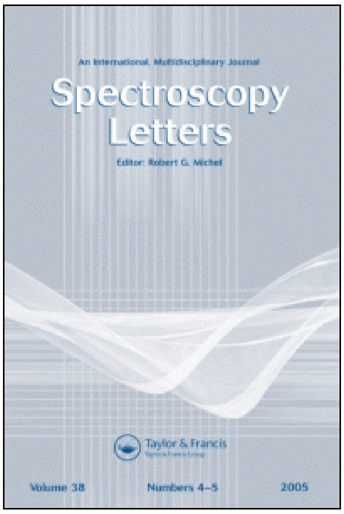

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The CN Stretch of Insoluble Metal Nitroprussides as a Sensor of Ligand-Outer Cation Interactions

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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 controled by electronic interactions of the CN ligand with the central and outer cations. Both interactions have been described in terms of two mechanisms[1-3]:

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 important[3] 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.

The method has been applied with sucess to ferricyanides and cobalticyanides[5], ferrocyanides[6] and acetonitrile complexes with cationic Lewis acids[7].

Nitroprussides are an important and interesting family of compounds in which the central divalent low spin Fe^{II} is coordinated to one NO^+ and five CN^- ligands. However, the actual charge of the Fe^{II} atom is increased by strong withdrawal of electrons by π^*-back donation to the NO^+ ligand[8]. This increases the polarizing power of the central cation and produces a greater withdrawal of electrons from the CN groups by the σ interaction mechanism, increasing its CN frequency more than 100 cm^{-1} above that of ferrocyanides and even 30-40 cm^{-1} higher than ferricyanides[9,10]

It would be interesting to explore the nature of the bonding of the CN group to the outer cations in nitroprussides using ν_{CN} *vs* cation parameters correlations[5-7]. Unfortunately, the lower symmetry of the $Fe^{II}[(CN)_5NO]^{2-}$ anion (C_{4v}), compared to that of the hexacyano anions (O_h), produces a splitting of the CN bands into four allowed transitions: ν_1CN(axial), ν_2CN(radial)(A_1), ν_{10}CN(radial)(B_1) ν_{16}CN(radial)(E_1) [11]. This makes it difficult to apply the method of frequency-cation parameters correlations. However, the insoluble transition metal nitroprussides from Mn to Zn, have only a single broad CN band and are amenable to be studied by this method.

In this communication we present the correlations and discuss the nature of CN-outer cation interactions in transition metal nitroprussides.

Experimental

The synthesis of nitroprussides was carried out by standard procedures as reported in previous works[12,13]. The products were characterized by IR spectroscopy. They were run as Nujol mulls in a FT-IR (Phillip) spectrometer. The frequency are precise to 1 cm^{-1}. The values of Z/r^2 are taken from the work of Zhang[14].

Results and discussion

The ν_{CN} frequencies of the insoluble nitroprussides from Mn^{2+} to Zn^{2+} are presented in Table 1. The CN stretch is a singlet in the range of 2170-2205 cm^{-1} with Mn^{2+} and Cu^{2+} at the extremes. If the interaction of the CN group with the outer cation is of σ nature, the shift in ν_{CN} should be linear with

Table 1. Frequency ν_{CN} for nitroprussides and unperturbed ν^o_{CN} for CH_3CN complexes

No.	Outer Cation	ν_{CN} Nitroprussides	ν^o_{CN} CH_3CN	p_σ Z/r^2
1	Mn^{2+}	2174	2290	3.287
2	Fe^{2+}	2179	2295	3.463
3	Co^{2+}	2188	2298	3.652
4	Ni^{2+}	2192	2302	3.858
5	Cu^{2+}	2205	2312	3.858
6	Zn^{2+}	2192	2298	3.652

the polarizing power of the outer cation which atracts the σ electrons of the N end of the ligand:

$$\nu_{CN} = \nu^o_{CN} + b_\sigma p_\sigma \qquad (1)$$

where p_σ is the polarizing power of the cation Z/r^2 and b_σ measures the sensitivity of the CN vibration to the σ interaction.

In Table 2 the correlation parameters for ν_{CN} *vs* Z/r^2 are presented. The correlation is good with a value of $r = 0.914$ for six experimental points, giving a confidence level of 99.0%. The errors of the intercept and slope are 1.8 and 22% respectively. We can assume that σ interaction is the predominant mechanism.

