symmetry point group.

On the basis of the observed excitation energies ΔE_i and the centre-of-gravity conservation rule, $\Sigma_i E_i = 0$, the relative energies of the frontier orbitals were estimated for the two niobocene dihalides. The energies are given relatively to the energy of the original degenerate molecular orbitals in the isotropic ligand field of the halide ligands (Fig. 4).

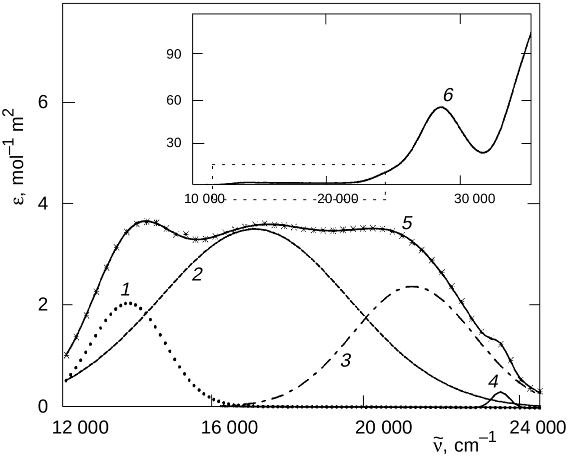

Fig. 2

Computerized resolution of the d–d transitions in the electronic absorption spectrum of niobocene dichloride. In the full spectrum (*6*), the d–d transition region is denoted by a box. Curves *1*–*4* correspond to the electronic transitions ${}^2A_1 \rightarrow {}^2B_1$, ${}^2A_1 \rightarrow {}^2B_2$, ${}^2A_1 \rightarrow {}^2A_1$, and ${}^2A_1 \rightarrow {}^2A_2$, respectively, *5* is the envelope curve

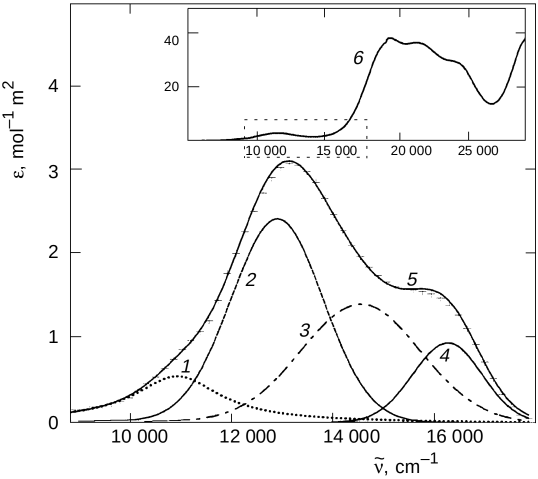

Fig. 3

Computerized resolution of the d–d transitions in the electronic absorption spectrum of niobocene diiodide. For labelling see Fig. 2

The term “isotropic ligand field” denotes a field which changes the energy of the niobium orbitals in contrast to that in the free ion, while not removing their degeneration.

The difference between the highest-energy d-orbital a_2 and the lowest-energy d-orbital $1a_1$, *i.e.* $E(a_2) - E(1a_1) = \Delta E_{max}$, is a measure of the overall splitting in the ligand field. The ΔE_{max} values for NBC and NBI are 23 490 and 16 440 cm^{-1}, respectively. The fact that the ΔE_{max} value is considerably lower for NBI than for NBC can be explained in terms of a larger destabilization of the $1a_1$ orbital of the Cp_2Nb moiety by two strong π-donor iodide ligands, in agreement with the positions of the iodide and chloride ligands in the spectrochemical series. Due to a larger π-donor interaction of the iodide ligands, the $1a_1$ MO, which has a larger antibonding character, is more delocalized with respect to the iodide ligands in the diiodide complex compared with the same orbital in Cp_2NbCl_2. This delocalization tendency correlates well with the observed mean values of the hyperfine interaction constant $\langle A \rangle$. This value is higher for

