

## The CN stretch of hexacyanometallates as a sensor of ligand–outer cation interactions—I. Ferricyanides and cobalticyanides

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**Abstract**—The CN frequencies of 39 hexacyanometallates (ferricyanides and cobalticyanides) are correlated with atomic parameters of the outer cation. Evidence is obtained of the presence of  $\sigma$  and  $\pi$  interactions in the bonding of the outer cation to the CN ligand. Quantitative estimation of the effect of these mechanisms on the shift of  $\nu_{\text{CN}}$  is presented.

### INTRODUCTION

The CN stretch in hexacyanometallates has been used as a sensor for bonding interactions of the central cation to the C end of the CN ligand [1–3]. This frequency has also been used to probe the interactions of the outer cation to the N end of the CN group [4]. The interactions have been described in qualitative fashion in terms of two bonding mechanisms,  $\sigma$  and  $\pi$  [2, 4]. In the present communication we report a correlational study of  $\nu_{\text{CN}}$  in ferricyanides and cobalticyanides with atomic parameters of the outer cations which provides clear evidence of the presence of  $\sigma$  and  $\pi$  interactions and a quantitative estimation of their effects on  $\nu_{\text{CN}}$ .

### THEORY

#### *Molecular orbitals of the complex*

Due to the symmetry of the molecular orbitals of the CN ligands, the energy diagram for their interactions with the central cation via the C atom or with outer cations via the N end are analogous [5, 6]. The only difference is that the strength of the interaction with the central cation is greater than with the outer cation. For this reason, the electronic distribution of the outer cation corresponds to a high spin species [6].

The  $\sigma$  interaction involves proper combinations of atomic orbitals of the CN group and the cation, forming the low energy levels  $A_{1u}$ ,  $E_g$  and  $T_{1u}$  (see Fig. 1). These levels are mainly of CN character and the interaction can be envisaged as a polarization of the N atomic orbitals towards the cation, leading to transfer of electronic charge from the ligand to the cation. The interaction also strengthens the CN triple bond and raises  $\nu_{\text{CN}}$  [2, 6, 7].

The  $\pi$  bonding interaction involves the  $T_{2g}$  electrons of the cation with the  $\pi$  and  $\pi^*$  orbitals of the CN ligand. It is supposed to transfer electronic charge from the cation to the empty  $\pi^*$  orbitals of the CN groups. This transfer, called “back donation”, weakens the CN bond and lowers its frequency [2, 6, 7].

#### *Model for the effect of $\sigma$ and $\pi$ interactions on $\nu_{\text{CN}}$*

We propose a simple model for the effect of  $\sigma$  and  $\pi$  interactions on  $\nu_{\text{CN}}$  in which each mechanism contributes independently to the  $\nu_{\text{CN}}$  shift. Each contribution in turn is factorable into ligand and cation factors. The equation describing the model is:

$$\nu = \nu_0 + b_\sigma p_\sigma + b_\pi p_\pi \quad (1)$$

The  $p_\sigma$  and  $p_\pi$  parameters correspond to the ability of the cation to promote  $\sigma$  and  $\pi$  interactions with the CN ligand, while the parameters  $b_\sigma$  and  $b_\pi$  measure the sensitivity of the CN vibration to these two mechanisms.

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