

The CN stretch of insoluble metal nitroprussides as a sensor of ligand-outer cation interactions

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Abstract- The CN frequencies of insoluble metal nitroprussides are correlated with the atomic parameters of the outer cations. The results indicate that the nature of the interaction is predominantly of the σ donor-acceptor type with no relevant π back-donation from the outer cations to the CN ligand.

Introduction

The CN stretching vibrational frequency in hexacyanometallates is controlled by electronic interactions of the CN ligand with the central and outer cations. Both interactions have been described in terms of two mechanisms¹⁻³:

- a) Donation of electrons from the σ orbitals of the CN ligand to the A_{1g} , E_g and T_{1u} orbitals of the cations;
- b) Back donation of T_{2g} electrons from the cations to the empty π^* orbitals of the CN group.

The σ -bonding mechanism increases ν_{CN} while π^* back donation should decrease this frequency^{2,4}. In the interaction of the central cation with the C end of the ligand, both mechanisms are important³ but in the bonding of the N end to the outer cation, the σ mechanism predominates, except in cases of cations with large number of T_{2g} electrons available and low polarizing power Z/r^2 to hold them back (e.g. Ag^+ and Cd^{2+})⁵.

The correlation of ν_{CN} with atomic parameters of the outer cations permits the calculation of the contributions of both mechanism to the CN frequency shifts.