

ESR OF LOW SPIN Co(II) AND Fe(I) WITH
CYANIDE AND ISOCYANIDE LIGANDS

A. O. Caride, S. I. Zanette and J. Danon
Centro Brasileiro de Pesquisas Físicas
Rio de Janeiro - Brazil

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The low spin $3d^7$ compounds presenting frequently square pyramidal and trigonal bipyramidal symetries have been object of considerable interest in the recent times.

The irradiation of single cristal of diamagnetic hexacyanides of Co(III) and Fe(II)^{1,3,4} allows the study of this type of molecules by ESR, in conditions of excellent resolution. This is because the very low concentrations of the paramagnetic species obtained by irradiation reduce to zero the magnetic dipolar broadening. On the other hand this technique made possible the finding of isocyanide bonds, as in the complex $\text{Co}(\text{CN})_4(\text{NC})_2^{4-}$, both as an intermediate and a stable species¹.

TABLE I

Compound	ϵ_{\parallel}	ϵ_{\perp}	A(G)	B(G)	Inter- action with N14	χ (au)	α^2	Assignment
Co(CN)_6 in KCl (a)	2.0067	2.1006	70.3	- 60.4	I=2 (3.5G)	- 1.4	.71	$\text{Co(CN)}_5(\text{C})_2^{4-}$
$\text{Co(CN)}_6\text{K}_3$ (I) (b)	2.006	2.095	54	- 70	I=2 (3.4G)	- 1.6	.68	$\text{Co(CN)}_5(\text{NC})_2^{4-}$ (unstable)
$\text{Co(CN)}_6\text{K}_3$ (II) (b)	2.004	2.174	89	- 25	-	- 2.7	.73	Co(CN)_5^{3-} (stable)
Co(CN)_5 in sol. (c)	2.003	2.165	87	- 28	-	- 2.5	.72	Co(CN)_5^{3-} (stable)
$\text{Co(CN)}_6\text{Cs}_2\text{Li}$ (a)	2.0070	2.1622	89	- 25	-	- 2.5	.71	Co(CN)_5^{3-} (stable)
$\text{Fe(CN)}_6\text{K}_4$ (d)	2.002	2.086	-	-	-	-	-	Fe(CN)_6^{5-} (unstable)
Fe(CN)_6 in KCl (e)	1.9998	2.0959	-	-	I=1 (6-11G)	-	-	$\text{Fe(CN)}_5(\text{NC})^{5-}$ (stable)
Fe(CN)_6 in NaCl (e)	2.0000	2.0766	-	-	I=1 (6-11G)	-	-	$\text{Fe(CN)}_5(\text{NC})^{5-}$ (stable)
Fe(CN)_6 in KBr (e)	1.9998	2.1035	-	-	I=1 (6-11G)	-	-	$\text{Fe(CN)}_5(\text{NC})^{5-}$ (stable)

(a) Present work; (b) Values from ref. (1); (c) Values from ref. (2); (d) Values from ref. (3);
(e) Values from ref. (4).

In table I the signs of the eigenvalues of the hyperfine interaction are those which give the maximum calculated value of α^2 , which is the fraction of time that the electron spends at the central ion and χ , the contribution in atomic units of the Fermi contact term to the hyperfine tensor.

The value of α^2 and χ are in agreement with those calculated by Mc Garvey⁵ and are consistent with a sigma bond such as the one corresponding to a d_{z^2} orbital, with small contributions from 4s orbital to the contact term, this arising from the fact that d_{z^2} belongs to the a_1 representation in D_{4h} and C_{4v} permitting its hybridization with 4s orbitals. Furthermore, the measures of g values agree with this assumption.

From the analysis of table I many features may be pointed out. The stability of the isocyanide bonds seems to be mainly related to the influence of the lattice since it has been impossible to obtain them in solution and they are unstable in the pure compound. However if the diamagnetic ion is introduced in a cubic lattice the isocyanide bonds formed by irradiation are stabilized. This can be explained by observing that the metal ion goes to a substitutional position in a cation site, while the CN^- ligands occupy approximately the six nearest Cl^- positions. Thus in order to achieve charge compensation in the crystal one K^+ vacancy must appear in the case of Fe(II) and two in the case of Co(III). We believe these vacancies to be responsible for the stabilization of the isocyanide bonds which

are closer to them. This is consistent with the fact that the esr spectra of iron and cobalt complexes shows HFS interaction with one and two nitrogen nuclei respectively.

Experimentally, the distortion appears only along the 100 directions, indicating that the vacancies placed along these directions are specially effective in stabilising the iso cyanide bonds.

The $\text{Co}(\text{CN})_5^{3-}$ ion has until now only been identified in solution. In the solid state it dimerizes to the diamagnetic $\text{Co}_2(\text{CN})_{10}$ complex ⁶. The irradiation procedure allows the obtention of the paramagnetic $\text{Co}(\text{CN})_5^{3-}$ ion, stabilized in a host lattice.

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REFERENCES:

1. J. Danon, R. P. A. Muniz, A. O. Caride and I. Wolfson, *J. Mol. Structure* 1 (1967-68) 127-130.
2. H. B. Gray, private communication 1969; J. J. Alexander and H. B. Gray, *J. Am. Chem. Soc.* 89, 3356 (1967).
3. S. I. Zanette, *Thesis, Centro Brasileiro de Pesquisas Físicas*, 1968.
4. K. D. J. Root and M. C. R. Symons, *J. Chem. Soc. (A)* 1968, 2366.
5. B. R. Mc Garvey, *J. Phys. Chem.* 71, 51 (1967).
6. A. W. Adamson, *J. Am. Chem. Soc.* 73, 5710 (1951).