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VIBRATIONAL SPECTROSCOPIC STUDY ON HOFMANN-Td-TYPE COMPLEXES: M(3,4-lutidine)2M'(CN)4 (M=Mn(II) or Cd(II), M'=Cd(II) or Hg(II))

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ABSTRACT

For new Hofmann-Td-type complexes M(3,4-lutidine)$_2$M'(CN)$_4$, where M=Mn or Cd M'=Cd or Hg, have been prepared and their infrared and Raman spectra are reported. The spectral data have been interpreted in accord with the structure similar to those found in Hofmann-Td-type host.

Key Words: Hofmann-Td-type complexes; 3,4-lutidine; IR and Raman spectra

M(3,4-lutidine)2M'(CN)4 (M=Mn(II) or Cd(II), M'=Cd(II) or Hg(II)) HOFMANN-Td TİPİ BİLEŞİKLERİN TİTREŞİM SPEKTROSKOPİSİ"

ÖZET

Genel formülü M(3,4-lutidine)$_2$M'(CN)$_4$, (M=Mn ve Cd M'=Cd ve Hg,) ile verilen Hofmann -Td-tipi bileşiklere 4 yeni örnek kazandırıldı. Elde edilen bileşiklerin kırmızı-altı ve Raman spektrumları kaydedilip titreşim frekans ve kipleri saptandı. Bu spektrumlar değerlendirilerek literatürdeki benzer Hofmann-Td-tipi çalışmalar ile karşılaştırıldı.

Anahtar Kelimeler : Hofmann-Td-tipi bileşikler; 3,4-lutidine; IR ve Raman spektroskopisi

1. INTRODUCTION

There is a group of complexes with the general formula CdL$_2$M'(CN)$_4$ among Hofmann-type and the analogous host lattices. In this formula, L$_2$ refers to be a bidendate or a pair of monodendate ligand molecules containing N-terminate donor atoms and M' refers to be Cd or Hg. In these compounds, the host lattice is formed from infinite -Cd-L$_2$-Cd-L$_2$- chains extending along a- and b-axes alternately and the tetrahedral M'(CN)$_4$ ions arranged between the consecutive crossing -Cd-L$_2$-Cd-L$_2$- chains with the N-terminate bound to the Cd atoms (1-3). This framework provides two kinds of cavities of and for the guest molecules. The cavity is a rectangular box similar to those in the Hofmann-type host, while the cavity is a twisted biprism as demostrated in previous papers (1-3). This is so-called Hofmann-Td-type host structure differs from the host structure of Hofmann-type clathrate, designated with a formula $M(NH_3)_2(CN)_4.2C_6H_6$ (M= Mn, Fe, Co, Ni, Cu, Zn or Cd; M' = Ni, Pd or Pt) as in the Hofmann-type. M and M' exhibit octahedral and square planer coordination,while in the Hofmann-Td-type the corresponding metals (M= Cd and M' = Cd or Hg) are octahedrally and tetrahedrally surrounded (4,5). Thus we have prepared four new dilutidinemetal(II) Tetracyanometallete (II) host complexes, $M(3,4\text{-lutidine})_2M'(CN)4$, (M= Mn or Cd M' = Cd or Hg). In this study, we report the IR spectra of Mn-Cd-lutidine, Mn-Hg-lutidine, Cd-Cd- lutidine and Cd-Hg-lutidine. In addition to that, we also report the Raman spectra of Cd-Cd-lutidine and Cd-Hg-lutidine, however, the Raman spectra of Mn-Cd-lutidine and Mn-Hg-lutidine could not obtained since there are dark brown compounds.

Table 1. Fundamental vibrational wavenumbers (cm^{-1}) of 3,4-lutidine in the complexes

