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An Infrared and Raman Spectroscopic Investigation of Copper(II) Tetracyanonickelate Complexes of α-, β- and γ-Picoline

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Abstract. Copper(II) dipicoline tetracyanonickelate complexes, $CuL_2Ni(CN)_4$ (L = α-, β- or γ-picoline), have been prepared for the first time and their infrared and Raman spectra are reported. Their structure consists of polymeric layers of $\{Cu{-}Ni(CN)_4\}_\infty$ with picoline molecules bound directly to the copper. It is proposed that the Cu—NC bonds are in two nonequivalent pairs in trans positions. Low temperature (83K) IR spectra have also been recorded and it is noted that the $Ni(CN)_4$ group frequencies increase with decreasing temperature while the picoline frequencies are insensitive to temperature.

Key words: IR and Raman spectra, tetracyanonickelate complex, α-, β- and γ-picoline complexes.

1. Introduction

The infrared and Raman spectra of Hofmann-type clathrates with the general formula $M(NH_3)_2M'(CN)_4 \cdot 2G$, where M is the metal being in six-coordination with two NH_3 molecules and four nitrogen atoms of CN ligands, M′ is the metal being in four-coordination with four carbon atoms of CN and G represents the guest molecules, have been studied in detail [1–5]. Based on this structure, several metal complex hosts, $ML_2Ni(CN)_4$, have been developed by replacing the ammonia molecules by other N-donor ligands (L) [6–10]. Among the series of metal (II) tetracyanonickelate host lattices, copper(II) complex hosts show in some cases [3,6] different spectral features in comparison with analogous complexes with other metals, due to the Jahn-Teller effect [11–12], which occurs in Cu^{2+} complexes and leads to two nonequivalent trans pairs of Cu—NC bonds with different lengths. For the Jahn-Teller effect in octahedral-type copper(II) complexes two bonds are either longer or shorter than the other four. When four of the ligands surrounding the metal are of one type (e.g. CN^-) and two of a second type (L), the four similar ligands may be expected to have equal metal-ligand bond lengths, but this is not always the case. Although in the cases of Hofmann type $Cu(NH_3)_2Ni(CN)_4 \cdot 2G$ (where G = benzene, pyrrole, or thiophene) clathrates, the four Cu—NC bonds were found to be equal [13], the $Cu(NH_3)_2Ni(CN)_4 \cdot 2C_6H_5NH_2$ clathrate [3] and the $Cupy_2Ni(CN)_4$ complex [6] have two pairs of nonidentical M—NC bond lengths. Thus, it is of interest to investigate the spectroscopic features of the new Cu(II) dipicoline tetracyanonickelate, $CuL_2Ni(CN)_4$ (L = α-, β- or γ-picoline) (abbreviated to Cu-Ni-L)

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complexes. These complexes can form inclusion compounds with various molecules. We will report our spectroscopic studies on these inclusion compounds in a future publication, but a necessary first task is the interpretation of the spectra of the pure complexes.

Table I. Fundamental vibrational wavenumbers (cm^{-1}) of α- and β-picoline in the Cu-Ni-L complexes

