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A Paramagnetic ^{1}H NMR Study of Tetrabromo(*N*-alkyl-methylpyridine-2-carbaldimine)tungsten(IV) and Related Complexes

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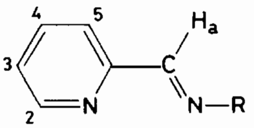
Abstract

Paramagnetic tetrabromo(R-pa)tungsten(IV) (R-pa = *N*-alkyl-methylpyridine-2-carbaldimine; R = Me, Et, Pr^n, Bu^n and Bu^i) as well as the 1,10-phenanthroline (phen) and 2,2-bipyridine (bpy) analogs were prepared by reaction of tetracarbonyl(R-pa, phen, or bpy)tungsten(0) with bromine. These d^2 complexes exhibited magnetic moments of 1.6–1.8 BM in the solid state at room temperature. Their ^{1}H NMR spectra in liquid sulfur dioxide showed sharp signals for all the protons. On the basis of the magnitudes and signs of the isotropic shifts together with Hückel molecular orbital calculations it is concluded that π-spin delocalization on the highest occupied molecular orbitals of phen and R-pa is dominant accompanied with some contribution of σ-delocalization, and that for the *N*-alkyl protons σ-spin polarization mechanism is operative.

Introduction

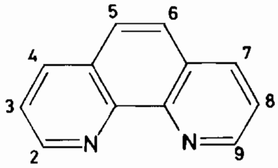
Previously several paramagnetic tungsten(IV) complexes were characterized in the solid state on the basis of magnetic moments and infrared spectra [1–7]. A few NMR studies on these paramagnetic complexes have been reported. Moss and Shaw [4] first reported the paramagnetic ^{1}H NMR of $WX_4(PMe_2Ph)_2$ (X = Cl, Br). Butcher *et al.* [6] measured the spectra of WCl_4L_2 (L = various alkyl-substituted phenylphosphines) and compared them with the spectra of the d^4-complexes based on rhenium(III) and osmium(IV), in which the chemical shifts varied linearly with temperature, indicating the excited state mechanism for the paramagnetism due to a second-order Zeeman effect. $WCl_4(PMe_3)_2$ and $WCl_4(PMe_3)_3$ were also reported to exhibit sharp paramagnetic ^{1}H NMR signals [8]. King and McCarley [7] reported the ^{1}H NMR spectral data of $WX_4(C_3H_7CN)_2$ (X = Cl, Br) and $WCl_4(SEt_2)_2$, suggesting that spin delocalization mechanism might differ in these complexes. Despite the paramagnetism of these complexes, their ^{1}H NMR spectra show interestingly narrow lines. However, poor solubility of these tungsten(IV) complexes in organic solvents have hindered further NMR studies, spin transmission in these complexes being not obvious. This is in a contrast to NMR studies on paramagnetic complexes of metal ions of the first transition series which have been extensively investigated in detail [9].

In this work several tetrabromotungsten(IV) complexes with *N*-alkyl-methylpyridine-2-carbaldimines (R-pa) (R - Me, Et, Pr^n, Bu^n, and Bu^i), 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen) have been prepared. Although they are almost insoluble in common organic solvents, the use of liquid sulfur dioxide as a solvent has made it possible to measure the ^{1}H NMR spectra of the R-pa and phen complexes. Spin transmission mechanisms in these complexes are discussed. The proton-labelling scheme in this work is illustrated in **A** and **B**.



A

N-Alkyl-methylpyridine-2-carbaldimine (R-pa)



B

1,10-Phenanthroline (phen)

(R = Me, Et, Pr^n, Bu^n, and Bu^i)

Experimental

Preparation of N-Alkyl-methylpyridine-2-carbaldimines (R-pa; R = Me, Et, Pr^n, Bu^n, and Bu^i)

R-pa compounds were prepared by reactions of pyridine-2-aldehyde with alkylamines by the method reported previously [10]: Me-pa, 76.5 °C/9 mmHg; Et-pa, 48–50 °C/1 mmHg; Pr^n-pa, 60–62 °C/2 mmHg; Bu^n-pa, 81–82 °C/2 mmHg; Bu^i-pa, 98 °C/7 mmHg. ^{1}H NMR spectra of all the prepared compounds in chloroform-d$_1$ showed no detectable signals due to impurities.