Assignments.	**3,4-lutidine***		**Cd-Cd-L**		**Cd-Hg-L**		**Mn-Cd-L**	**Mn-Hg-L**
	IR	**Raman**	**IR**	**Raman**	**IR**	**Raman**	**IR**	**IR**
a' ν_1	3055vs	___	3074w	___	3074w	___	3072w	3073w
ν_2	3021vs	3027m	3026vw	___	3026w	___	___	3026vw
ν_3	3010vs	___	3014w	___	3013w	___	3014w	___
ν_4	1594vs	1594s	1609s	1610s	1608s	1610m	1609s	1608s
ν_5	1560s	1563w	1560w	___	1560w	___	1561w	1559w
ν_6	1492vs	1493w	1499s	___	1501m	___	1500s	1501s
ν_7	1405vs	1403w,sh	1418s	___	1417s	___	1416s	1416s
ν_8	1349w,sh	1347w	___	___	___	___	___	___
ν_9	1305m	1304w	1314m	___	1313w	1313w	1314m	1313m
ν_{10}	1237m	1240s	1242vw	1243m	1243w	1244m	1243vw	1244w
ν_{11}	1194vs	1191m	1200s	1199w	1201s	1202w	1200s	1199s
ν_{12}	1176m	1175m	1177m	1176w	1176m	1179w	1175w	1175w
ν_{13}	1066s	1068w	1084vs	1082m	1084vs	1083m	1082s	1082s
ν_{14}	839vs	842w	862vs	___	862s	___	857s	861s
ν_{15}	751m	758vs	754w	753vs	754sh	756vs	752sh	754w
ν_{16}	600m	604s	611m	608m	610m	609m	610m	610m
ν_{17}	524s	528sh	533s	___	532m	___	533m	533m
ν_{18}	409w	409vw	405vw	___	405vw	___	407vw	405w
ν_{19}	258m	260m	266m	___	267w	___	279vw	269sh
a'								
ν_{20}	985m	984m	987vw	___	988vw	___	985sh	986sh
ν_{21}	918w	920w	921w	___	921w	___	920w	921w
ν_{22}	821vs	829w	828vs	___	828s	___	828s	826s
ν_{23}	726vs	733vw	723vs	___	724s	___	724vs	724vs
ν_{24}	506s	509m	533sh	519w	522sh	523w	521vw	523sh
ν_{25}	422s	426w	426m	___	426m	___	426m	427m
ν_{26}	___	308w	___	___	___	302w	___	___
ν_{27}	___	181m	___	190w	___	189m	___	___
$\nu_{as}(CH_3)$	2971vs	2976m	2992sh	___	2993sh	___	2991m	2992m
$\nu_{as}(CH_3)$	2947vs	2947m	2967m	2967w	2967m	2965w	2967m	2967m
$\nu_s(CH_3)$	2923vs	2920m	2928m	2927s	2928m	2929m	2928m	2928m
$\delta_{as}(CH_3)$	1447vs	1449m	1443vs	___	1445vs	___	1447vs	1446vs
$\delta_s(CH_3)$	1384vs	1385s	1386s	1308m	1387m	1389m	1387m	1387m
(CH_3) rock	1048m	1048sh	1061w	___	1062w	___	1062w	1063w
(CH_3) rock	1020s	1015w	1024m	___	1024s	___	1024m	1023m
(CH_3) rock	1001m	___	1006w	___	1006w	___	1005w	1005w
(CH_3) rock	918w	920w	921w	___	921w	___	920w	921w

* Taken from Ref.(6); v = very, s = strong, m = medium, w = weak, sh = shoulder, L=3,4-lutidine

2. EXPERIMENTAL

The complexes were prepared by adding slightly more than two milimoles of 3,4-lutidine and one milimole of potassium tetracyanometallete $K_2M(CN)_4$ (M= Cd or Hg) solution in water to one milimole M(II) (M = Mn or Cd) chloride solution in water. The precipitate was filtered, washed with water, ethanol and ether successively, and kept in a desiccator. Infrared spectra of the compounds were recorded between 4000-200 cm^{-1} on perkin-Elmer 1330 spectrometer which calibrated using polystyrene. The samples were prepared as mulls in nujol and hexachlorobutadiene between CsI windows, and KBr discs. The Raman spectra of the Cd-Cd-lutidine and Cd-Hg-lutidine were obtained using the 514.5 nm line of a Spectra-Physics Model 2016-4S Ar$^+$ ion laser and recorded on Jobin-Yvon U1000 (wavelength drive) spectrometer. The freshly prepared samples were analyzed for Mn and Cd by Philip 49200 atomic absorption spectrophotometer, and for C,H and N by Leco CHN-600 Model analyzer with the results are given in Table 3.

