

Study of the nature of the interaction of CH₃CN with Lewis acids

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Abstract—The unperturbed ν^0 (CN) stretching frequencies of CH₃CN in 18 complexes with Lewis acids are correlated with ν (CN) frequencies in cobalticyanides and with cation parameters which measure σ and π interactions. The results indicate that the nature of the interaction is predominantly of the σ donor–acceptor type with no detectable π back-donation from the cation to the CN ligand.

INTRODUCTION

THE CN vibrational stretch ν (CN) in cyano complexes is dependent on the interactions of the central cation with the C atom and of the outer cations with the N end of the cyano ligand [1–5]. The bonding of the C end to the central cation has been interpreted in terms of σ and π interactions [1–5]. The association of the N end with outer cations in hexacyanometallates has been interpreted in analogous fashion, but the interactions are weaker than with the central cation, and σ interactions predominate [6, 7].

The CN stretch of CH₃CN has been used as a sensor of molecular interactions in solutions and complexes with Bronsted and Lewis acids [8–10]. The CN frequency of the complex increases with the strength of the acid or the polarizing power of the cation [10]. The CN stretch fundamental in CH₃CN is perturbed by the binary combination of the symmetric CH₃ deformation and the C–C stretch [8, 9]. This Fermi resonance interaction repels the unperturbed frequencies and shifts intensity from the allowed to the forbidden band due to the mixing of the vibrational wave functions. Therefore, the observed frequencies do not correspond to pure CN or pure binary combination. In inert and basic solvents, the low frequency doublet corresponds to ν (CN), and with increasing acid strength, the resonance intensifies and more CN character is withdrawn from the lower component to the upper frequency one. With highly charged cations, the upper component is now predominantly the CN fundamental. In order to study the behavior of ν (CN) in CH₃CN we present in this paper a compilation of unperturbed ν^0 (CN) frequencies of CH₃CN with 18 Lewis acid complexes [8, 9]. These unperturbed frequencies are correlated with ν (CN) of cobalticyanide salts and with outer cation parameters which gauge the σ and π interactions with the CN group [6, 7].

RESULTS AND DISCUSSION

(A) Correlation of ν (CN) frequencies of Co(CN)₆^{3–} salts and CH₃CN Lewis acid complexes

The ν (CN) values of 13 cobalticyanides from previous work in our laboratory [6] and the ν (CN) values of the unperturbed CN stretch of acetonitrile complexed with 18 Lewis acids from analogous sources [8, 9] are collected in Table 1. The observed cobalticyanide frequencies are accurate to ± 1 cm^{–1}, while the calculated acetonitrile unperturbed frequencies have an uncertainty of ± 2 cm^{–1}. See Refs [6–9]. The unperturbed ν^0 (CN) corresponds to the lower frequency component for cations with 1+ and 2+ charges, while for higher cationic charges the upper frequency component is the allowed fundamental [8, 9].

If the ν (CN) frequencies of both families are compared, we obtain an excellent correlation, which indicates analogous interactions of the CN group with outer cations in CH₃CN and the cobalticyanide complexes (see Table 2).