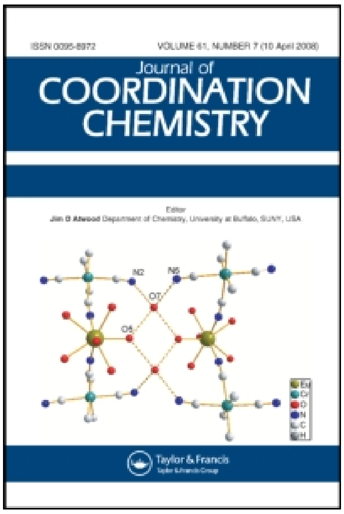

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

A VIBRATIONAL SPECTROSCOPIC STUDY OF TRANSITION METAL TETRACYANONICKELATE COMPLEXES OF 2-CHLOROPYRIDINE AND 2-BROMOPYRIDINE

Sevim Akyüz[a]; Meric Bakiler[b]; J. Eric[c]; D. Davies[c]
[a] Department of Physics, Faculty of Science, Istanbul University, Istanbul, Türkiye [b] Department of Physics, Mimar Sinan University, Istanbul, Türkiye [c] Environmental Science Division, Lancaster University, Lancaster, UK

To cite this Article Akyüz, Sevim , Bakiler, Meric , Eric, J. and Davies, D.(1996) 'A VIBRATIONAL SPECTROSCOPIC STUDY OF TRANSITION METAL TETRACYANONICKELATE COMPLEXES OF 2-CHLOROPYRIDINE AND 2-BROMOPYRIDINE', Journal of Coordination Chemistry, 37: 1, 1 — 6

To link to this Article: DOI: 10.1080/00958979608023535

URL: http://dx.doi.org/10.1080/00958979608023535

J. Coord. Chem., 1996, Vol 37, pp. 1-6
Reprints available directly from the publisher
Photocopying permitted by license only

A VIBRATIONAL SPECTROSCOPIC STUDY OF TRANSITION METAL TETRACYANONICKELATE COMPLEXES OF 2-CHLOROPYRIDINE AND 2-BROMOPYRIDINE

SEVIM AKYÜZ*

Department of Physics, Faculty of Science, Istanbul University, Vezneciler 34459, Istanbul, Türkiye

MERIÇ BAKILER

Department of Physics, Mimar Sinan University, Besiktas 80690, Istanbul, Türkiye

and J. ERIC D. DAVIES

Environmental Science Division, Lancaster University, Lancaster LA1 4YQ, UK

(Received February 8, 1995; in final form June 7, 1995)

The FT-IR and Raman spectra of eight new complexes of formula $ML_2Ni(CN)_4$ (where M = Mn, Fe, Co, Ni, Cu or Cd and L = 2-chloropyridine; M = Ni or Cd and L = 2-bromopyridine) are reported. The spectroscopic results indicate that the complexes have structures consisting of corrugated polymeric layers of $[M\text{-}Ni(CN)_4]_\infty$ with 2-substituted pyridine molecules bound directly to the metal (M). For a given ligand (2-Clpy or 2-Brpy) the effects of metal-ligand bond formation on the ligand modes are examined. Metal-ligand bond strengths of the halo-derivatives of pyridine (L = 2-Clpy or 2-Brpy), inferred by the effects on frequency shifts of certain ligand modes, have also been compared.

KEYWORDS: tetrocyanonickelate, vibrational spectroscopy, transition metal

INTRODUCTION

In a recent paper[1] we reported the vibrational spectra of transition metal tetracyanonickelate complexes of 3-chloropyridine. In this paper we report the vibrational spectra of eight new tetracyanonickelate complexes of 2-chloropyridine and 2-bromopyridine, $ML_2Ni(CN)_4$ (M = Mn, Fe, Co, Ni, Cu or Cd, L = 2-Clpy; M = Ni or Cd, L = 2-Brpy, abbreviated henceforth as M-Ni-L). The aim of this study is to provide further examples of tetracyanonickelate hosts. We also want to compare the vibrational results of isomorphous complexes formed by halide-substituted pyridines. The information available in the literature on metal complexes of halopyridines is scarce.[1-4] and there is no complete vibrational study on 2-chloro- or 2-bromopyridine complexes with transition metals.