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TABLE 1. Colors, melting points and elemental analyses of the W(CO)$_4$(N-N) complexes

Complex	Color	Melting point (°C)	Found(calc.) (%)		
			C	H	N
W(CO)$_4$(R-pa)					
R = Me	dark green	167–170	31.49 (31.75)	1.92 (1.94)	6.81 (6.73)
Et	dark green	168–170	33.46 (33.51)	2.32 (2.35)	6.66 (6.52)
Pr^n	dark green	164–167	34.84 (35.16)	2.61 (2.73)	6.40 (6.31)
Bu^n	dark green	123–125	36.45 (36.70)	2.75 (3.09)	6.02 (6.12)
Bu^i	dark maroon	189–191	36.83 (36.70)	3.19 (3.09)	6.07 (6.12)
W(CO)$_4$(phen)	maroon	>230	40.58 (40.36)	1.56 (1.70)	6.06 (5.89)
W(CO)$_4$(bpy)	maroon	>230	36.99 (37.19)	1.79 (1.84)	6.44 (6.20)

Preparation of W(CO)$_4$(N-N) Complexes (N-N = R-pa, phen and bpy)

W(CO)$_4$(R-pa) complexes were synthesized according to the method described previously [11]. A benzene solution containing W(CO)$_6$ and 1.2 molar amounts of R-pa was irradiated by UV light at room temperature until two molar amounts of carbon monoxide were evolved. The solvent was evaporated under reduced pressure to give a purple–violet precipitate, which was recrystallized from a dichloromethane–diethyl ether or n-hexane mixture (35–45% yields). W(CO)$_4$(phen) and the bpy analog were prepared according to the literature [12]. Colors, melting points and elemental analyses of the complexes are summarized in Table 1.

Preparation of WBr$_4$(N-N) Complexes (N-N = R-pa, phen and bpy)

Dry nitrogen was bubbled through the solvents prior to use and all the reactions were carried out in nitrogen atmosphere. To a rapidly stirred dichloromethane (15 cm^3) solution of W(CO)$_4$(R-pa) (R = Me, Et, Pr^n, Bu^n, and Bu^i) (200 mg) was added dropwise an excess amount of bromine in dichloromethane (15 cm^3) at room temperature. The vermilion solution turned dark green. After 10 min petroleum ether (40–60 °C) (100 cm^3) was added slowly to precipitate dark green solids of the Bu^n-pa and Bu^i-pa complexes or black microcrystals of the Me-pa, Et-pa and Pr^n-pa complexes. The phen and bpy analogs were also prepared in the same way. Colors and elemental analyses of the complexes obtained are listed in Table 2.

TABLE 2. Colors and elemental analyses of the WBr$_4$(N-N) complexes

Complex	Color	Found(calc.) (%)		
		C	H	N
WBr$_4$(R-pa)				
R = Me	black	13.95 (13.48)	1.35 (1.29)	4.58 (4.49)
Et	black	15.50 (15.07)	1.66 (1.58)	4.56 (4.39)
Pr^n	black	16.65 (16.59)	1.96 (1.86)	4.52 (4.30)
Bu^n	dark green	18.34 (18.04)	1.99 (2.12)	4.28 (4.21)
Bu^i	dark green	18.48 (18.04)	2.19 (2.12)	4.35 (4.21)
WBr$_4$(phen)	black	21.32 (21.08)	1.18 (1.18)	4.14 (4.10)
WBr$_4$(bpy)	dark maroon	18.01 (18.21)	1.33 (1.23)	4.41 (4.25)

Physical Measurements

^{1}H NMR spectra were recorded on a Jeol JNM-PS-100 (100 MHz) spectrometer with a variable temperature probe and a temperature control. Temperature of the probe was calibrated from the signals of methanol [13]. The NMR spectra of W(CO)$_4$(N-N) complexes (N-N = R-pa and phen) were measured

TABLE 3. ^1H NMR chemical shifts (δ, ppm)[a] of the $W(CO)_4(R\text{-pa})$ complexes in chloroform-d_1 at 24 °C