α-picoline		β-picoline				Assignment	
Liquid[a]	Cu-Ni-α pic	Liquid[a]		Cu-Ni-β pic			
IR	IR	IR	Ra	IR	Ra		
3080	3087	–	3085	3086	3090	A′	ν_1 CH str.
3046[b]	3070	–	3054	3062	3070		ν_2 CH str.
1233	1220	1227	1227	1249	–		ν_3 X-sens.
1590	1607	1595	1594	1613	1613		ν_4 ring str.
1475	1487	1479	1477	1484	–		ν_5 ring str.
1143	1162 1153	1188	1190	1201	1199		ν_6 CH bend i.p.
1047	1071	1043	1041	1061	–		ν_7 CH bend i.p.
800	804 790	–	810	833 822	825		ν_8 X-sens.
994	1016	1028	1025	1035	1039		ν_9 ring str.
548	550	538	535	539	542		ν_{10} X-sens.
3080	3087	3085	–	3108	–		ν_{11} CH str.
3030	3026	–	3030	3049	–		ν_{12} CH str.
1565	1569	1578	1575	1584	–		ν_{13} ring str.
1440	1449	1414	1409	1422	–		ν_{14} ring str.
1376	1382	1340	1336	1344	–		ν_{15} ring str.
1291	1303	–	1286	1274	–		ν_{16} CH bend i.p.
358	390	338	338	366	–		ν_{17} X-sens.
1099	1109	1106	1103	1109	–		ν_{18} CH bend i.p.
628	639	630	628	658	657		ν_{19} ring def. i.p.
972	968	987	984	–	–	A″	ν_{20} CH bend o.p.
883	–	923	919	922	–		ν_{21} CH bend o.p.
403	433	399	398	417	–		ν_{22} ring def. o.p.
940	948	941	942	943	–		ν_{23} CH bend o.p.
751	754	788	795	792	–		ν_{24} CH bend o.p.
729	723	708	710	699	–		ν_{25} ring def. o.p.
470	473	457	454	–	–		ν_{26} CH bend o.p.
207	–		217	–	221		ν_{27} X-sens.
2950	2955	2980	2975	2969 2942	–		ν_a (CH_3)
2925	2919	–	2923	2920	2920		ν_s (CH_3)
1440	1449	1452	1453	1452	–		δ_a (CH_3)
1376	1381	1385	1380	1384	1386		δ_s (CH_3)
1040	1042	1043	1041	1039	–		CH_3 rock
					244		ν(M—N)pic.

[a] Taken from ref. 14 except ν_{11} in the case of β-picoline.

[b] Raman line.

2. Experimental

The complexes were prepared employing a method analogous to that used for quinoline complexes [9]. The samples were analysed for metal content using the X-ray fluorescence method.

The IR spectra of mulls and discs were recorded on a Perkin-Elmer 621 spectrometer. The Raman spectra of the samples were excited with the 488 nm line of an argon ion laser and

Table II. The fundamental vibrational wavenumbers (cm^{-1}) of γ-picoline in the Cu-Ni-γ-pic. complex

Liquid[a]		Cu-Ni-γ pic		Assignment[a]	
IR	Ra	IR	Ra		
3050	3051	3083	–	A′	ν_1 CH str.
3050	3051	3062	–		ν_2 CH str.
1211	1212	1218 1207	1221 1212		ν_3 X-sens.
1606	1606	1626	–		ν_4 ring str.
1497	1497	1504	–		ν_5 ring str.
1222	1221	1245 1231	1231		ν_6 CH bend i.p.
1070	1071	1066	1070		ν_7 CH bend i.p.
802	803	814	818		ν_8 X-sens
996	996	1033	1032		ν_9 ring str.
516	516	550	–		ν_{10} X-sens.
3070	–	3090	–	A″	ν_{11} CH str.
3029	3034	3039	–		ν_{12} CH str.
1564	1565	1562	–		ν_{13} ring str.
1413	1413	1432	–		ν_{14} ring str.
1360	–	1360	–		ν_{15} ring str.
1280	1280	–	–		ν_{16} CH bend i.p.
–	344	357	358		ν_{17} X-sens.
1100	1094	1118	–		ν_{18} CH bend i.p.
–	671	670	673		ν_{19} ring def. i.p.
973	971	979 958	–		ν_{20} CH bend o.p.
870	874	875	–		ν_{21} CH bend o.p.
–	383	396	394		ν_{22} ring def. o.p.
870	874	875	–	A′	ν_{23} CH bend o.p.
799	803	802	–		ν_{24} CH bend o.p.
727	–	718	–		ν_{25} ring def. o.p.
486	487	494	–		ν_{26} CH bend o.p.
–	214	–	217		ν_{27} X-sens.
2962	2964	2978	–		$\nu_a (CH_3)$
2924	2923	2924	2929		$\nu_s (CH_3)$
1445	1454	1438	–		$\delta_a (CH_3)$
1381	1381	1381	1382		$\delta_s (CH_3)$
1041	1045	1033	–		CH_3 rock
			275		$\nu(M{-}N_{pic})$

[a] Taken from ref. 15.

the spectra were recorded on a SPEX Ramalog spectrometer with a slit width of 3 cm^{-1} by use of a spinning cell.