---

* Author for correspondence.

EXPERIMENTAL

The complexes were prepared using a method analogous to that given in the literature.[5] The samples were analyzed for metal content using an X-ray fluorescence method. The FT-IR spectra of nujol mulls between CsI plates or KBr discs were recorded on Nicolet MX IE, Nicolet 510 and Jasco 5300 FT-IR spectrometers. The Raman spectra of the samples were measured with a Cary 81 spectrometer using a slit width of 4 cm^{-1} by use of a spinning cell. The samples were excited using 514.5 or 488 nm lines of an Ar^+ laser.

RESULTS AND DISCUSSION

The vibrational spectra of the M-Ni-L complexes are very similar indicating that they have analogous structures. The FT-IR spectrum of Cu-Ni-2Clpy is given in Figure 1 as a typical example of M-Ni-L complexes. Because of rapid decomposition of the M = Cu, Fe and Co samples under laser excitation we were not able to record their Raman spectra.

$Ni(CN)_4$ Group Vibrations

The vibrational wavenumbers of the $Ni(CN)_4$ group for the complexes studied are

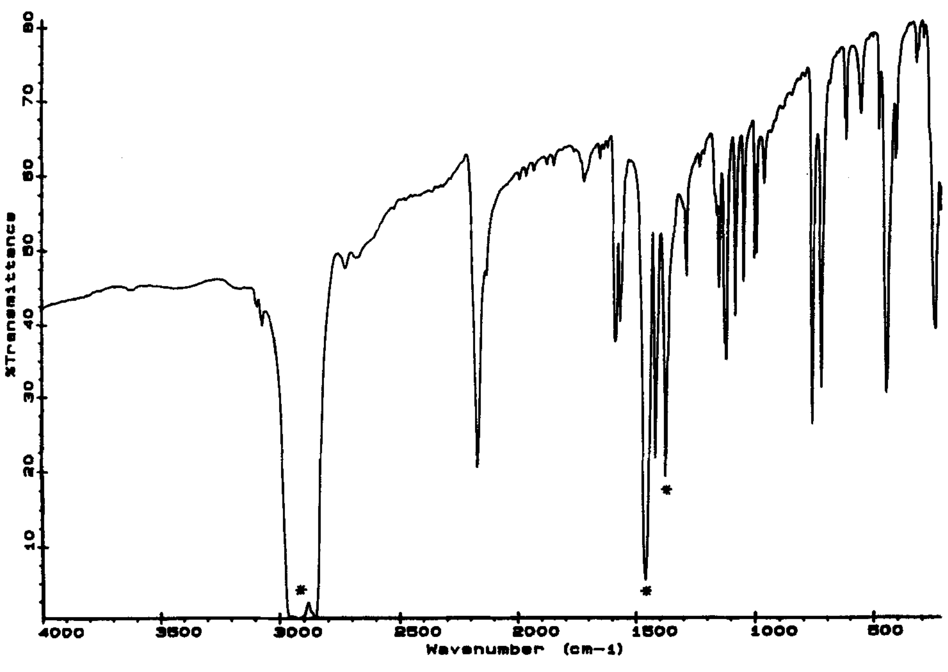

Figure 1 FT-IR spectrum of $Cu(2Clpy)_2 Ni(CN)_4$ $Cu(2Clpy)_2 Ni(CN)_4$. Nujol bands are indicated (*).

given in Table 1. The characteristic wavenumbers of the υ(CN) and δ(NiCN) modes are found to be similar to those of Hofmann-type clathrates[6] and Hofmann pyridine complexes,[7] indicating that $[M\text{-}Ni(CN)_4]_\infty$ layers have been preserved. Moreover, observation of one IR active (E_u) and two Raman active (A_{1g} and B_{1g}) vibrational modes of υ(CN) shows that cyanide groups around the nickel atom have a local D_{4h} environment.