Table 2. The vibrational wavenumbers (cm-1) of M'(CN)4 group for Cd-Cd-L, Cd-Hg-L, Mn-Cd-L, Mn-Hg-L

Assignments	**$K_2Cd(CN)_4$***		**$K_2Hg(CN)_4$***		**Cd-Cd-L**		**Cd-Hg-L**		**Mn-Cd-L**	**Mn-Hg-L**
	IR	**Raman**	**IR**	**Raman**	**IR**	**Raman**	**IR**	**Raman**	**IR**	**IR**
A_1 υ_1(CN)	---	2149	---	2149	---	2178vs	---	2177vs	---	---
F_2 υ_5(CN)	2145	---	2146	---	2164vs	2163sh	2166vs	2168sh	2162s	2163vs
Hot band	---	---	---	---	---	---	---	---	2130vw	2155vw
$A_1\upsilon_2$(MC)	---	---	---	---	---	---	---	---	---	---
$F_2\upsilon_6$ (ν(MC)+δ(NCM))	316	---	330	---	356vs	---	354vs	---	384s	362s

Taken from Ref.(7); v = very, s = strong, w = weak, sh = shoulder, L=3,4-lutidine

Table 3. Analytical data of M-M'-3,4-lutidine complexes (M=Mn or Cd M'=Cd or Hg)

Compounds	**Found%**					**Calculated%**				
	Mn	**Cd**	**C**	**H**	**N**	**Mn**	**Cd**	**C**	**H**	**N**
Mn-Cd-lutidine	11.85	22.15	43.00	3.97	16.70	11.31	23.14	44.51	3.73	17.30
Mn-Hg-lutidine	9.61	---	37.65	3.37	14.40	9.57	---	37.67	3.16	14.64
Cd-Cd-lutidine	---	41.73	38.54	3.20	14.97	---	41.39	39.80	3.34	15.47
Cd-Hg-lutidine	---	18.02	34.67	2.46	12.94	---	17.80	34.24	2.87	13.31

3. RESULTS and DISCUSSION

The spectral features of Mn-Cd-L, Mn-Hg-L, Cd-Cd-L and Cd-Hg-L complexes are found to be very similar, suggesting that they have isomorphous crystal structures. Owing to the lack of structural data the assignments were made by treating the lutidine molecule (L) and the M'(CN)$_4$ moities as isolated units.

A detailed IR and Raman spectroscopic study of 3,4-lutidine have been reported (6) and confirmed by the normal coordinate calculations (7). To the best of our knowledge IR or Raman measurements have been reported for metal complexes of 3,4-lutidine in the 4000-200cm-1 region (8). The assignments and the wavenumbers of the vibrational bands of 3,4-lutidine observed in the spectra of the compounds studied are listed in Table 1, together with the wavenumbers of 3,4-lutidine in liquid (6) on which the assignments are based. The designation of the species and the numbering of the vibrations are the same as that used by Green et al. (6). We made the assignment for coordinated 3,4-lutidine by making a one-to-one comparison with the assignments for liquid 3,4-lutidine (Table 1). On complexing, lutidine vibrational frequencies generally increase and the inplane modes are the most strongly perturbed. These increases in frequency when compared to those of free molecule mainly was explained in term of coupling of the internal vibrational modes of 3,4-lutidine with M-N vibrations. The spectra in Table 1 shows that each of the fundamental frequencies of Cd (3,4-lutidine)2M'(CN)$_4$ are reproduced with only minor shifts in the spectra of the complexes studied. The striking correspondence between these frequencies indicates that the 3,4-lutidine molecules in our complexes coordinate to Mn (or Cd).

In the Td-type clathrates and Td-type host compleses studied previously (1-3,9), the metal atom

M' in $M'(CN)_4$ is tetrahedrally surrounded by the carbon ends of four CN ions. Therefore, it is reasonable to assume that the complexes studied here also have tetrahedral $M'(CN)_4$ moeities In assigning the bands attributable to the $M(CN)_4$ (M= Cd or Hg) ions in the spectra of our compounds, we refer to the work of Jones (7) who presented vibrational data for the salts $K_2M(CN)_4$ (M= Cd, Hg) in the solid state (7). The vibrational data for $M'(CN)_4$ groups in the compounds studied are given in Table 2, together with the vibrational wavenumbers of $K_2Cd(CN)_4$ and $K_2Hg(CN)_4$. The assigned wavenumbers of the $M'(CN)_4$ groups of the compounds appear to be much higher than for isolated $M'(CN)_4$ ion (7). Therefore, they can be used as references to account for the units. Such frequency shifts have been observed for Td-type (9,10) and Hofmann-type (11-14) compounds, and are attributed to the mechanical coupling of the internal modes of $M'(CN)_4$ with metal vibrations (Mn-NC or Cd-NC). it follows that the N-terminate of the $M'(CN)_4$ groups are also bound to an Mn (or Cd) atom in our complexes.