R	H_2	H_3	H_4	H_5	H_a	α-CH	β-CH	γ-CH	δ-CH
Me	9.21 (+0.60)	7.35 (+0.10)	7.90 (+0.23)	7.76 (−0.17)	8.70 (+0.35)	4.18 (+0.80)			
Et	9.24 (+0.63)	7.39 (+0.15)	7.94 (+0.33)	7.82 (−0.14)	8.78 (+0.40)	4.21 (+0.52)	1.69 (+0.29)		
Pr^n	9.23 (+0.63)	7.37 (+0.13)	7.93 (+0.27)	7.80 (−0.13)	8.72 (+0.37)	4.15 (+0.52)	2.11 (+0.36)	1.01 (+0.07)	
Bu^n	9.18 (+0.54)	7.33 (+0.01)	7.90 (+0.17)	7.76 (−0.25)	8.68 (+0.29)	4.13 (+0.44)	2.04 (+0.31)	1.36 (−0.04)	0.98 (+0.04)
Bu^i	9.24 (+0.60)	7.37 (+0.11)	7.94 (+0.26)	7.82 (−0.19)	8.68 (+0.32)	3.95 (+0.44)	2.69 (+0.63)	0.97 (+0.00)	

[a] Values in parentheses are ($\delta_{complexed} - \delta_{free}$).

in chloroform-d_1. WBr_4(N-N) complexes were too insoluble in common organic solvents to measure the ^1H NMR spectra. The measurements were carried out in liquid sulfur dioxide at low temperature, dichloromethane being added as the internal standard. However, the bpy analog was too insoluble in the solvent to measure the spectrum. Magnetic moments of the WBr_4(N-N) complexes were determined by the Gouy method using a Mettler H-20 balance at room temperature.

Results and Discussion

^1H NMR of $W(CO)_4(R\text{-pa})$ Complexes (R = Me, Et, Pr^n, Bu^n and Bu^i)

Chemical shifts of $W(CO)_4(R\text{-pa})$ complexes in chloroform-d_1 are summarized in Table 3, together with differences of the chemical shifts between the complexed and free ligands.

All the ligand proton signals except for the H_5 signals move to lower fields upon complex formation, which is due to the inductive effect of the $W(CO)_4$ moiety. The H_5 signals occur at higher fields upon complexation. As was reported previously [14], this is due to the resultant of the two mutually opposite effects on the H_5 proton; a downfield shift caused by the inductive effect of the $W(CO)_4$ moiety and an upfield shift caused by the disappearance of the paramagnetic effect of the azomethine nitrogen atom upon coordination.

Magnetic Moments of WBr_4(N-N) Complexes

These complexes exhibit magnetic moments (μ_{eff}) in the range of 1.6–1.8 BM at room temperature (see Table 4), which are close to those (1.5–2.2 BM) reported for $WX_4(RCN)_2$ (X = Cl and Br; R = Me, Et and Pr^n) [1], WX_4(bpy) (X = Cl and Br) [3], and $WX_4(PRR'_2)_2$ (X = Cl, Br; RR'_2 = $PhMe_2$, $MePh_2$, $PhEt_2$, $EtPh_2$, $PhPr^n_2$, Pr^nPh_2, Bu^nPh_2 and $PhBu^n_2$) [6]. Large deviation of the magnitudes of the observed μ_{eff} from the value expected on the basis of a d^2 spin-only system may be due to a large spin–orbit coupling [15] in the tungsten complexes. In tungsten(IV) complexes μ_{eff} was estimated as 1.5 BM for a perfect octahedral symmetry and 2.84 BM for a large distortion or asymmetrical fields [16]. Therefore, the values of WBr_4(N-N) (N-N = R-pa and phen) which are rather close to 1.5 BM suggest a nearly octahedral symmetry of these complexes.

TABLE 4. Magnetic moments of the WBr_4(N-N) complexes

Complex	μ_{eff} (BM)
$WBr_4(R\text{-pa})$	
R = Me	1.78
Et	1.69
Pr^n	1.73
Bu^n	1.80
Bu^i	1.81
WBr_4(phen)	1.63