Although we were not able to record a Raman spectrum of the Cu-Ni-2Clpy complex, the observation of one single band in the υ(CN) (E_u) and δ(Ni-C≡N)(E_u) regions of the IR spectrum indicates that, in spite of the Jahn-Teller effect, the Cu-Ni-2Clpy complex has the same sheet structure as the other M-Ni-2Clpy complexes. In previous studies on $CuL_2Ni(CN)_4$ complexes (where L = pyridine, 2-, 3- and 4-methylpyridine, 3,5-dimethylpyridine or aniline),[7-10] two strong bands rather than one were observed in the υ(CN)(E_u) and δ(Ni-C≡N) (E_u) regions of the IR spectra. The additional IR activity in E_u modes of the $Ni(CN)_4$ group vibrations observed in all copper tetracyanonickelate complexes except the present case, was explained by the removal of the degeneracy by the Jahn-Teller effect and proposed non-equivalent *trans* pairs of Cu-NC bonds with different lengths were proposed. For the Jahn-Teller effect in octahedral type complexes, two bonds are either longer or shorter than the other four. Therefore it is proposed that in the case of Cu-Ni-2Clpy, four equal Cu-NC bond lengths are shorter and two equal Cu-N(2Clpy) bond lengths are longer in comparison with those of other M-Ni-2Clpy complexes. This result is also confirmed by analysis of the frequency shifts of the 2-Clpy vibrational modes, due to complex formation as will be discussed in the following section.

2-Chloropyridine and 2-Bromopyridine Vibrations

The vibrational wavenumbers of 2-chloropyridine and 2-bromopyridine observed in the IR and Raman spectra of M-Ni-L complexes are given in Tables 2 and 3, respectively, together with the IR and Raman wavenumbers of the liquid halopyridines.[11] It is noted that certain vibrations of 2-chloropyridine and 2-bromopyridine show significant shifts (up to 32 cm^{-1}) to higher wavenumber when compared to the same vibrations of the neat liquids. The shifts are metal dependent. Analogous shifts on coordination were observed in pyridine[7,12] and substituted

Table 1 The wavenumbers (cm^{-1}) of the $Ni(CN)_4$ vibrations of the M-Ni-L complexes.[a]

Assignment	L = 2-Clpy						L = 2-Brpy		Relative Intensity
	Mn	Cd	Fe	Co	Ni	Cu	Cd	Ni	
A_{1g} ν(CN)	(2176)	(2184)	-	(2184)	(2189)	-	-	-	vs
B_{1g} ν(CN)	(2165)	(2171)	-	(2175)	(2177)	-	-	-	s
E_u ν(CN)	2158	2160	2139	2163	2167	2172	2159	2166	vs
ν(^{13}CN)	2118sh	2121	2117sh	2123sh	2131sh	2132	2118	-	vw
E_u ν(NiC)	553	552	556m	556m	560	562m	550	561	w
A_{2u} π(NiCN)	452	445	456	459	459	408	449vw	460	sh
E_u δ(NiCN)	436	431	440	444	445	454	432	445	vs

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

Abbreviations: vs = very strong; s = strong; m = medium; w = weak; vw = very weak; sh = shoulder

Table 2 The fundamental vibration wavenumbers(cm^{-1}) of 2-Clpy in M-Ni-2Clpy complexes.