TABLE I
Parameters of the d–d bands of Cp_2NbX_2

ΔE_1, cm$^{-1,a}$	$w/2$, cm$^{-1,b}$	Band shape	Electron transition (orbital excitation)
	Cp_2NbCl_2		
13 860	2 695	Gaussian	$^2A_1 \rightarrow {}^2B_1$ $(1a_1 \rightarrow b_1)$
17 060	7 060	Gaussian	$^2A_1 \rightarrow {}^2B_2$ $(1a_1 \rightarrow b_2)$
21 310	4 492	Gaussian	$^2A_1 \rightarrow {}^2A_1$ $(1a_1 \rightarrow 2a_1)$
23 490	642	Gaussian	$^2A_1 \rightarrow {}^2A_2$ $(1a_1 \rightarrow a_2)$
	Cp_2NbI_2		
10 718	2 061	Lorentzian	$^2A_1 \rightarrow {}^2B_1$ $(1a_1 \rightarrow b_1)$
13 104	2 510	Gaussian	$^2A_1 \rightarrow {}^2B_2$ $(1a_1 \rightarrow b_2)$
15 444	2 057	Gaussian	$^2A_1 \rightarrow {}^2A_1$ $(1a_1 \rightarrow 2a_1)$
16 440	1 336	Gaussian	$^2A_1 \rightarrow {}^2A_2$ $(1a_1 \rightarrow a_2)$

[a] Excitation energy (band position in the spectrum); [b] band half-width.

Cp_2NbCl_2, $\langle A \rangle = 108.2 \cdot 10^{-4}\,cm^{-1}$, suggesting a larger localization of the $1a_1$ HOMO at the central atom in the dichloride complex (the $\langle A \rangle$ values were calculated from the A values in Table II).

Electron Spin Resonance Spectra

The ESR spectra of the two niobocene dihalides are shown in Figs 5 and 6 along with the results of computational simulation. The difference between the observed and simulated spectra for niobocene diiodide is due to the measurement in a frozen solution,

TABLE II
Parameters of EPR spectra of Cp_2NbX_2

Parameters	Direction		
	x	y	z
	Cp_2NbCl_2		
g_i[a]	1.983	1.950	2.010
$\lvert A\rvert \cdot 10^{-4}\,cm^{-1}$,[b] ($I_{Nb} = 9/2$)[d]	107.0	162.0	55.5
$\lvert A'\rvert \cdot 10^{-4}\,cm^{-1}$,[b] ($I_{Cl} = 3/2$)[d]	6.5	2.0	4.8
$\Delta H_{pp} \cdot 10^{-4}$ T[c]	4.2	4.5	3.0
	Cp_2NbI_2		
g_i[a]	2.070	2.145	1.999
$\lvert A\rvert \cdot 10^{-4}\,cm^{-1}$,[b] ($I_{Nb} = 9/2$)[d]	69	125.0	66.1
$\Delta H_{pp} \cdot 10^{-4}$ T[c]	2.5	2.0	3.0

[a] Diagonal component of ***g***-tensor; [b] absolute value of the diagonal component of ***A***-tensor of hyperfine splitting; [c] band half-width in the derivative spectrum; [d] nuclear spin values.

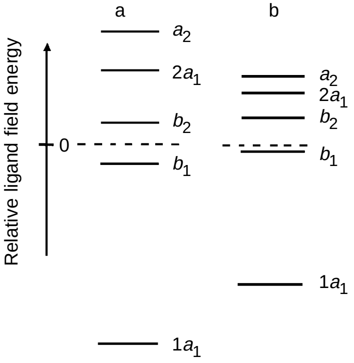

FIG. 4
Order of frontier orbital energies in niobocene dichloride (a) and diiodide (b) relative to the corresponding energies in the isotropic ligand field of the halide ligands. The MO orbital energies were obtained by analysis of the electronic absorption spectra using the excitation energies ΔE_i given in Table I

which had to be used due to lack of any suitable diamagnetic matrix. Interaction of components tensor in associates possibly formed in a frozen solution of NBI can decrease the ESR spectral resolution. This, along with the unresolved superhyperfine splitting, which probably occurs (interaction of the d^1 electron with the nuclear spin of the iodide ligands), can bring about an appreciable band half-width increase (Table II) and distortion of the ESR spectrum. The **g**-tensor and **A**-tensor components of hyperfine splitting obtained by computer simulation of the EPR spectra are given in Table II.