^1H NMR Spectra of the WBr_4(N-N) Complexes

In spite of the paramagnetism of these complexes, they show sharp ^1H NMR signals, some of which are clearly resolved. Figure 1 shows the spectra of WBr_4(phen) and $WBr_4(Pr^n\text{-pa})$ in liquid sulfur dioxide at −42 °C. In the spectrum of WBr_4(phen) the sharp singlet at −1.5 ppm can be assigned to H_5(=H_6) based on the fact that these protons have no spin–spin coupling with the other protons. On the other hand, both H_4(=H_7) and H_2(=H_9) signals are expected to occur as an apparent doublet owing to the coupling with H_3 and H_8, respectively. Since

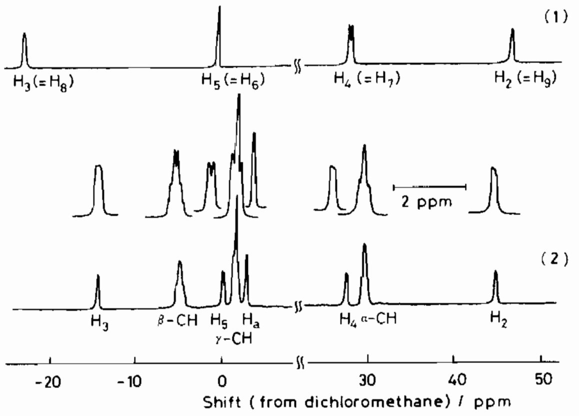

Fig. 1. ^1H NMR spectra of (1) WBr_4(phen) and (2) WBr_4(Pr^n-pa) in liquid sulfur dioxide at −42 °C.

the coupling constant $J_{3,4}$ (=$J_{7,8}$) is larger than $J_{2,3}$ (=$J_{8,9}$) ($J_{3,4}/J_{2,3} = 1.5$) in phen [17]. Thus, a clear doublet at 27.1 ppm is assignable to H_4(=H_7). Since irradiation of the signal at −23.8 ppm with a signal separation of 8 Hz has changed the doublet due to H_4(=H_7) to a singlet, revealing that the signal at −23.8 ppm is ascribed to H_3(=H_8), the signal at 46.5 ppm can be assigned to H_2(=H_9).

In the spectrum of WBr_4(Pr^n-pa), the triplet signal at 2.2 ppm and the signals at −5.4 and 29.2 ppm are assigned to the γ-methyl, β-methylene and α-methylene protons of the *N*-n-propyl group on the basis of their relative intensities and the irradiation experiment. The H_2 and H_5 signals would occur as an apparent doublet due to spin–spin coupling with H_3 and H_4, respectively. In view of the relative magnitude of $J_{4,5}/J_{2,3}$ [=1.6 for diamagnetic $W(CO)_4$(R-pa) complexes], the clear doublet at 0 ppm is assigned to H_5. Since the irradiation of the signal at 27.6 ppm has changed the doublet signal due to H_5 to a sharp singlet, it is assignable to H_4. The signal at the lowest field is due to H_3 because its irradiation has resulted in a clear doublet of the H_4 signal. The signal at the highest field (44.9 ppm) is attributed to H_2 by comparing with the position of the H_2(=H_9) signal of WBr_4(phen) and on the basis of the fact that irradiation of the H_3 signal leads to no change in the signal at 3.0 ppm. Thus, this signal is assigned to H_a. The spectral assignment for the other complexes has been carried out similarly.

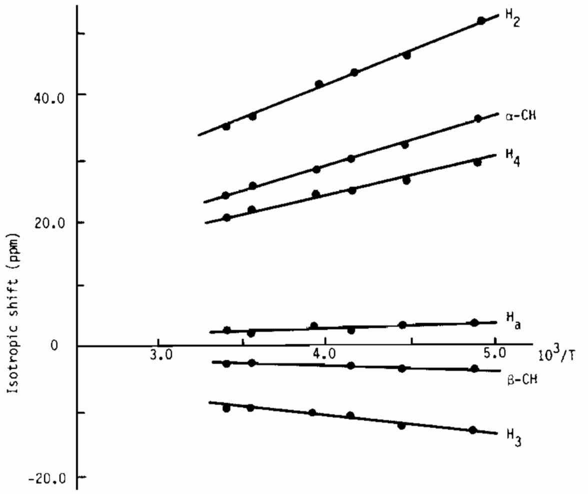

Fig. 2. Temperature dependence of isotropic shifts for WBr_4(Et-pa) in liquid sulfur dioxide.