Assignment (11)	Wilson No(13)	2-Clpy(11) IR	2-Clpy(11) Ra	2-Clpy IR	Mn IR	Mn Ra	Cd IR	Cd Ra	Fe IR	Co IR	Ni IR	Ni Ra	Cu IR
A′(A_1)													
υ(CH)	2	3082sh	3071s	3075sh	3071s	-	3079sh	3076vs	3080sh.	3075sh	-	-	3076sh
υ(CH)	20a	3059s	3058vs	3055vs	-	-	3069m	3074sh	3071m	3071s	-	-	3070s
υ(CC)	8a	1577s	1582s	1577vs	1594s	1598m	1593s	-	1594s	1595vs	1596s	1599s	1589vs
υ(CC)	19a	1452s	1459m	1453vs	1461vs	-	1461s	-	1461vs	1462vs	1463vs	1467m	1459vs
δ(CH)	9a	1148s	1153s	1149vs	1155s	1156m	1153s	1154m	1155vs	1156vs	1157vs	1160m	1153s
δ(CH)	18a	1044s	1045vs	1045s	1053vs	1058s	1052s	1056s	1054vs	1055vs	1057vs	1060s	1051s
υ_{ring}	1	992s	995vs	991s	1004s	1009vs	1006s	1009vs	1005s	1006vs	1008vs	1011vs	1005s
x-sens	13	1117vs	1121s	1117vs	1133vs	1137m	1132vs	1136m	1134vs	1134vs	1136vs	1140m	1129vs
x-sens	12	725s	728s	724vs	731s	738vs	731vs	733s	732s	732vs	734vs	739s	729vs
x-sens	6a	425m	428vs	426m	-	443vs	-	440s	-	-	443vs	446vs	-
(B_2)													
υ(CH)	20b	3082sh	3071s	3084sh	3104m	-	3103m	3076vs	-	3113m	-	-	3089m
υ(CH)	7b	3059s	3058vs	3003m	3013vw	-	-	3074sh	-	-	-	-	-
υ(CC)	8b	1568s	1573s	1568s	1565s	1562m	1566s	-	1560s	1560s	1561s	1565s	1566vs
υ(CC)	19b	1420s	1423m	1420vs	1418vs	-	1419vs	-	1419vs	1420vs	1422vs	-	1420vs
υ(CC)	14	1363w	1367w	1365	1374vw	-	1373vw	-	1394vw	1397sh	1395sh	-	1378s
δ(CH)	3	1286m	1291s	1286s	1295s	1301m	1294s	1297m	1296s	1297vs	1298s	1303m	1289m
δ(CH)	18b	1083s	1085s	1083vs	1087s	1092m	1088s	1091m	1089vs	1089vs	1091vs	1095m	1085s
δ_{ring}	6b	617m	621s	617m	629s	634m	629s	631m	629m	629s	631m	635s	622m
x-sens	15	-	313m	312w	333m	-	333m	335m	341	340	344m	341s	330w
A″(A_2)													
γ(CH)	17a	960w	967w	961m	961m	-	961m	-	962m	962s	963m	-	967m
γ(CH)	10a	881w	889m	878w	-	-	-	-	-	884vw	883m	-	-
γ_{ring}	16a	406w	-	407m	416s	435m	414s	-	418s	421s	426sh	-	416m
(B_1)													
γ(CH)	5	-	-	914w	-	-	920w	-	920m	922m	920w	-	-
γ(CH)	10b	767s	772w	767vs	759vs	-	759vs	-	758vs	758vs	758vs	-	768s
γ_{ring}	4	-	-	691w	694w	-	692m	-	692m	693s	692s	-	694vw
γ_{ring}	11	480m	481w	480s	481m	477m	480m	-	481m	481s	483m	-	485m
x-sens	16b	-	190vs	-	-	-	-	-	-	-	-	-	-
Total Shifts of all ring and CH modes except 6a, 14, 10a, 5 and 16b					121		115		132	142	172		109

Table 3 The fundamental vibrational wavenumbers (cm^{-1}) of 2-Brpy in M-Ni-2Brpy complexes.

Assignment	Wilson No	2-Brpy IR	Cd IR	Ni IR
A'(A_1)				
υ(CH)	2	3069	3075m	—
υ(CH)	20a	3056s	3070m	—
υ(CC)	8a	1573s	1587vs	1589vs
υ(CC)	19a	1452s	1458s	1465
δ(CH)	9a	1146m	1155s	1158
δ(CH)	18a	1042w	1051s	1056
υ_{ring}	1	989m	1003vs	1006
x-sens.	13	1104s	1118vs	1118
x-sens.	12	700s	706s	709
x-sens.	6a	—	330w	—
(B_2)				
υ(CH)	20b	3069	3099w	—
υ(CH)	7b	3056	3070m	—
υ(CC)	8b	1563s	1558vs	1557
υ(CC)	19b	1417s	1415vs	1417
υ(CC)	14	1363w	—	—
δ(CH)	3	1282m	1294m	1294
δ(CH)	18b	1076s	1082s	1083s
δ_{ring}	6b	613m	626m	628m
x-sens.	15	265	286	296
A"(A_2)				
γ(CH)	17a	960w	959w	960
γ(CH)	10a	882m	—	—
γ_{ring}	16a	404w	412m	420m
(B_1)				
γ(CH)	5	934m	932w	934w
γ(CH)	10b	761vs	755vs	757
γ_{ring}	4	724w	723m	723
γ_{ring}	11	466s	468m	469m
x-sens.	16b	—	—	—
Total Shifts			119	168

