

Carbon-13 EPR Hyperfine Interaction in the Complex $[\text{Rh}(\text{CN})_6]^{4-}$ in a KCl Host Lattice

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The hyperfine interaction with ^{13}C in nonenriched $[\text{Rh}(\text{CN})_6]^{4-}$, in a KCl host lattice at 7 K, is measured by continuous-wave X- and Q-band electron paramagnetic resonance, allowing, for the first time, a comparative study of spin densities on the carbon of the axial cyanide in this complex and in the similar $[\text{Co}(\text{CN})_6]^{4-}$ complex. From the experimental data corrected for dipolar interactions, $A_{\text{iso}} = 79.80 \times 10^{-4} \text{ cm}^{-1}$ and $A_{\text{anis}} = 0.76 \times 10^{-4} \text{ cm}^{-1}$.

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In previous papers (1, 2) we reported on the $[\text{Rh}(\text{CN})_6]^{4-}$ complex in a KCl host lattice. This complex is produced by X-ray or 2 MeV electron irradiation on KCl single crystals doped with a 0.5% molar proportion of $\text{K}_3\text{Rh}(\text{CN})_6$. The EPR spectra of this $4d^7$, low-spin, D_{4h} symmetry complex reveal a hyperfine interaction between the unpaired electron occupying a d_{z^2} antibonding orbital and the $I = \frac{1}{2}$ rhodium nucleus, in addition to a superhyperfine interaction with two equivalent nitrogens of the axial cyanides.

Carbon-13 hyperfine interactions are usually very difficult to observe in the EPR spectra of nonenriched transition-metal cyanide complexes, due to the low natural abundance of this isotope (about 1%). Experiments performed by Shock and Rogers at 77 K on the ^{13}C isotopically enriched $[\text{Co}(\text{CN})_6]^{4-}$ $3d^7$ low-spin complex in a KCl host lattice (3) led to the measurement of the hyperfine splitting due to the carbons of the axial cyanides. In this work we report on the ^{13}C hyperfine tensor in nonenriched $[\text{Rh}(\text{CN})_6]^{4-}$ in a KCl host lattice, at 7 K, allowing, for the first time, a comparative study of spin densities on the carbons of the axial cyanides in these complexes.

The EPR experiments were performed at X band (9.680 GHz) and at Q band (35.56 GHz). For X band we used a Bruker ESP380E spectrometer equipped with a dielectric cavity inserted into an Oxford CF-35 variable-temperature cryostat with 100 kHz modulation. For Q band the measurements were made in a Bruker ESP300 under similar conditions. The cubic crystals were mounted on a small Teflon cylinder in a quartz tube. The sample was aligned in such a way that one of the principal axes of the crystal is perpendicular to the magnetic field so that one can obtain both the

parallel and the perpendicular features of the spectrum with the magnetic field parallel to either of the other axes.

Figure 1 compares the X- and the Q-band parallel spectra taken at 7 K. The central part of the spectrum corresponds to the interaction between the unpaired electron and the rhodium nucleus as well as with two equivalent nitrogens of the axial cyanides. It is flanked by two low-intensity satellites, whose spacing is frequency independent. Angular-dependence experiments on these very well-defined satellite lines show that their spacing is almost isotropic. This isotropy immediately refutes the hypothesis of a pair interaction as the source for these lines. The ratio of the intensity of the satellite lines to the central lines is as expected for ^{13}C lines in natural abundance. Consequently we interpret these satellite lines as arising from the interaction between the unpaired electron and a ^{13}C nucleus belonging to an axial cyanide. The probability of finding two ^{13}C nuclei in the same molecule is considered negligible.

Table 1 shows the spin-Hamiltonian parameters measured for divalent rhodium and divalent cobalt hexacyanides. Experiments with T_2 -based selection of species, performed in field-swept pulsed EPR at 7 K, show that the perpendicular multiplets are formed by six lines instead of seven lines as reported in Ref. (1). As a consequence, the measured perpendicular component of the hyperfine interaction with the rhodium nucleus is $3.9 \times 10^{-4} \text{ cm}^{-1}$ and not $8 \times 10^{-4} \text{ cm}^{-1}$. Dipolar interactions between the unpaired electron and the ^{13}C nucleus, as well as between the unpaired electron and the ^{14}N nucleus, considering a point dipole model, are not negligible when compared to the small hyperfine anisotropies. The dipolar correction, along the bond axis, for ^{13}C , is $1.67 \times 10^{-4} \text{ cm}^{-1}$ for a 2 Å Rh–C bond length, and $1.97 \times 10^{-4} \text{ cm}^{-1}$ for a 1.89 Å Co–C distance. For ^{14}N , considering the distance Rh–C–N = 3.1 Å, the dipolar correction is $0.3 \times 10^{-4} \text{ cm}^{-1}$, and it is $0.33 \times 10^{-4} \text{ cm}^{-1}$ for a distance Co–C–N = 2.99 Å.