REFERENCES

1. Kuroda, R.,."Metal ammine cyanide aromatic clathrates XV. new type clathrates. new type clathrates compound crystal structure of Cd(NH3)2Hg(CN)4.2C6H6", ***Inorg. Nucl. Chem. Lett.***, 9,13 (1973).

2 Iwamoto, T., "Recent developments in the chemistry of hofmann-type and analogous clathrates", ***J. Mol. Struct.***, 75,51 (1981).

3. Nishikiori, S., and Iwamoto, T., "Crystal Structure of Etilendiamine Cadmium (II) Tetracyanocadmate (II)-Benzene (1/2) and Etilendiamine Cadmium (II) Tetracyanocadmade(II)", ***J. Incl. Phenom.***, 3,283 (1985).

4. Iwamoto, T., Kiyoki, M. and .Matsuura, M., "Cyclohexadienly radicals in - irradiated catena -cyanomercurate (II) benzene (1/2) and the analogous clatharates" ***Bull. Chem. Soc.Jpn.***, 51,390 (1978).

5. Nishikiori, S., Iwamoto, T. and Yoshino, Y., "Three dimensional metal complex structure with ambident propylenediamine ligands saving as the hosts of the aromatic guest molecules hofmann-Pn and Pn-Td type clatrates" ***Bull. Chem. Soc. Jpn.***, 53,2236 (1980).

6. Green, J. H. S., Harrison, D.J., Kynaston, W., Paisley, H. M., "The vibrational spectra of the dimethylpyridines", ***Spectrochim. Acta.***, 26 A, 2139 (1969).

7. Jones, L. H., "Vibrational spectrum and structure of metal cynide complexes in the solit state V. K2Zn(CN)6, K2Hg(CN)4 and K2Cd(CN)4" ***Spectrochim. Acta***, 17, 188(1961)

8. Özbay, A. and Yurdakul, Ş., "Vibrational spectroscopic studies of 3,4-lutidine metal (II) tetracyanonickelate complexes" ***Spectroscopy Letters***, 28(4), 611-619 (1995).

9. Bahat, M. and Yurdakul, Ş., "Fourier transform infrared and raman studies on metal (II)-di(3,5-dimethylpyridine) tetracyanometalate complexes" ***J. Mol. Struct.***, 408/409,395-398 (1997).

10. Kasap, E and Kantarcı, Z., "Vibrational spectrocopic studies on the hofmann-Td-type clathrates", ***J. Incl. Phenom.***, 20,33(1995).

11. Kasap, E., Özbay, A. and Özçelik, S., "Infrared spectroscopic study of the hofmann-diam-type clathrates: M(1,6-diaminohexaneNi(CN)4.C6H6 (M=Ni, Co or Cd)" ***Spectroscopy Letters***, 30(3), 491(1997).

12. Kasap, E., Özbay, A. and Özçelik, S., "Infrared and raman spectroscopic study of the hofmann-type clathrates M(1,7-DiaminoheptaneNi(CN)4.G(M=Ni or Co; G = chlorobenzene, m-xylene or naphthalene)" ***J. Mol. Struct.***, 408/409,13 (1997).

13. Kasap, E. and . Özbay, A.,"Infrared spectroscopic study of the hofmann-daon-type clathrates: M(1,8-diaminooctane)Ni(CN)4.G (M=Co, Ni or Cd; G = aromatic guest molcules)" ***J. Incl. Phenom.***, 28: 335 (1997).

14. Özbay, A. and Yurdakul, Ş., "Vibrational spectroscopic studies of 2,4-lutidine metal (II) tetracyanonickelate complexes" ***J. Mol. Struct.***, 349,13 (1995).

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