Table 5 summarizes isotropic shifts of the paramagnetic WBr_4(N-N) complexes measured in liquid sulfur dioxide at −42 °C, which are defined as the chemical shift differences relative to those of the corresponding diamagnetic $W(CO)_4$(N-N) complexes (see Table 3).

Temperature dependence of the isotropic shifts has been investigated on WBr_4(R-pa) (R = Me, Et and Bu^n). The isotropic shifts of all the protons vary proportionally to $1/T$, as shown for WBr_4(Et-pa) in Fig. 2. The observed behavior obeyed by

TABLE 5. Isotropic shifts (ppm)[a] of the WBr_4(N-N) complexes in liquid sulfur dioxide at −42 °C

Complex	H_2(=H_9)	H_3(=H_8)	H_4(=H_7)	H_5(=H_6)	H_a	α-CH	β-CH	γ-CH	δ-CH
WBr_4(phen)	+50.7	−21.3	+30.4	+1.3					
	+50.8[b]	−21.2[b]	+30.5[b]	+1.4[b]					
WBr_4(R-pa)									
R = Me	+50.3	−13.4	+33.6	+1.2	+5.4	+41.2			
Et	+46.2	−12.3	+29.9	+1.4	+4.7	+30.8	−6.7		
Pr^n	+48.8	−11.9	+30.2	+2.5	+6.4	+28.1	−8.6	−2.1	
Bu^n	+46.7	−11.9	+29.2	+2.5	+8.9	+26.8	−8.4	−1.4	+0.6
	+46.5[b]	−11.8[b]	+29.2[b]	+2.5[b]	+8.9[b]	+26.8[b]	−8.4[b]	−1.5[b]	+0.5[b]
Bu^i	+47.2	−11.9	+28.8	+2.9	+7.7	+23.7	−8.3	−1.8	

[a] Referenced to the chemical shifts (in chloroform-d_1) of the corresponding $W(CO)_4$(N-N) complexes. [b] Measured in nitromethane at 24 °C.

the regular Curie law suggests that any equilibria between different conformers of the complexes or between species in different spin states are very unlikely [18].

Origin of the Isotropic Shifts of the $WBr_4(N\text{-}N)$ Complexes

The isotropic paramagnetic shift is a sum of contributions from the nuclear–electron dipolar interaction and the scalar (or Fermi) isotropic hyperfine contact interaction. Assuming the dipolar interaction is operative in the paramagnetic shifts, the linewidths of the proton signals should be dominated by electron–proton dipolar relaxation mechanism; that is, the linewidth is proportional to r^{-6}, where r is a metal–proton distance [19]. On the basis of this mechanism, the relative linewidths for WBr_4(phen) are estimated to be in the ratio 37:3.1:1.3:1.0 for H_2:H_3:H_4:H_5 signal (the magnitude for the H_5 signal is normalized to unity), using the reported bond distances of phen [20] and estimating the metal–nitrogen bond distance of 2.20 A [21]. However, the observed linewidths are within 12–18 Hz for all the signals. This suggests that the dipolar contribution is essentially minor in the WBr_4(N-N) complexes, the observed shifts being primarily from a contact nuclear–electron interaction.

The contact interaction has three possible mechanisms; σ-spin polarization, σ-delocalization and π-delocalization. Both the σ-mechanisms result in the rapid attenuation of paramagnetic shifts as the position of a proton is further separated from the paramagnetic metal center [9].

For the *N*-alkyl chains of WBr_4(R-pa), the shift would reflect σ-mechanism due to the absence of π-system. As shown in Table 5, α-methylene proton signals occur at considerably high fields and β-methylene proton signals, on the contrary, at low fields. This sign alternation in the isotropic shifts seems to be explicable predominantly on the basis of σ-spin polarization mechanism; that is, the negative spin density is induced on the α-methylene protons and then positive spin density on the β-methylene protons by correlation effect [22]. The spin polarization mechanism was reported to be dominant in hexacoordinate nickel(II) complexes with alkylamines [23].

For the pyridyl ring protons of WBr_4(R-pa), the H_2 signal occurs at the highest field, the H_3 one at the lowest, and the H_4 one again at a high field. In spite of a large H_4 proton–metal distance compared with H_2 proton– and H_3 proton–metal distances, the H_4 signal occurs at a considerably high field. This finding and the sign alternation in the shifts of these protons are strongly in disagreement with the contribution of only σ-mechanism. The isotropic shifts of H_2, H_3 and H_4 protons of WBr_4(phen) also alternate in their signs.