In order to evaluate the possible contribution of Π^* back-donation, we correlate ν_{CN} with both σ and Π^* parameters[5-7]. Since back donation depends on the availability of T_{2g} electrons (n) and the facility of transfer to the Π^* orbital of the CN group is inversely proportional to the polarizing power of the cation (Z/r^2), we use nr^2/Z as the p_π parameter of the cation. The correlation equation is now:

$$\nu_{CN} = \nu^o_{CN} + b_\sigma p_\sigma + b_\pi p_\pi \qquad (2)$$

where p_π is nr^2/Z and b_π is the sensitivity of the CN vibration in the Π interaction.

Table 2. Correlation of ν_{CN} of nitroprussides with p_σ and p_π of outer cations

Correlation Coefficient (r)	Confidence Level (%CL)	Correlation parameters (bo, bσ, bπ)		
		bo	bσ	bπ
0.91	99	2026 ± 36	45 ± 10	
0.92	99	2050 ± 67	35 ± 25	9 ± 20

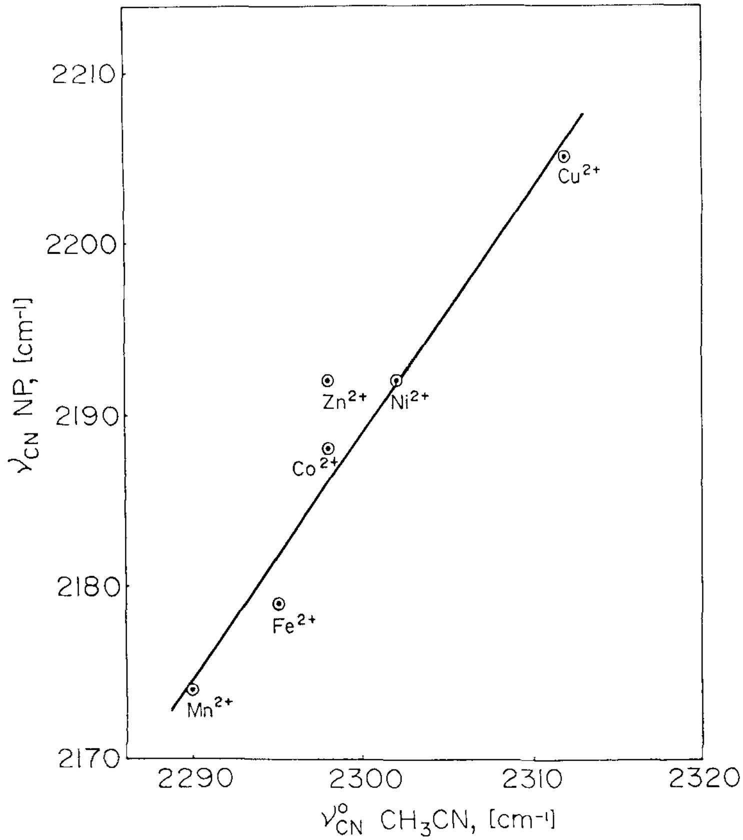

Figure 1. Correlation of ν_{CN} for nitroprussides (ν_{CN} NP) vs ν^{o}_{CN} for CH3CN complexes.

As we can observed in Table 2 the value of r is practically the same and the confidence level remains at 99%. Further more, the errors in the intercep (3.2%) and the coefficients b_π and p_π (71% and 222%) are much higher than in the previous correlations with Z/r^2. This clearly indicates that back-donation is not relevant in this CN-outer cation interaction.

We know that the interactions of CH_3CN with Lewis acid cations are due only to σ interactions[7]. In Figure 1 we present a plot of ν_{CN} of nitroprussides *vs* ν^o_{CN} of CH_3CN. The excellent correlation with r =0.961 has a confidence level close to 99.9% which is in agreement with σ bonding being the dominant mechanism in the interaction of outer cations with the CN ligands in nitroprussides.

Conclusions

The electronic interactions of CN ligands with the outer cations in transition metal nitroprussides is governed by the polarizing power of the cation Z/r^2, indicating σ bonding, with no relevant contribution of the back-donation mechanism.

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