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AN INFRARED SPECTROSCOPIC STUDY ON A DIVALENT METAL SALT OF p-AMINOBENZOIC ACID [ABA(Mg)] TETRACYANONICKELATE

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**AN INFRARED SPECTROSCOPIC STUDY
ON A DIVALENT METAL SALT
OF p-AMINOBENZOIC ACID [ABA(Mg)]
TETRACYANONICKELATE**

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ABSTRACT

Infrared spectra of $MLNi(CN)_4$ [$M=Mn, Fe, Co, Ni, Zn$ or Cd and $L=$ Divalent metal of p-Aminobenzoic Acid or ABA (Mg)] are reported. Their structure consists of polymeric layers of $[M-Ni(CN)_4]_n$ with the divalent metal of p-aminobenzoic acid [ABA(Mg)] molecules bound directly to the metal (M).

Key Words: Infrared spectroscopy; Tetracyanonickelate; p-Aminobenzoic acid; Hofmann-type complex; Clathrate

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INTRODUCTION

The structure of the Hofmann type complexes given by the formula $ML_2Ni(CN)_4$, where M is a divalent metal and L is a ligand molecule, consists of infinite polymeric layers $[M-Ni(CN)]_a$ formed of $Ni(CN)_4^{-2}$ anions bridged by ML_2^{+2} cations¹⁻². The nickel atoms are surrounded by four carbon atoms of the cyanide groups and coordinated to M. The ligand molecules lie above and below the layers³.

This paper reports seven newly prepared $M[ABA(Mg)-Ni(CN)_4]$ ($M = Mn, Fe, Co, Ni, Cu, Zn$ or Cd) compounds. In a previous publication, Divalent Metal Salt of p-Aminobenzoic Acid $[ABA(Mg) = C_{14}H_{12}N_2O_4Mg]$ ligand molecule containing an ionic band formed between $-COO^-$ and Mg^{++} , and two terminal amino groups has been reported⁴.

EXPERIMENTAL

All chemicals used were reagent grade (Merck) and used without further purification. The compounds $M[ABA(Mg)Ni(CN)_4]$ ($M = Mn, Fe, Co, Ni, Cu, Zn$ or Cd) were prepared by adding slightly more than 1 mmol of solid $ABA(Mg)$ to $K_2Ni(CN)_4$ and 1 mmol MCl_2 solution in water. These complexes were filtered and washed. Infrared spectra of the compounds as KBr discs were recorded in the range of 4000 to 400 cm^{-1} on a MATTSON 1000 FTIR spectrometer. The freshly prepared compounds were analyzed for C; H and N by a LECO CHNS -932 analyzer. Realative amounts of elements in percentage are as follows (% found/% calculated):

Mn	$(C_{14}H_{12}N_2O_4Mg)Ni(CN)_4$:	C = 41.88/42.03,	H = 2.18/2.33,
		N = 16.17/16.28;	
Fe	$(C_{14}H_{12}N_2O_4Mg)Ni(CN)_4$:	C = 41.96/42.12,	H = 2.28/2.33,
		N = 16.31/16.33;	
Co	$(C_{14}H_{12}N_2O_4Mg)Ni(CN)_4$:	C = 40.96/41.70,	H = 2.33/2.31,
		N = 16.23/16.21;	
Ni	$(C_{14}H_{12}N_2O_4Mg)Ni(CN)_4$:	C = 41.86/41.72,	H = 2.33/2.31,
		N = 16.30/16.22;	
Cu	$(C_{14}H_{12}N_2O_4Mg)Ni(CN)_4$:	C = 40.86/41.33,	H = 2.27/2.28,
		N = 15.90/16.07;	
Zn	$(C_{14}H_{12}N_2O_4Mg)Ni(CN)_4$:	C = 41.26/41.19,	H = 2.27/2.28,
		N = 15.96/16.02;	
Cd	$(C_{14}H_{12}N_2O_4Mg)Ni(CN)_4$:	C = 37.63/37.80,	H = 2.12/2.10,
		N = 14.73/14.70;	



RESULTS AND DISCUSSION

The vibrational wavenumbers of the Ni (CN)₄ group of the complexes are given in Table 1. Characteristic frequencies $\nu(\text{CN})$ and $\delta(\text{NiCN})$ are found to be similar to those of the Hofmann type clathrate and complexes⁵⁻⁶. The similarity indicates that the [M-Ni(CN)₄]_a layers have been preserved. The presence of just one IR active CN stretching vibrations in the vibrational spectra of all the complexes except Cu-Ni-ABA(Mg) indicates that local symmetry around the Ni atom is D_{4h}. However, for Cu-Ni-ABA(Mg), two strong bands rather than one, are observed in the $\nu(\text{CN})$ and $\delta(\text{NiCN})$ region of the IR spectrum. The $\nu(\text{CN})$ and $\delta(\text{NiCN})$ vibrations are both doubly degenerate in the complexes that have D_{4h} symmetry. The splitting of these bands in the Cu-Ni-L complex points directly to a change of symmetry and removal of the degeneracy. The ABA(Mg) modes of the Cu-Ni-ABA(Mg) complex do not differ from those in the other complexes. Therefore, we propose that only the sheet structure of the Cu-Ni-ABA(Mg) complex differs from the structure in other complexes.

