Electron Paramagnetic Resonance Investigation of Transition Metal Complexes. XII. Bisnaphthalene Complexes of Vanadium(0), Chromium(I), Chromium(–I), and Chromium(–III)

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Abstract: Bisnaphthalene complexes of V(0) and Cr(I) ("sandwich complexes") have been detected by epr spectroscopy, and their *g* values and hyperfine coupling constants have been measured. Comparison with the previously reported data for bisbenzene, bistoluene, and bismesitylene complexes shows that only one ring of each naphthalene is involved in the bonding. Two bisnaphthalene complexes of chromium in valence states lower than 0 have also been observed and spectroscopically characterized. Valence states –I and –III are suggested based on epr evidence.

In a former communication[1] we showed that in bisarene "sandwich" complexes of V(0) and Cr(I) the coupling of the unpaired spin with the aromatic hydrogen nuclei is virtually the same for the three arenes investigated (benzene, toluene, and mesitylene); namely $a_H = 10.8 \pm 0.3$ MHz for the V(0) complexes, and $a_H = 9.7 \pm 0.3$ MHz for the Cr(I) complexes. Within the resolution capacity of the method, all ring hydrogen nuclei were found equivalent, and no methyl splitting was observed. Also the *g* value, 1.987 for both the V(0) (second-order correction applied; apparent *g* value, 1.992; the corrected value in ref 1 is erroneous) and the Cr(I) species, as well as the interaction of the unpaired spin with the metal nucleus in the case of the V(0) complexes ($a_V = 175 \pm 3$ MHz) were found to be independent of the arene molecule. Thus the bisarene complexes of V(0) and Cr(I) may be said to be experimentally defined by the data given above.

Several suggestions have been made as to how unpaired spin density is delocalized to such a considerable extent onto the aromatic hydrogens: by out-of-plane bending of the hydrogen atoms;[1,2] by direct overlap of metal orbitals with ring protons ("through space coupling");[3] or by metal-to-ligand electron delocalization in σ orbitals of the aromatic compound.[1,4,5]

Recent extended Hückel molecular orbital calculations of Prins and Reinders[6] and of Drago, *et al.*,[7,8] have made it very probable that, at least in the cases of V and Cr complexes, the overlap of metal orbitals with an extensively delocalized σ molecular orbital of the aromatic compound is the most important mechanism by which spin is placed on the hydrogen nuclei.

In the present communication we wish to report on bisnaphthalene and bisanthracene complexes of vanadium and chromium in different valence states. The epr signals are perfectly in line with our former results and should provide an experimental base for further theoretical work on this type of compound.

Bisnaphthalene and Bisanthracene Complexes of V(0)

The reduction of VCl_3 with lithium naphthalide (LiNp) in tetrahydrofuran ($LiNp/VCl_3 = 3$) leads to a dark, homogeneous solution which exhibits the epr signal represented in Figure 1. The epr spectroscopic parameters a_H, a_V, and *g* are identical with those mentioned above, thus indicating strongly the formation of a bisarene complex. Number and intensity distribution of the hydrogen hyperfine lines show that only one ring of each of the two naphthalene molecules is in interaction with the metal. This is best seen from the second-derivative representation, Figure 1c (2 × 4 hydrogens, 9 lines, 1:8:28:56:70:56:28:8:1).

The presence of a bisnaphthalenevanadium(0) complex could unequivocally be confirmed by the epr spectrum of the complex prepared from perdeuterated LiNp; see Figure 2. The signal shows exactly the shape and line width as predicted by computer simulation. The simulated signal of Figure 2c was obtained by varying the line width, for the given a_H, until best fit with the experimental signal, Figure 2a, was observed (Lorentzian line shape). For the signal of Figure 2d this line width was maintained, and the hyperfine splitting constant a_H was replaced by $a_D = (g_D/g_H)a_H = 0.153a_H$.

If the VCl_3 is reduced with lithium anthracenide instead of LiNp, an epr signal identical with that shown in Figure 1, although with less intensity, is observed, indicating that the bisarene complex is also formed with anthracene, making use only of one of the outer rings of each molecule.

The formation of the bisarene complexes may be formulated (for the naphthalene case) as

$$VCl_3 + 3LiNp \longrightarrow (C_{10}H_8)_2V^0 + 3LiCl + C_{10}H_8$$

If LiNp is present in excess, bisnaphthalenevanadium(0) is further reduced and the epr signal disappears. Up to six further electrons may be taken up by the complex,

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[1] G. Henrici-Olivé and S. Olivé, *Z. Phys. Chem.* (Frankfurt am Main), **56**, 223 (1967).