The octahedral d^2 complexes are considered to be in the $(t_{2g})^2$ electronic configuration, and in the tungsten(IV) complexes the t_{2g} level is likely no more degenerated owing to the large spin–orbit coupling as expected from the observed magnetic moments. The t_{2g} level is able to overlap with ligand π-orbitals. Thus, the metal 5d-orbitals may possibly interact with the highest occupied bonding and the lowest unoccupied antibonding π-orbitals of the ligand. The former interaction corresponds to the ligand-to-metal charge transfer, resulting in the net negative or positive spin in the ligand highest bonding orbital for the metal complexes with less than half-filled d-shells. On the contrary, the latter interaction may indicate the metal-to-ligand charge transfer, which causes positive spin densities on the lowest antibonding orbital of the ligand.

As mentioned above, the observed isotropic shifts of the pyridyl ring protons are not reasonably explained only by a σ-mechanism, an important contribution of the π-mechanism is deduced. The large upfield shift of the H_2 signal, as well as the α-methylene signals, would be based on the positive spin densities on the C_2 and N-α-methylene carbons. π-Spin delocalization mechanism causes the sign alternation of the isotropic shifts. The signs of the $H_2(+)$, $H_3(-)$ and $H_4(+)$ isotropic shifts of the pyridyl ring protons in both the R-pa and phen complexes support this mechanism. The isotropic shifts of $H_2(+)$, $H_3(-)$ and $H_4(+)$ protons for WBr_4(phen) are explained by the net α-spin produced through the ligand-to-metal β-spin transfer. Hückel molecular orbital (HMO) calculations indicate that the π-spin densities on C_2, C_3, C_4 and C_5 of the highest occupied bonding orbital of phen are 0.141, 0.012, 0.203 and 0.397, respectively [24]*, which are close to those reported previously [25, 26]. The density on C_3 is very small, resulting in some negative spin density by the correlation effect. Thus, these findings seem to be consistent with the observed isotropic ^{1}H NMR shifts, except for the small observed shift of H_5 in spite of the large positive spin density at C_5. This inconsistency between the observed H_5 isotropic shifts and the HMO-calculated spin density at C_5 also resemble that for the $[Cr^{II}(phen)_3]^{2+}$ complex [25], in which π-spin delocalization is predominant. On the other hand, π-spin densities on C_2, C_3, C_4 and C_5 of the lowest unoccupied antibonding orbital of phen have been calculated to 0.118, 0.295, 0.003 and 0.258, which are appreciably inconsistent with the observed isotropic shifts.

For the R-pa complexes, π-spin delocalization also seems to be predominant. The signs of the isotropic shifts of $H_2(+)$, $H_3(-)$, $H_4(+)$ and $H_5(+)$ of WBr_4(Me-pa) (see Table 5) are qualitatively consis-

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*Hückel eigen vectors were calculated using the parameters $\alpha_N = \alpha_C + 0.5\beta_{CC}$ and $\beta_{CN} = \beta_{CC}$.

tent with calculated π-spin densities on C_2, C_3, C_4 and C_5 for the highest occupied bonding orbital of Me-pa, although the H_5 signal exhibits the small ^1H isotropic shift and the large positive spin density is calculated at C_5 (spin densities: C_2, 0.286; C_3, 0.040; C_4, 0.589; C_5, 0.473). Furthermore, the isotropic shift of H_a of WBr_4(Me-pa) is appreciably positive, although the π-spin density on the azomethine carbon (C_a) is very small (0.012), indicating some negative spin density by the correlation effect. Thus, a downfield shift should be observed for the H_a signal assuming only π-spin delocalization. However, the H_a signal occurs at an appreciably high field, which may partially come from σ-spin delocalization. This effect was reported for tris(salicylaldimines)vanadium(III) [27] which contains the d^2 metal ion isoelectronic to tungsten(IV).

Thus, both the π-spin and the σ-spin delocalizations contribute to the isotropic shifts of WBr_4-(N-N) complexes. The observed large upfield isotropic shift at H_2 protons of phen and R-pa ligands may be caused by the sum of both the contributions.

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