The distortion of the crystalline structure which occurs in Cu⁺², may be the result of a Jahn-Teller effect⁸. This leads to two non-equivalent trans pairs of Cu-NC bonds with different length. In this situation there would also be two non-equivalent pairs of C=N bonds. Such a spectroscopic feature is also observed in the CuL₂Ni(CN)₄ (L = pyridine or methylpyridine)⁹.

No complete vibrational assignment has been reported for the free ABA(Mg) molecule in the literature. The assignments and wavenumbers of the vibrational bands of the free ABA(Mg) molecule observed in the spectra of the compound studied are given in Table 2. The NH₂ stretching frequencies which are lower than the corresponding values of the free

Table 1. The Vibrational Wavenumbers (cm⁻¹) of the Cyanide Group for the M-Ni Compounds

Assignment ^a	Na ₂ Ni(CN) ₄	Mn	Fe	Co	Ni	Cu	Zn	Cd
$\nu(\text{CN})$	2132 2128	2156 vs	2157 vs	2156 vs	2156 vs	2156 vs 2178 m	2179 vs	2145 vs
$\nu(\text{NiCN})$	543	551 w	545 w	5546 sh	545 w	574 vw	544 vw	550 sh
$\nu(\text{NiCN})$	—	—	541 vw	—	547 vw	563 vw	543 vw	—
$\delta(\text{NiCN})$	543	437 m	441 m	450 s	451 s	446 m	441 s	433 m

^a Taken from [7].

^b Taken from [12].

v = very, s = strong, m = medium, w = weak, br = broad, sh = shoulder.



Table 2. The Vibrational Wavenumbers (cm^{-1}) of ABA(Mg) in the M-Ni-ABA(Mg) Complexes

Assignment ^a	ABA(Mg)*	Mn-Ni	Fe-NiL	Co-NiL	Ni-NiL	Cu-NiL	Zn-NiL	Cd-NiL
$\nu(\text{NH}_2)$	3492 vs	3390 s	3393 s	3391 s	3390 s	3249 s	3385 s	3389 s
$\nu(\text{NH}_2)$	3390 s	3320 s	3318 s	3321 s	3320 s	3144 w	3245 w	3331 w
$\nu(\text{CN})$	2966 s	2966 s	2979 s	2979 s	2977 s	2975 s	2976 s	2974 s
$\nu(\text{CN})$	2910 s	2914 w	2932 w	2934 w	2931 w	2928 w	2925 w	2926 w
$\nu(\text{CN})$	1666 vs	1667 vs	1662 vs	1667 vs	1667 vs	1678 vs	1676 vs	1665 vs
$\nu(\text{CN})$	1610 s	1631 s	1602 w	1605 w	1603 w	1603 w	—	1607 w
$\delta(\text{NH}_2)$	1596 vs	1579 vs	1561 s	1555 s	1579 s	1578 s	1584 s	1567 s
ν	1567 w	1555 w	1538 w	1539 w	1536 w	1537 w	1536 w	1537 w
$\delta(\text{CN})$	1434 vs	1432 vs	1432 vs	1430 vs	1432 vs	1426 vs	1435 vs	1437 s
$\nu_t(\text{CN})$	1337 w	1315 w	1314 w	1312 w	1313 w	—	1312 w	1335 w
$\nu_t(\text{NH}_2)$	1284 vs	1290 vs	1291 vs	1291 vs	1291 vs	1286 vs	1288 vs	1291 vs
ν	1167 vs	1173 vs	1172 vs	1173 vs	1174 vs	1168 vs	1172 vs	1173 vs
$\nu(\text{CN})$	1128 w	1126 w	1126 w	1125 w	1127 w	1120 w	1126 w	1129 w
$\nu(\text{CN})$	1073 w	1015 vw	1014 vw	1015 vw	1015 vw	1013 vw	1014 vw	1016 vw
ν	955 vs	958 vs	926 vs	956 vs	956 vs	954 vs	953 vs	961 vs
$\nu_t(\text{CN})$	838 s	833 w	833 w	827 w	832 w	841 w	843 w	839 w
$\nu_t(\text{CN})$	767 s	768 s	768 s	767 s	769 s	744 s	776 s	758 s

^a Taken from [7].

* The infrared spectra of KBr disc of ABA(Mg).

v = very, s = strong, m = medium, w = weak, vs = very strong, vw = very weak.

ABA(Mg) molecule (in Table 2) show that ligand molecules bound directly to the metal M (M= Mn, Fe, Co, Ni, Zn or Cd). Several modes of the coordinated ABA(Mg) molecule have upward shifts in frequency in comparison with those of the normal shifts that are metal dependent. The general increase in frequency of the ABA(Mg) modes with the different metals in our compounds are in the following order: Mn < Cd < Fe < Co < Zn < Ni < Cu, which is in agreement with increasing order of the second ionization potential of the metals. Similar observations were also reported in other complexes¹⁰⁻¹¹. We conclude that the order of the M-N[ABA(Mg)] stretching frequencies follows the same regularity and this order reflects the increasing strength of the M-N bond.

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