[2] K. E. Schwarzhans, *Angew. Chem.*, **81**, 433 (1969).

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[6] R. Prins and F. J. Reinders, *Chem. Phys. Lett.*, **3**, 45 (1969).

[7] M. F. Rettig and R. S. Drago, *J. Amer. Chem. Soc.*, **91**, 3432 (1969).

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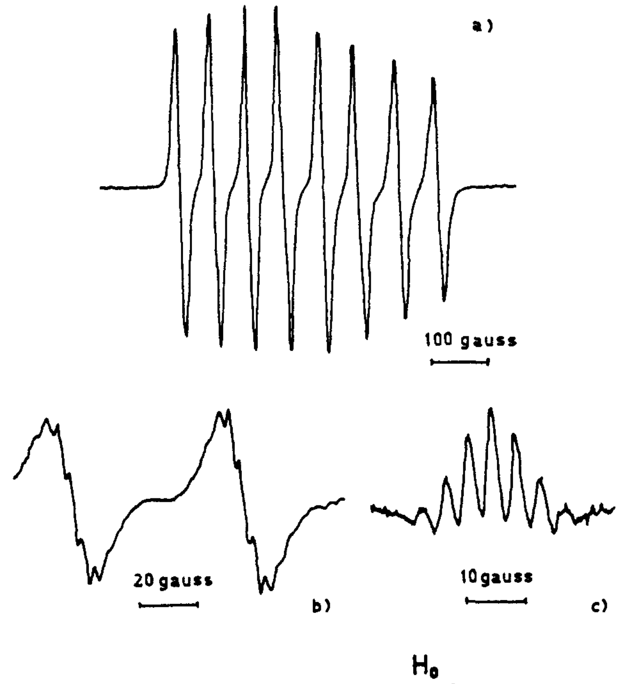

Figure 1. Epr signal of bisnaphthalenevanadium(0) in THF, temperature 20°: (a) total spectrum, (b) third and fourth lines at higher dilution, (c) fourth line in second-derivative representation.

as demonstrated formerly[9] by hydrolysis and deuterolysis experiments.

Bisnaphthalene Complexes of Cr(I), Cr(−I), and Cr(−III)

In contrast to the bisnaphthalenevanadium(0), the isoelectronic Cr(I) species cannot be obtained directly by adding the correct amount of LiNp (Li/Cr = 2). The epr signal of the Cr(I) complex (Figure 3a) is, however, observed if the $CrCl_3$ solution is added to an excess of LiNp (Li/Cr $\simeq$ 5), the reaction product is then hydrolyzed with a small amount of water (H_2O/Cr $\simeq$ 50), and the chromium is oxidized with O_2 (the amount of O_2 present in the water is mostly sufficient; excess oxygen should be avoided to prevent epr line broadening). The bisnaphthalenechromium(I) complex is identified by its epr spectroscopic data: g = 1.987, a_H = 10.0 ± 0.3 MHz (*cf.* the values reported in the first section of this paper).

In the range of $5 \leqslant \mathrm{Li/Cr} \geqslant 6$ a relatively strong epr spectrum is observed (corresponding to some 30% of the chromium, assuming one unpaired electron per Cr). The spectrum appears at a somewhat lower field than that of the Cr(I) complex (see Figures 3b–d; the dotted line marks the place of the center of the Cr(I) signal in Figure 3a). No LiNp signal appears, indicating that the LiNp is used up for further reduction of the Cr species; the resemblance of the epr spectra of Figures 3b–d to that of Figure 3a points to further reduced bisnaphthalene–chromium species. The aspect of the spectrum depends on the ratio Li/Cr. At Li/Cr = 5 two odd-numbered sets of lines may be discerned. This is seen especially well from the second-derivative representation on the right of Figure 3d, where the two sets are marked by ○ and ×. The number of lines in each set cannot be determined exactly, since in this relatively well-resolved spectrum ^{53}Cr satellite lines overlap with the outer lines of the main spectra, especially on the low-field side. However, the intensity distribution seems to be binomial and in line with that to be expected for bisnaphthalene complexes (compare the vanadium case). At a higher Li/Cr ratio the right-hand side of the spectrum gains importance, suggesting that the set of lines marked with × belongs to a more reduced species. At higher Li/Cr the lines also become broader, and much of the hyperfine structure gets lost. (This is not a concentration broadening effect, since dilution does not improve resolution.)