pyridine complexes.[1,5,8,9] These were explained by coupling of the internal modes of the ligand with the M-N (ligand) vibrations.[12] In our previous papers we proposed a correlation between the sum of the differences between the liquid and ligand values of pyridine or pyridine derivative and the strength of the M-N (ligand) bond.[1,7] We will therefore use this approach for all the observed ring modes in the IR spectra of 2-Clpy and 2-Brpy complexes which are available for both. The total shifts are shown at the bottom of Tables 2 and 3. We note that the general increase in wavenumber for the 2-Clpy modes with different metals in M-Ni-2Clpy complexes is in the order Mn≈Cd<Fe<Co<Ni> Cu. For M-Ni-2Clpy complexes we infer that the order of the M-N(2Clpy) stretching frequency follows the same trend and this order reflects the increasing strength of the M-N bond. In the previous studies on tetracyanonickelate complexes with a series of transition metals, including Cu(II),[7,9,12] this order was found to be the same as the increasing order of the second ionization potentials of the metals (Mn≈Cd<Fe<Co<Ni<Cu). However, in the present case, the Cu-N(2Clpy) bond strength, contrary to all previously studied Cu-Ni-L complexes,[7,9] is found to be less than those of other metals (M-Ni-2Clpy). But as mentioned before, Cu-Ni-2Clpy exhibited different IR

spectral feature in comparison to other Hofmann type copper complexes.[7,8–10] Therefore the drop for copper is further evidence for our prediction that Cu-2Clpy bond lengths are longer than regularly expected values for this series of compounds.

The total IR shift values of a given metal with 2-Clpy and 2-Brpy as ligands (M = Ni or Cd) are also compared and found to be similar, which indicates that these metal ligand bond strengths are almost the same.

Acknowledgements

This work was supported by the Research Fund of The University of Istanbul. Project number Ö.30. S.A. and M.B. thanks Professor Çakil Erk for allowing them to use the FT-IR spectrometer in his laboratory.

References

1. S. Akyüz, T. Akyüz and J.E.D. Davies, *J. Mol. Struct.*, **265**, 85 (1992).
2. G.V. Quedraogo, C. More, Y. Richard and D. Benlian, *Inorg. Chem.*, **20**, 4387 (1981).
3. W.R. Scheidt, D.K. Geiger, Y. Ja. Lee, C.A. Reed and G. Lang, *Inorg. Chem.*, **26**, 1039 (1987).
4. D.E. Billing, *J. Inorg. Nucl. Chem.*, **31**, 137 (1969).
5. S. Akyüz, *J. Incl. Phenom.*, **3**, 403 (1985).
6. S. Akyüz, A.B. Dempster and R.L. Morehouse, *Spectrochim. Acta*, **30A**, 1989 (1974).
7. S. Akyüz, A.B. Dempster, R.L. Morehouse and S. Suzuki, *J. Mol. Struct.*, **17**, 105 (1973).
8. S. Akyüz, *J. Incl. Phenom.*, **4**, 219 (1986).
9. S. Yurdakul, S. Akyüz and J.E.D. Davies, *J. Mol. Struct.*, **156**, 91 (1987).
10. S. Akyüz, *J. Mol. Struct.* **68**, 41 (1980).
11. J.H.S. Green, W. Kynaston and H.M. Paisley, *Spectrochim. Acta*, **19**, 549 (1963).
12. S. Suzuki and W.J. Orville Thomas, *J. Mol. Struct.*, **37**, 321 (1977).
13. E.B. Wilson, *Phys. Rev.*, **45**, 706 (1934).