From the order of the frontier orbitals (Table I, Fig. 4), the orientation of the **g**-tensor components can be determined. For the spin-orbital interaction of the ground and excited states, we have[7]

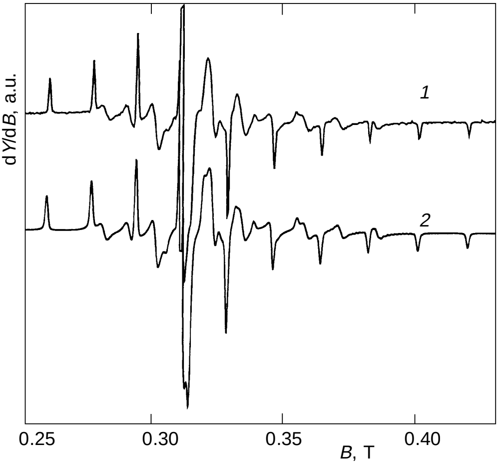

FIG. 5
Experimental (*1*) and simulated (*2*) ESR spectra of niobocene dichloride in a titanocene dichloride matrix (liquid nitrogen temperature; microwave frequency 9.283 GHz)

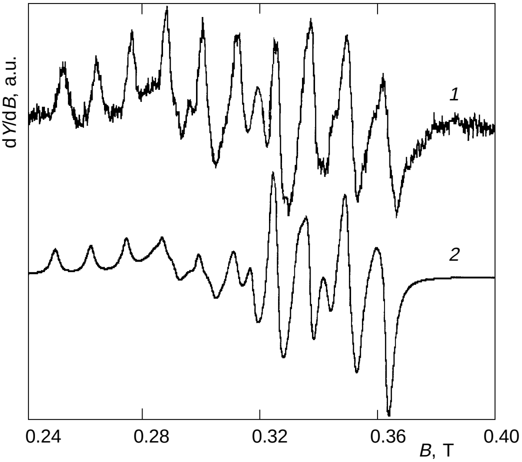

FIG. 6
Experimental (*1*) and simulated (*2*) ESR spectra of niobocene diiodide in a frozen dichloromethane solution (liquid nitrogen temperature; microwave frequency 9.282 GHz)

$$\langle \Psi_i \,|\, \hat{L} \,|\, \Psi_j \rangle \neq 0 \ , \tag{1}$$

where ψ_i and ψ_j are the wave functions of the ground and excited states, respectively, and $\hat{L}$ is the angular momentum operator. If the HOMO orbital symmetry is $1a_1$, then, for the C_{2v} symmetry point group, the a_1 orbital will be affected by the spin-orbital interaction between the a_2 or b_1 or b_2 orbitals during rotation around the z or y or x axis, respectively. Since Δg is inversely proportional to the energy difference between the ground and excited states[8], then, taking into account the energy order of the frontier orbitals, we have $|\,\Delta g_y\,| > |\,\Delta g_x\,| > |\,\Delta g_z\,|$ where $\Delta g_i = g_i - g_e$ ($i = x, y, z$; $g_e = 2.00232$).

The absolute values of the difference between the z-component of the ***g***-tensor for the niobocene dihalides and the corresponding value for a free electron ($g_e = 2.00232$) are different for the dichloride and diiodide but are very low in either case. Since the orbital magnetic moment of the d_{z^2} orbital is zero in the z direction[9], the similar g_z and g_e values implies that the molecular orbital of the $1a_1$ symmetry, at which the d^1 unpaired electron is localized, is mainly formed by the contribution of the d_{z^2} orbital.

The above conclusions are also borne out by the values of mixing coefficients c_1^2 and c_2^2 as defined by Eq. (*2*), describing the participants of the d_{z^2} and $d_{x^2-y^2}$ orbitals in the resulting molecular orbital $1a_1$:

$$\Psi_{\mathrm{HOMO}} = c_1\,|d_{z^2}\rangle + c_2\,|d_{x^2-y^2}\rangle \ . \tag{2}$$

Coefficients c_1 and c_2 can be calculated by spectral parameter analysis using equations[9] derived on the basis of second-order perturbation theory. Our experimental data support an appreciable d_{z^2} nature (about 93%) of the resulting HOMO for NBC. For NBI, the contributions of the two atomic orbitals are changed (about 83 and 17% for d_{z^2} and $d_{x^2-y^2}$, respectively).