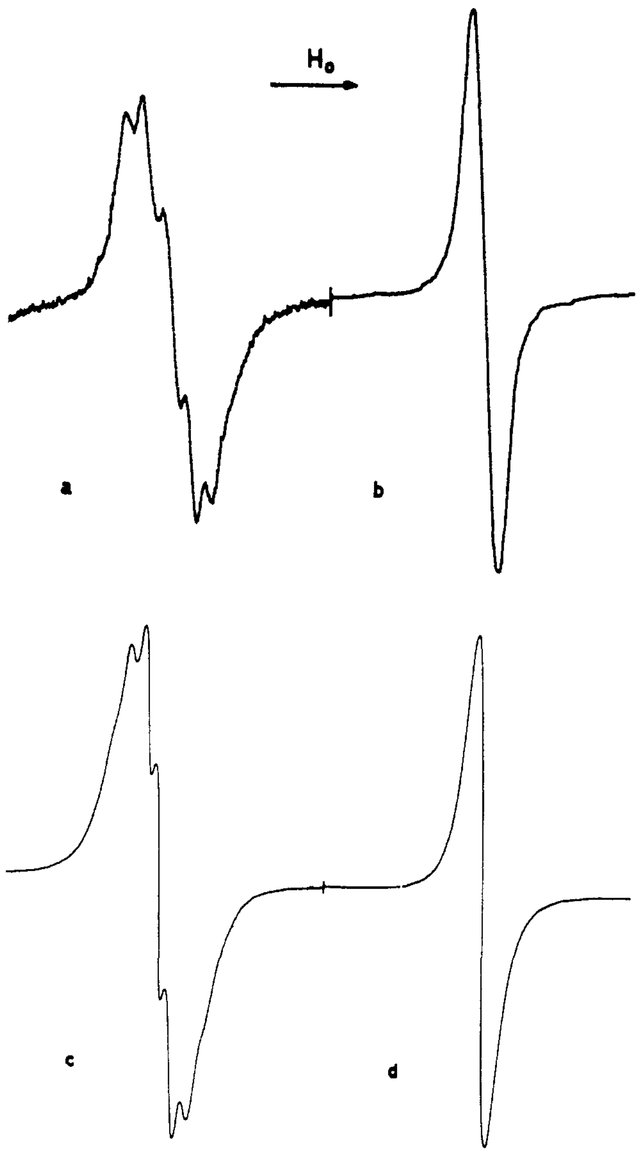

Figure 2. Measured (a and b) and computer-simulated (c and d) epr signals of $(C_{10}H_8)_2V^0$ and $(C_{10}D_8)_2V^0$, fourth line.

As in the case of the vanadium, signals with the correct appearance and line width are obtained if perdeuterated LiNp is used. The hyperfine structure from the aromatic deuterium nuclei is not resolved, and only one broadened line appears for each chromium species. At Li/Cr = 5 (Figure 4, signal a), the low-field line predominates and the high-field line appears

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(9) G. Henrici-Olivé and S. Olivé, *J. Organometal. Chem.*, **9**, 325 (1967).

