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The CN stretch of hexacyano metallates as a sensor of ligand–outer cation interactions—II. Ferrocyanides

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Abstract—The CN stretching frequencies of 14 ferrocyanides are correlated with atomic parameters of the outer cations. The contributions of σ and π interactions to the CN frequency shifts are calculated.

INTRODUCTION

THE vibrational frequency of the CN ligands in hexacyano metallates are dependent on the electronic interactions of the ligands with the central cation [1, 2]. The outer cations have a lesser but significant influence on ν_{CN} [3]. Both effects can be described in terms of σ and π interaction mechanisms between the CN ligand and the inner and outer cations.

In a recent publication we have shown how the σ and π contributions to the CN shifts can be calculated by correlation ν_{CN} with atomic parameters of the outer cation [4]. The model has been applied with success to ferricyanides and cobalticyanides, obtaining reliable and physically significant values of the interaction parameters [4].

In this paper, the second of the series, we apply this model to a family of ferrocyanides. The results are compared with those of ferricyanides and cobalticyanides.

THEORY

The model used to describe the effect of σ and π interactions on ν_{CN} is rather simple [4]. Both mechanisms are supposed to contribute independently to ν_{CN} and in turn each contribution is factorable into ligand and cation factors. The equation is

$$\nu = \nu_0 + B\sigma P\sigma + B\pi P\pi. \tag{1}$$

The $P\sigma$ and $P\pi$ parameters correspond to the ability of the outer cation to promote σ and π interactions with the CN ligands, while the parameters $B\sigma$ and $B\pi$ measure the sensitivity of the CN vibration to these mechanisms.

For $P\sigma$ we have selected the polarizing power of the outer cation measured by Z/r^2. (Z = cation charge; r = ionic radius.) For $P\pi$ we have selected the parameter nr^2/Z, where n is the number of electrons in the T_{2g} level of the cation available to be transferred to the ligand, this "back donation" being opposed by the polarizing power of the cation Z/r^2. The $B\sigma$ and $B\pi$ parameters will be calculated from the correlation of ν_{CN} with $P\sigma$ and $P\pi$ according to Eqn (1).

EXPERIMENTAL

The synthesis of ferrocyanides was carried out by standard procedures [4]. The products were characterized by i.r. spectroscopy. They were run as Nujol mulls in a UR-20 Carl Zeiss spectrometer.

The broadness of the bands makes the frequencies uncertain by $\pm 2\ cm^{-1}$. In favourable cases the error is $\pm 1\ cm^{-1}$.

The values of Z/r^2 used for $P\sigma$ and $P\pi$ are taken from the work of ZHANG [5].

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