

RAMAN, INFRARED, FAR-INFRARED AND THEORETICAL STUDIES OF OCTAHEDRAL ACETONITRILE COMPLEXES OF Mn(II) AND Cu(II)

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Abstract: Vibrational spectra of $[M(\text{NCCH}_3)_6]^{2+}$ complexes (where $M=\text{Mn}^{2+}$ and Cu^{2+}) have been recorded involving $[\text{Mn}(\text{NCCD}_3)_6]^{2+}$ species. Complete assignments and force constant calculations have been performed.

An interesting and useful phenomenon in coordination chemistry is the alteration of ligand vibrations upon coordination to different metal ions. In many cases the magnitudes of the wavenumber shifts give information about the bonding forces between the ligand and the metal ion. Generally the shifts of stretching frequencies of the donating groups ($>\text{C}=\text{O}$, $>\text{S}=\text{O}$, $\equiv\text{P}=\text{O}$ etc.) are negative upon coordination.

However, methyl cyanide shows a positive shift in the $\text{C}\equiv\text{N}$ stretching frequency when coordinated to metal ions, due to the rehybridization at the nitrogen atom. In spite of the practical and theoretical interest of acetonitrile complexes, there have been relatively few reports on the vibrational spectra [1]. Previous spectroscopic investigations have been mainly concerned with the infrared spectra, very few Raman or far-infrared studies have been reported. We now report the complete vibrational spectroscopic and force field studies of $[\text{Mn}(\text{NCCH}_3)_6]^{2+}$, $[\text{Mn}(\text{NCCD}_3)_6]^{2+}$ and $[\text{Cu}(\text{NCCH}_3)_6]^{2+}$ complexes, combined with various anions ($[\text{BF}_4]^-$, $[\text{B}(\text{C}_5\text{F}_5)_4]^-$).

Both the Mn^{2+} [2] and Cu^{2+} [3] complexes have an octahedral symmetry due to the X-ray studies. Considering the CH_3 and CD_3 groups of the acetonitrile as point masses, the distribution of the so called “skeletal” vibrations among symmetry species are (O_h -point group):

$$\Gamma(\text{complex}) = 3A_{1g} + 3E_g + 2F_{1g} + 3F_{2g} + 6F_{1u} + 3F_{2u}.$$

Where A_{1g} , E_g and F_{2g} are Raman and F_{1u} species are infrared active modes.

Five infrared and four Raman features were observed in the CN stretching region (Table 1). Overtones and Fermi resonances made very complicated this spectral range. Overtones and combination bands of CH_3 deformation and C-C stretching vibrations were completely removed from the CN stretching region due course of deuteration of acetonitrile ligand, and only a single band at 2296 cm^{-1} has been recorded for $[\text{Mn}(\text{NCCD}_3)_6]^{2+}$ complex.

Fundamental infrared and Raman modes of skeletal vibrations of the complexes are summarized in Table 2.

Force filed calculations have been performed for complexes, considering methyl groups as point masses. Coordination (bonding) properties, *trans*- influence and special vibrational behavior will be discussed in this paper.

TABLE 1. Assignment of the CN stretching region.

$[\text{Mn}(\text{NCCH}_3)_6]^{2+}$		$[\text{Mn}(\text{NCCD}_3)_6]^{2+}$	ASSIGNMENT
Infrared	Raman	Infrared	
2404 vw			1374 + 1031 ^a
	2314 s		A_{1g} CN stretches
2313 vs 2285 vs } ^b		2296 vs	F_{1u}
	2290 vs } ^c 2279 s }		E_g
		2271 m,s	CD ₃ asym str
2246 w, sh		2248 vw	¹³ CN stretch (F_{1u})
	2119 w, m		CD ₃ sym str
2065 m			2x1031 ^a

^a The bands at 1374, 1031 and 940 cm⁻¹ are the fundamental vibrations of coordinated acetonitrile, namely CH₃ umbrella, CH₃ rocking and C – C stretching modes, respectively.

^b Spilling of the bands due to Fermi resonance with 1374+940 cm⁻¹ combination.

^c Solid state splitting.

TABLE 2. Infrared and Raman active skeletal vibrations of $[\text{Mn}(\text{NCCH}_3)_6]^{2+}$ complexes (M= Mn²⁺, Cu²⁺)

$[\text{Mn}(\text{NCCH}_3)_6]^{2+}$		$[\text{Mn}(\text{NCCD}_3)_6]^{2+}$	$[\text{Cu}(\text{NCCH}_3)_6]^{2+}$	Assignment	
IR	Raman	IR	IR	Raman	
	2314 s			2306 m	A_{1g} CN stretches
2299 s ^a		2296 vs	2297 s		F_{1u}
	2284.5 ^a			2271 s	E_g
940 m		849 m	928 w		F_{1u} C–C stretches
	942 m			940 m	A_{1g}
	935 sh			934 w	E_g
384 s		362 s	388 m		F_{1u} M–N stretches
	395 s			395 s	A_{1g}
	294 m			270 m	E_g
378 s		340 m	360 w		F_{1u} NCC deform
	370 w,sh			406 m,sh	F_{2g}
	252 w			236 w	F_{2g} MNC deform
232 s		230 w	233 w		F_{1u}
	126 m			127 w	F_{2g} NMN deform
94 s		90 m	94 ms		F_{1u}

^a Averaged values of frequencies listed in Table 1.

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