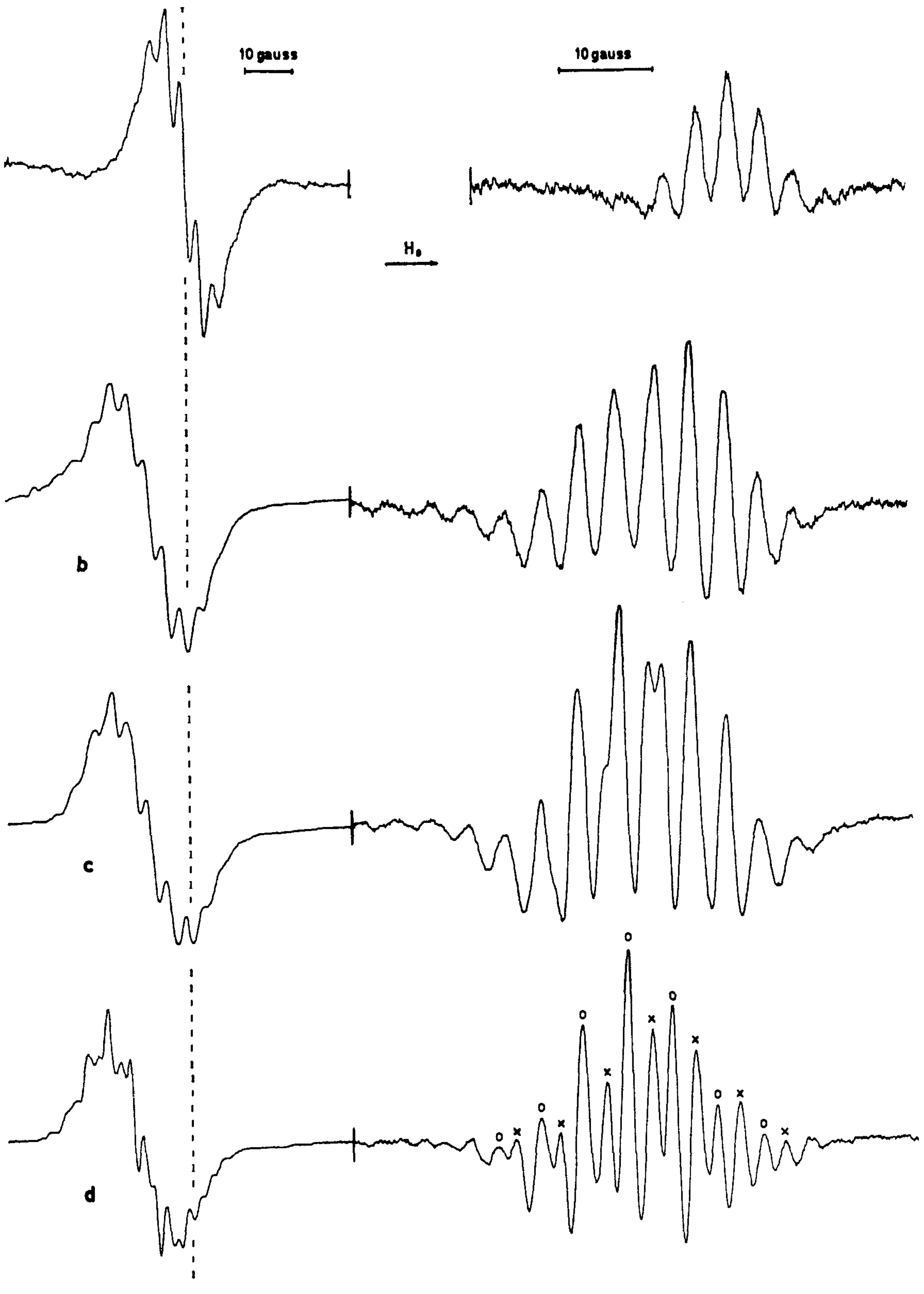

Figure 3. Epr spectra of bisnaphthalene complexes of chromium: (a) bisnaphthalenechromium(I), (b) signal at Li/Cr = 6.0, (c) signal at Li/Cr = 5.5, (d) signal at Li/Cr = 5.0; left = first-derivative, right = second-derivative representation.

only as a shoulder. At Li/Cr = 6 (signal b), the low- and high-field lines have about the same intensity. The spectra of Figure 4 show, therefore, even more clearly than those of Figure 3 that the high-field part of the spectra belongs to a more reduced species, since it appears with higher relative intensity at higher Li/Cr ratio.

The two lines of the perdeuterated species are some 7 G apart and have *g* values of 1.995 and 1.990. The position of the low-field line is identical with that of the most intense line of the set marked with ○ in Figure 3d. The *g* value of the high-field line, however, indicates that in the set marked with ×, not the apparently most intense, but the third marked line from the right must

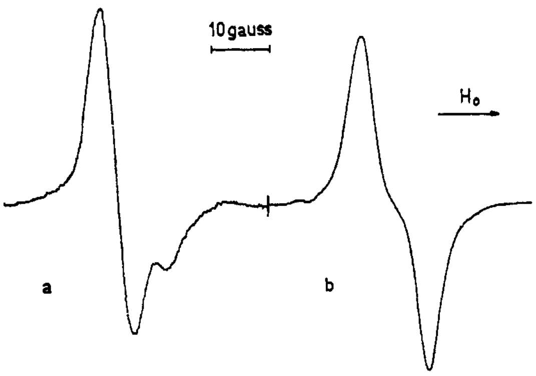

Figure 4. Epr signals obtained with perdeuterated LiNp: (a) Li/Cr = 5, (b) Li/Cr = 6.

be the central line. The true intensity distribution of this set is obviously somewhat masked by incomplete resolution.

