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AN INFRARED SPECTROSCOPIC STUDY OF SOME METAL UREA TETRACYANONICKELATE COMPLEXES

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ABSTRACT

The results of an infrared spectroscopic study are reported for four new urea complexes of the form M $(\text{urea})_2$ Ni(CN)_4 (M=Ni, Co, Cd or Mn). Their structure consists of polymeric layers of (M-Ni $(\text{CN})_4$) with urea molecules bound to metal, M, through oxygen, similar to the structure found in Hofmann type host complexes.

INTRODUCTION

Infrared spectroscopic technique alone has long been recognized to be of value in revealing the Structure of Hofmann type host complexes. The structure of these complexes designated with a general formula $ML_2M'(CN)_4$ (M is a divalent transition metal, Zn or Cd, M'is divalent Ni, Pd, or Pt, and L_2 is a bidentate or a pair of monodentate Ligands) consists of two dimensional polymeric layers composed of M' $(CN)_4$ anions and ML_2 cations. The M' atoms are coordinated to the 4C atoms of the CN groups. The M atoms are octahedrally surrounded by CN groups, 4 are from the CN groups, and the other two are from two ligand molecules. The ligand molecules lie above and below the layers. The layers and the linagds as bloching unit provide empty spaces of varying shapes and dimensions, in which guest molecules may be imprisoned [IWAMOTO, 1981].

The complexes of this type have generally been prepared with nitrogen donor ligands. Regarding the oxygen donor ligands, only dioxane and dimethylsulphoxide complexes have been reported so far

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[DEMPSTER and USLU, 1978; KANTARCI, 1983]. In order to increase the number of available complexes with oxygen donor ligands, we have prepared four new complexes of the form M $(urea)_2$ $Ni(CN)_4$, where, M is Mn, Co, Ni or Cd. In this paper, we report an infrared spectroscopic study on these complexes, with the aim of searching any similarity in structure between our complexes and the Hofmann type host complexes.

EXPERIMENTAL

Materials: The chemicals used for preparations were reagent grade (Merck) and used without further purification. The complexes were prepared by the method analogous to that used for dimethylsulphoxide complexes [KANTARCI, 1983].

Spectra: The infrared spectra of the compounds in nujol and polychlortrifluorenthylen mulls were recorded on a Perkin-Elmer 1330 spectrometer, which was calibrated using polystrene films.

RESULTS AND DISCUSSION

In the infrared spectra of complexes $M(urea)_2$ $Ni(CN)_4$ (M=Mn, Co,Ni or Cd), the wavenumbers of the bands assignable to $Ni(CN)_4$ (D_{4h}) ion are given in Table 1.

The Spectra of $[M\text{–}Ni(CN)_4]_\infty$ Structure: The assignment of the observed bands in Table 1 is made on the basis of D_{4h} symmetry assu-

Table 1. The wavenumbers of the fundamental modes of tetracyanonickelate group in metal complexes* (cm^{-1}).

Assignment	$Ni\text{-}Ni(CN)_4$	$Co\text{-}Ni(CN)_4$	$(Cd\text{-}Ni(CN)_4$	$Mn\text{-}Ni(CN)_4$
$\nu_8 E_4 \nu(CN)$	2162 vs	2158 vs	2152 vs	2150 vs
Hot Band?	no	2138 vw	2135 vw	no
$\nu(^{13}CN)$	2122 w	2118 w	2112 w	2118 w
$\nu_9 E_u \nu(Ni,CN)$	538 w	535 w	528 w	532 w
$A_{2u}\pi(Ni\ CN)$	463*	460*	462*	458*
$\nu_{10} E_u\ \delta(Ni\ CN)$	445 s	441 s	431 s	430 s

* no= not observed, v= very, w= weak, s= strong.

* also assigned to $A_2\omega(NH_2)$ (See Table 2).

med for $Ni(CN)_4$ group in the complexes studied here. This is in agreement with the assignments made ofr other Hofmann-type complexes.

The existence of $[M\text{--}Ni(CN)_4]$ polymeric sheet structure in Hofmann-type complexes is generally indicated by two strong infrared bands, antisymmetric CN stretching vibration of E_u $\upsilon(CN)$ and NiCN bending (in plane) vibration of E_u $\delta(NiCN)$ found at higher frequencies than those of free $Ni(CN)_4^{2-}$ ion found at 2128 cm^{-1} (E_u,υ_8) and at 421 cm^{-1} (E_u, υ_{10}), respectively [McCULLOUGH et al., 1960]. As is clear from Table 1, considerable upward shifts in frequencies occur for the CN stretching (υ_8) and the NiCN bending (υ_{10}) vibrations of our complexes. A similar shifts have been observed in other Hofmann-type complexes e.i., with pyridine [SUNGUR et al., 1987]. Then, these frequency shifts appear consistent with the infinite polymeric sheets, $([M\text{--}Ni(CN)_4]_\infty$, formed from planar $Ni(CN)_4$ anions bridged by M cations.