3. Results and Discussion

The vibrational wavenumbers of α-, β- or γ-picoline in the IR and Raman spectra of the Cu-Ni-L complexes are given in Tables I and II, together with the IR and Raman wavenumbers of the liquid picolines [14, 15]. It is noted that certain vibrations of α-, β- or γ-picoline show significant shifts (up to 34 cm^{-1}) to higher frequency when compared to the same vibrations in the neat liquids. Analogous shifts on coordination were observed in pyridine [6, 16] and α-, β- and γ-picoline complexes [8, 10, 15]. These were explained by the coupling of the internal modes of the ligand with the M—N (ligand) vibrations [17]. Since the vibrational spectra of the Cu-Ni-L complexes show all the characteristics of coordinated picoline, we propose that picoline molecules are directly bonded to the metal (Cu).

When the vibrational wavenumbers of Cu-Ni-L complexes (where L = α-, β- or γ-picoline) are compared with the previously reported analogous complexes M-Ni-L (M = Ni or Cd, L = α-, β- or γ-picoline) [8, 10] it is found that the differences between liquid and ligand values of α-, β- and γ-picoline are metal dependent and are greater in the copper complexes.

Cu-Ni-L (L = β- or γ-picoline) complexes are stable in air and do not show signs of decomposition, however the Cu-Ni-α pic complex is unstable once removed from the solution in which it is crystallized. Because of the rapid decomposition of the Cu-Ni-(α-pic) sample under laser excitation we were not able to record its spectrum.

The vibrational wavenumbers of the $Ni(CN)_4$ group are given in Table III together with the vibrational wavenumbers of the $Cupy_2Ni(CN)_4$ complex [6]. The ν(CN) and δ(NiCN) vibrational frequencies are found to be similar to those of Hofmann-type clathrates [3] and pyridine complexes [6] indicating that $\{Cu{-}Ni(CN)_4\}_\infty$ layers have been preserved. If the cyanide groups around the nickel atom have a local D_{4h} environment, one ν(CN) (E_u) band only is expected in the IR spectrum and two other ν(CN) (A_{1g} and B_{1g}) vibrations are expected in the Raman spectrum. However, two strong bands, rather than one are observed in the ν(CN) (E_u) and also the δ(NiCN) (E_u) regions of the IR spectra of the Cu-Ni-L complexes.

Table III. The wave numbers (cm^{-1}) of the $Ni(CN)_4$ group vibrations of the $CuL_2Ni(CN)_4$ (L = α-, β- or γ-picoline) and $Cupy_2Ni(CN)_4$ complexes[a]

Cu-Ni-α pic	Cu-Ni-β pic	Cu-Ni-γ pic	Cu-Ni-py[b]	Relative intensity	Assignment
n.m.	(2183)	(2179)	(2187)	vs	$\nu_1 A_{1g}\ \nu(CN)$
n.m.	(2150)	(2149)	(2154)	s	$\nu_4 B_{1g}\ \nu(CN)$
2175	2171	2164	2174	vs	$\nu_8 E_u\ \nu(CN)$
2142	2136	2136	2142		
559	554	n.o.	558	w	$\nu_9 E_u\ \nu(NiC)$
n.o.	454	n.o.	450	vw	$\nu_{12} A_{2u}\ \pi(NiCN)$
445	439	437	441	vs	$\nu_{10} E_u\ \delta(NiCN)$
426	422	424	426		

[a] The bands observed in the infrared spectra are given without parentheses; the bands observed in the Raman spectra are given in parentheses.

[b] Taken from ref. [6].

n.m. = not measured; n.o. = not observed; vs = very strong; s = strong; w = weak; vw = very weak.

The splitting points directly to a change of symmetry and removal of the degeneracy. This splitting was observed previously in the $Cu(NH_3)_2Ni(CN)_4 \cdot 2C_6H_5NH_2$ clathrate [3] and in the $Cupy_2Ni(CN)_4$ complex [6] and was accounted for in terms of a Jahn-Teller distortion which leads to two pairs of trans, non-identical Cu—NC bond lengths.

The ν(CN) frequencies are found to be slightly dependent on the ligand (L). This is probably due to the changes of the strength of the Cu—NC bonds, since it is known that there is a mechanical coupling between the M—N and C≡N stretching modes [6].

We also recorded the low temperature (83 K) IR spectra of the samples. It is found that whilst the picoline frequencies are insensitive to temperature, $Ni(CN)_4$ frequencies increase with decreasing temperature (up to 8 cm^{-1}). This is thought to be due to a slight contraction in the cavity size with decreasing temperature. We still have not observed Raman active modes in the IR spectra at 83 K.

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