The epr spectroscopic data of the different Cr species are summarized in Table I, where the V(0) data are also included. The chromium complexes are specified as Np$_2$-Cr(I), Np$_2$-Cr($-$I), and Np$_2$-Cr($-$III). This specification needs some comment.

Table I. Epr Spectroscopic Data of the Bisnaphthalene Complexes[a]

Complex	g value	a_H, MHz	a_V, MHz
Np$_2$-Cr(I)	1.987	10.0 ± 0.3	
Np$_2$-Cr($-$I)	1.995	13.4 ± 0.6	
Np$_2$-Cr($-$III)	1.990	13.6 ± 0.6	
Np$_2$-V(0)	1.987	10.6 ± 0.3	175 ± 3

[a] Temperature 20°.

The electronic configuration of a bisarene–chromium(I) complex as well as that of a bisarene–vanadium(0) complex is $\ldots(e_{1u})^4(e_{2g})^4(a_{1g})^1$, with the unpaired electron in the $a_{1g}(3d_{z^2})$ orbital. The lowest empty orbital is an e_{2u} (ligand) orbital (see ref 6 and literature therein). Although calculated explicitly only for the bisbenzene complexes (D_{6h} symmetry), this MO level ordering may also be taken as a fairly good first approximation for the bisnaphthalene–chromium(I) and the bisnaphthalene–vanadium(0) complexes, given the close similarity of the g values and the hyperfine constants (compare the first and last rows of Table I with the data given in the first section of the papers).

On the other hand, the similarity of the epr spectroscopic data within the three observed Cr species strongly suggests a similar electronic population at the metal in each case. This requires that the more reduced species store the extra electrons provided by the LiNp in ligand orbitals. (This has already been suggested in ref 9, based on hydrolysis experiments.)

Fischer and Piesbergen[10] reported that the bisarene–chromium(0) complexes are diamagnetic. No epr signal is to be expected; the electronic configuration is most probably $\ldots(a_{1g})^2$. Addition of another electron may lead to $\ldots(a_{1g})^1(e_{2u})^2$. The e_{2u} (ligand) level is assumed to be made up predominantly of the lowest antibonding π orbitals of the two naphthalene ligands. Sufficient overlap should be provided to cause the coupling of the two spins, particularly if the Np molecules are eclipsed. The $\ldots(a_{1g})^1(e_{2u})^2$ configuration is assumed to be responsible for the set of epr lines marked with ○ in Figure 3d, which predominates at Li/Cr = 5 and corresponds formally to Np$_2$-Cr($-$I). The next electron leads to Np$_2$-Cr($-$II), which could have the following configurations: $\ldots(a_{1g})^2(e_{2u})^2$, $\ldots(a_{1g})^1(e_{2u})^3$ (singlet), or $\ldots(a_{1g})^1(e_{2u})^3$ (triplet). From the first two configurations no epr signal is to be expected; in the last case zero-field splitting would most probably broaden the epr lines beyond observability. It is therefore suggested that the set of lines marked with × in Figure 3d represents Np$_2$-Cr($-$III), which has the configuration $(a_{1g})^1(e_{2u})^4$.

It should be noted that the presented epr evidence for the delocalization and pairing of the extra electrons in ligand orbitals corroborates the MO level ordering given by Prins and Reinders ($a_{1g} < e_{2u} < e_{1g}^*$), which otherwise was somewhat doubtful, according to the cited authors.[6]

The smearing out of the hyperfine structure at Li/Cr > 5 may perhaps be due to the formation of even higher reduced chromium species. Hydrolysis and deuterolysis experiments reported earlier[9] have in fact shown that, as in the case of the bisnaphthalene–vanadium complexes, up to six electrons [counted from Cr(0)] may be taken up by the chromium species. The negatively charged complexes of Cr as well of V are interesting intermediates, *e.g.*, for the fixation and reduction of molecular nitrogen.[11,12]

Experimental Section

Solutions of the bisarene complexes were prepared adding the metal salt in THF (concentration 10^{-2}–10^{-3} mol/l.) in an argon countercurrent to the solution in THF (concentration 10^{-1}– 10^{-2} mol/l.).

A varian X-band spectrometer with 100-kHz field modulation was used for the epr measurements. The characteristic parameters (g values, hyperfine coupling constants) were obtained by comparison with a standard sample of peroxylamine disulfonate (g = 2.0055; $a_N = 13.0 \pm 0.1$ G = 36.5 ± 0.3 MHz).

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