It is interesting to note that the frequency values of CN stretching (υ_8) and NiCN bending (υ_{10}) modes are metal dependent and follows the sequence of the second ionization potantials of the metals as follows [ORGEL, 1967]: $Mn < Cd < CO < Ni$. A similar sequence has also been found in other works: the increase in several modes of metal-pyridine complexes [AKYÜZ, et al., 1973], the increase in NH, rocking and M–N stretching frequencies in metal-hexamine chlorides [NAKAMOTO, 1970], the heats of formation of the MCl_4^{2-} ions [PAOLETTI AND VACCA, 1964]. This spectral sequence reflects the increasing strength of bridging M–NC, Ni bond.

The Spectra of Coordinated Urea: In the solid phase, urea is a planar molecule with C_{2v} symmetry [VAUGHAN and DONOHUE, 1952, WORSHAM et al., 1957, PRYOR and SANGER, 1970]. Based on this symmetry, the normal modes of vibration of free urea and their activity (R = raman active, IR = infrared active) are as follows:

$7A_1(R,IR) + 6B_2(R,IR)$ — 13 in plane vibrations

$3B_1(R,IR) + 2A_2(R)$ — 5 out of plane vibrations.

When urea is complexed with a metal ion, C_{2v} symmetry is lowered, causing two vibrations of A_2 to be IR-active. Then, 18 fundamental bands of urea must be expected in the infrared spectra of our complexes. In order to aid in the identification of these modes in the spectra considered here, the liteature data should be consulted.

A number of vibrational spectroscopic studies as well as normal coordinate analyses have been performed on urea in solid phase [YA-

MAGUCHI et al., 1957; SHTEINBERG et al, 1972; DUNCAN, 1971, SAITO et al., 1971; DIAZ and CAMPOS, 1981; ARENAS et al., 1984; BHOOPATHY et al., 1988] and in solition [HADZI et al., 1976]. The solid phase spectral data are not appropriate for our purposes, since in the condensed state the urea molecules are subject to very strong inter-molecular hydrogen bonds which affect very appreciably the C=O stretching and NH_2 stretching and deformation vibrations. In comparison to solid phase there have been relatively few solution studies on urea in soliton [YAMAGUCHI et al., 1957, R.M. BADGER and R.D. WALDRON 1957; STEWARDT, 1957; R.B. PENLAND et al., 1957; LAULICHT et al 1965; AGGARWAL and SINGH, 1965; DUNCAN, 1971; SAITO et al., 1971; SHTEINBERG et al., 1972; HADZI et al., 1976; DIAZ and CAMPOS 1981; ARENAS et al., 1984; LIAPIS et al., 1985; BHOOPATHY et al., 1988]. Among these, the most detailed and relevant work is that of Hadzi et al., [HADZI et al., 1976], although their assignment is limited only to in plane vibrations. These authors recorded the infrared spectra of solution of urea and thiourea in acetonitrile and compared with those of their ^{15}N and ^{2}H ısotopic species. Their assignment is supported by normal coordinate analyses based on Wilson's GF Matrix method and the Urey-Bradly force field. These spectral data are contained in Table 2, where they are compared with infrared data of our complexes.

Urea can form a coordinate bond to a metal through either N or O atom depending on the nature of the metal, and this preference may be modified by the presence of other ligands or by whether the complex is in the solid state or in solution. If there is nitrogen coordination, the lone electron pair on a nitrogen atom is involved, resulting in a increase of C=O streching frequency and a decrease in N–C and N–H stretching frequencies with the presence of two N–H and two N–C–N deformation bands due to free and coordinated CNH_2 groups (in the same coordinated urea). If there is Oxygen coordination, however, the bond order of C=O diminishes and the bond order of CN increase, resulting in a decrease in C=O stretching frequency and an increase in C–N stretching frequency, with unaltered N–H Stretching frequency [RAO, 1963].

On examination of Table 2, the following Spectral features indicate that oxygen-to-metal bonds are present in our complexes: a) the frequencies assigned to asymmetric N–H and symmetric N–H streching vibrations corresbond to the bands of free urea of almost the same

Table 2. The wavenumbers of the fundamental modes of coordinated urea* (cm^{-1}).