The difference between the two niobocene dihalides can be explained in terms of the fact that the iodide ligands are bulkier than the chloride ligands, so that the I–Nb–I bond angle can be expected to be larger than the Cl–Nb–Cl angle, bringing about a certain increase in the contribution of the $d_{x^2-y^2}$ component to the $1a_1$ orbital.

The fact that the signs of the maximum difference between the g_y component of the ***g***-tensor and the g_e value are different for the two niobocene dihalides (Table I) suggests a change in the sign of the spin-orbital interaction of the HOMO orbital with the nearest localized MO (ref.[8]). For niobocene dichloride, this difference is negative, which can be explained by the spin-orbital interaction[8] of the HOMO orbital $1a_1$ with the higher-lying unoccupied orbital b_1, whereas for niobocene diiodide, the difference has an appreciable positive value, $\Delta g_y = 2.1450 - 2.0023 = 0.1427$, which can be interpreted in terms of the spin-orbital interaction of the $1a_1$ orbital with the nearest lower-lying occupied molecular orbital[8]. Due to the higher principal quantum number of iodine and its lower electronegativity compared with chlorine, the energy of the set of pσ and pπ orbitals of the iodide ligands will be raised to the energy level of the Cp(π) orbitals of the cyclopentadiene ligands or even above it. Thus it can be inferred that, compared with niobocene dichloride, the energy diference between the molecular orbital $1a_1$ and the nearest lower-lying occupied molecular orbital, which mainly consists of the atomic orbitals of the halide ligands (presumably one of the three molecular orbitals b_1, a_2, b_2, with energies approaching each other closely[2]), will be lower in niobocene diiodide. The observed effect of the halide ligands on the energy of the valence orbital set correlates with the energy trend inferred from the photoelectron spectra of some chemically related compounds and with the qualitative MO schemes of metallocene dihalides suggested on the basis of the spectra[10].

Stewart and Porte[3] estimated energies of the one-electron d-d transitions of bent metallocenes of the Cp_2MX_2 type (M = V or Nb, X = Cl, SCN, or CN) by MO calculations. Their conclusions are in a good agreement with our experimental data.

This work was supported by the Grant Agency of the Czech Republic, grants No. 203/97/0502 and No. 203/96/0876.

REFERENCES

1. Lauher J. W., Hoffmann R.: *J. Am. Chem. Soc.* **1976**, *98*, 1729.
2. Petersen J. L., Dahl L. F.: *J. Am. Chem. Soc*. **1975**, *97*, 6433.
3. Stewart C. P., Porte A. L.: *J. Chem. Soc., Dalton Trans*. **1973**, 722.
4. Kopf-Maier P., Leitner M., Kopf H.: *J. Inorg. Nucl. Chem*. **1980**, *42*, 1789.
5. Hunter J. A., Lindsell W. E., Mc Coullough K. J., Parr R. A., Scholes M. L.: *J. Chem. Soc., Dalton Trans*. **1990**, 2145.
6. Holubova J., Cernosek Z., Pavlik I.: *Collect. Czech. Chem. Commun*. **1996**, *61*, 1767.
7. Goodman B. A., Raynor J. B.: *Adv. Inorg. Chem. Radiochem*. **1970**, *13*, 135.
8. Gordy W. in: *Theory and Applications of Electron Spin Resonance* (W. West, Ed.), Vol. XV, p. 305. Wiley and Sons, Chichester 1980.
9. Casey A. T., Raynor J. B.: *J. Chem. Soc., Dalton Trans*. **1983**, 2057; and references therein.
10. Cauletti C., Clark J. P., Green J. C., Jackson S. E., Fragala I. R., Ciliberto E., Coleman A. W.: *J. Electron Spectrosc. Relat. Phenom*. **1980**, *18*, 61.