From Table 1 the axial ^{13}C hyperfine interaction is clearly almost isotropic. An isotropic hyperfine interaction (A_{iso}) may arise from inner-*s*-shell polarization or from direct unpaired electron delocalization on available *s* orbitals. If A_{iso}

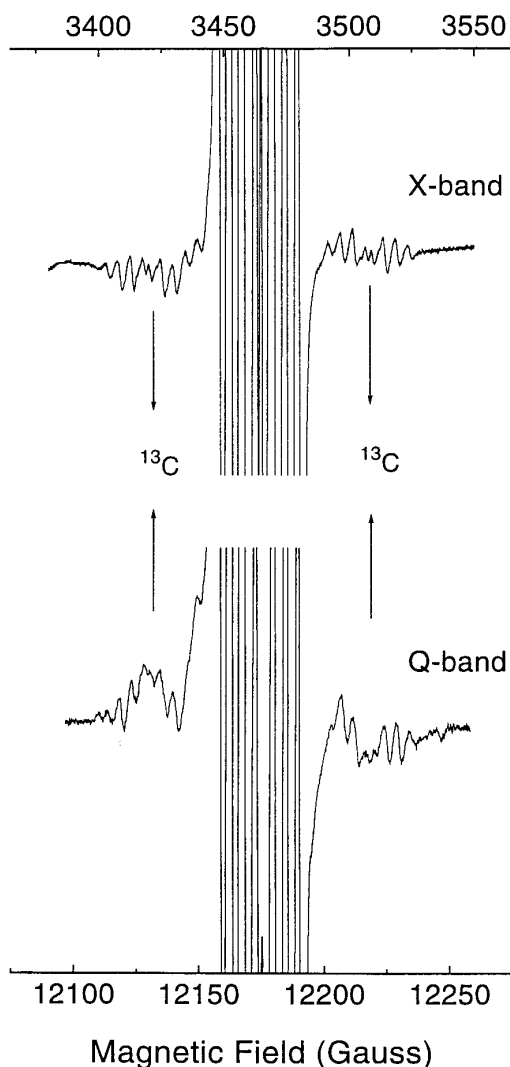


FIG. 1. Comparison between X-band (9.680 GHz) and Q-band (35.56 GHz) EPR spectra of the $[\text{Rh}(\text{CN})_6]^{4-}$ complex in a KCl host lattice taken at 7 K on the same magnetic field scale, centered at the same g value. The external magnetic field is parallel to the principal symmetry axis of the complex.

^{13}C arises mainly via the polarization mechanism, we would expect a similar value for this interaction both in Co and in Rh complexes. This is obviously not the case, suggesting that

TABLE 2
Unpaired Electron Densities

Species	C_s^c	C_p^c	N_s^c	N_p^c	$ \alpha ^2$
$[\text{Rh}(\text{CN})_6]^{4-}$	0.077	0.025	0.008	~ 0	0.61 ^a
$[\text{Co}(\text{CN})_6]^{4-}$	0.027	0.007	0.006	0.014	0.68 ^b

^a This work.

^b Reference (3).

the main contribution to A_{iso} comes from unpaired electron density on the carbon $3s$ orbitals. In this way, A_{iso} will have the same sign as the nuclear g factor of ^{13}C , which is positive. This leads to the conclusion that both A_{\parallel} and A_{\perp} are also positive. From our experimental data corrected for dipolar interactions we calculate $A_{\text{iso}} = 79.80 \times 10^{-4} \text{ cm}^{-1}$ and $A_{\text{anis}} = 0.76 \times 10^{-4} \text{ cm}^{-1}$.

The unpaired electronic densities on carbon $3s$ and $3p$ orbitals, C_s^c and C_p^c , may be estimated by taking the ratio between the measured A_{iso} and A_{anis} and the values calculated assuming one unpaired electron occupying a $3s$ or a $3p$ orbital (4). These values are respectively 1033.4×10^{-4} and $30.17 \times 10^{-4} \text{ cm}^{-1}$. The results are shown in Table 2. Data for the cobalt complex differ from those reported in Ref. (3) as a consequence of dipolar correction. Unpaired electron densities on the metal, $|\alpha|^2$, are calculated with a ligand-field model described in Refs. (1, 3).

Molecular-orbital calculations should, at least in principle, be more adequate for the understanding of the electronic distribution in these complexes. Unfortunately, accurate hyperfine interaction calculations are not available in the literature. The ligand-field model, on the other hand, presents good internal consistency if the unpaired electron densities in the two complexes under study are compared. The $4d$ radial wavefunction is significantly more spread out than the $3d$ function (5). As a consequence, and also because of the slightly smaller $|\alpha|^2$ value for the rhodium complex, there is much more transferred spin density on the carbon $3s$ and $3p$ orbitals for this complex than for the cobalt complex. On the other side, the calculated transferred spin density on the farther axial nitrogen, which is roughly the same in the $3s$ orbitals of both complexes, is smaller in the $3p$ orbitals for

TABLE 1
Spin-Hamiltonian Parameters

Species	Host	g_{\parallel}	g_{\perp}	$^M A_{\parallel}^a$	$^M A_{\perp}^a$	$^C A_{\parallel}^a$	$^C A_{\perp}^a$	$^N A_{\parallel}^a$	$^N A_{\perp}^a$
$[\text{Rh}(\text{CN})_6]^{4-}$ ^b	KCl	1.997	2.081	-11.4	3.9	83.0	78.2	4.2	4.2
$[\text{Co}(\text{CN})_6]^{4-}$ ^c	KCl	2.008	2.102	69.96	-61.85	28.32	26.15	3.49	2.52

^a Hyperfine interactions measured in 10^{-4} cm^{-1} . Signs have been assigned as described in the text. Ligand values are corrected for dipolar interactions.

^b This work.

^c Reference (3).

the rhodium complex. This suggests a different degree of bending of the axial cyanides (6) in these complexes.

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