Serial No	Symmetry type	Assignment	Urea	M $(urea)_2$ $Ni(CN)_4$				relative intensity
				M=Ni	M=Co	M=Cd	M=Mn	
1	A_1	$\nu_a(NH_2)$	3503*	3488	3490	3485	3483	m
2	B_2	$\nu_a(NH_2)$	3503*	3488	3490	3485	3478	m
3	A_1	$\nu_s(NH_2)$	3390*	3390	3388	3380	3390	m
4	B_2	$\nu_s(NH_2)$	3390*	3390	3388	—	3378	m
5	A_1	ν (CO)	1695*	1638	1641	1648	1652	m
6	B_2	δ (NH_2)	1614*	1628	1626	1630	1635	m
7	A_1	δ (NH_2)	1614*	1587	1583	1578	1588	m
8	B_2	ν (CN)	1419*	1490	1490	1490	1488	w
9	B_2	ϱ (NH_2)	1167*	1168	a1165	1165	1166	vw
10	A_1	ϱ (NH_2)	1167*	1145	1143	1148	1142	m
11	A_1	ν (CN)	969*	1020	1020	1025	1020	vw
12	B_2	δ (NCO)	576*	617	615	602	608	w
13	A_1	δ (NCN)	509*	558	560	555	552	w
14	B_1	Π (CO)	790+	761	760	768	770	w
15	B_1	ζ (NH_2)	705+	730	730	730	730	vw
16	B_1	ω (NH_2)	495+	507	509	507	508	w
17	A_2	ζ (NH_2)	714+	730	730	730	730	vw
18	A_2	ω (NH_2)	554+	463	460	462	458	w

* $a, s, \nu, \delta, \varrho, \Pi, \zeta$ and ω stand for asymmetric, symmetric, stretching, deformation, rocking, out of plane, torsion, and wagging vibrations, respectively; v= very, w= weak, m= medium, s= strong.

* from urea in solution (HADZI et al., 1976).

\+ from normal coordinate analyses (SAITO et al., 1971).

frequencies. b) the upwards shifts in frequency of asymmetric C–N stretching and symmetric C–N stretching modes compared with those in solution. c) the absence of any band in the higher frequency side of C=O streching frequency of uncoordinated urea. d) the assignment of C=O stretching frequency to the bands in the carbonly region on the low frequency side of free urea (this assignment is reasoned below).

The carbonyl region where expected three strong bands are observed presents little difficulty in differentiating the C=O stretching band from two NH_2 deformation bands. The strong bands at 1652, 1641, 1638 and 1648 cm^{-1} in the complexes with Mn, Co, Ni and Cd, respectively, are assigned to C=O stretcing vibration. This assignment is based on the fact that the frequency value of CO band with different metals in our complexes is in the order Mn<Cd<Co<Ni. This order agrees well with the heats of formation of the MCl_4^{2-} ions [PAOLETTI AND VACCA, 1964], the order of which can be considered as a criterion of electron acceptor power of the transition metals. A similar trends has been found in other works, such as the second ionization potentials of transition metals [ORGEL, 1967] and metal depended frequency shifts in a number of coordination compounds [NAKAMOTO, 1970; CLARK and WILLIAMS, 1965; GOLDSTEIN and UNSWORTH, 1972].

The assignments of OCN and NCN in-plane deformation motions are based on the normal coordinate analyses performed on planar XYZ_2 and metal bounded $M\ldots XYZ_2$ type molecule models with C_{2v} symmetry using Wilson's GF matrix tmethod and diagonal force field [HAMAN, 1988]. The results show that the bending OCN and NCN frequencies must increase on going from free ligand to cordinated ligand.

All in plane vibrations of NH_2 groups but NH_2 bending of A_1 show small frequency shifts. These may be due to the change in environment or consequence of the breaking of the couplings between NH_2 bending and OCN_2 skeleton vibrations. A number of normal coordinate analyses of urea indicate that substantial vibrational mixing of C=O stretching and NH_2 bending is present in urea [YAMAGUCHI et al., DUNCAN, 1971, SAITO et al., 1971; HADZI, et al., 1976; DIAZ and CAMPOS, 1981; ARENAS et al., 1984; BHOOPATHY et al., 1988]. However, on formation of metal-to oxygen bond ,the coupling between the C=O stretching and NH_2 bending vibrations decreases, causing them to be more separable. Therefore, the NH_2 bending vibrations of A_1 in complexes are assigned to bands appear in the region of 1585 cm^{-1}.

There remain the out of plane vibrations: Because of the lack of appropriate spectral data concerning with out of plane vibrations of uncoordinated urea which we refer to, we made a assignment of five bands observed below 800 cm^{-1} by arranging them in such a way that their order of frequency values consistent with the order of those obtained from anormal coordinate analyses [SAITO et al., 1971; DIAZ and CAMPOS, 1981]. It should be noted that this assignment is tentative possibly speculative but it is consistent with our spectral data and the results of a study of single-crystal and Raman, incoherent neutron Scattering and infrared data on urea which indicate that the inadequacies of an isolated-molecule approach to the interpretation of the spectra of solid urea and related normal coordinate analyses [LIAPIS et al., 1985].

The preceding discussion based on the experimental data available, considered together, lead us to conclude that the structure of our complexes are similar to those of Hofmann- type host structures.

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