

Vibrational Spectroscopic Studies of 4-*tert*-Butylpyridine Tetracyanonickelate Dioxane Clathrates

ŞENAY YURDAKUL* and MEHMET BAHAT

Gazi Üniversitesi, Fen-Edebiyat Fakültesi, Teknikokullar, 06500 Ankara, Turkey.

(Received: 22 November 1995; in final form: 2 April 1996)

Abstract. Two new dioxane clathrates of the form $M(4\text{-}i\text{-tert-bupy})_2 \text{Ni}(\text{CN})_4 \cdot \text{dioxane}$ ($M = \text{Ni}$ or Co) have been prepared in powder form. Their spectral data were compared with those of the corresponding host complexes and found to be consistent with the host structure found in Hofmann type clathrates.

Key words: 4-*tert*-Butylpyridine, IR and Raman spectra, tetracyanonickelate clathrates.

1. Introduction

Detailed studies have been published [1–4] on the IR and Raman spectra of Hofmann-type clathrates with the general formula $M(\text{NH}_3)_2 M'(\text{CN})_4 \cdot 2\text{G}$, 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 in four-coordination with four carbon atoms of CN, and G represents the guest molecules. Based on this structure, several metal complex hosts, $[\text{ML}_2\text{Ni}(\text{CN})_4]$ and clathrates $[\text{ML}_2\text{Ni}(\text{CN})_4 \cdot 2\text{G}]$, have been developed by replacing the ammonia molecules by other N-donor ligands (L) [5, 6].

We have previously reported [7] the vibrational spectra of samples of some Hofmann 4-*tert*-butylpyridine complexes and their formula are given as $M(\text{L})_2\text{Ni}(\text{CN})_4$ [$M = \text{Mn}, \text{Cd}, \text{Fe}, \text{Co}, \text{Ni}$, L = 4-*tert*-butylpyridine]. We now report the results of IR and Raman spectroscopic studies of two new clathrates $M(\text{L})_2\text{Ni}(\text{CN})_4 \cdot \text{dioxane}$ [$M = \text{Ni}(\text{II})$ and $\text{Co}(\text{II})$, L = 4-*tert*-butylpyridine] [abbreviated henceforth as Ni-Ni-L-dio and Co-Ni-L-dio]. The evidence from these vibrational data suggests that the compounds belong to the Hofmann-type group of clathrates.

* Author for correspondence.

Presented at the Sixth International Seminar on Inclusion Compounds, Istanbul, Turkey, 27–31 August, 1995.

2. Experimental

The complexes were prepared by adding slightly in excess of one mole of 4-*tert*-butylpyridine dissolved in a liquid guest (dioxane) and this solution, together with an aqueous solution of one mole of $K_2Ni(CN)_4$, were added to an aqueous solution of the metal(II) chloride, with constant stirring. The precipitate was filtered and washed with water and acetone.

The freshly prepared compounds were analyzed for C, H and N by a CHN analyser (LECO, CHN-600) with the following results (*found %/calculated %*): $NiL_2Ni(CN)_4 \cdot dioxane$: C = 52.15/53.79, H = 5.69/5.92, N = 13.99/14.49, $CoL_2Ni(CN)_4 \cdot dioxane$: C = 52.08/53.83, H = 5.98/5.92, N = 13.29/14.48. Results are normal because one water molecule also behaves as guest in the resulting lattice.

The IR spectra of mulls and discs were recorded on Mattson 1000 FTIR and Perkin-Elmer 1330 spectrometers which were calibrated using polystyrene bands. The Raman spectrum of the $NiL_2Ni(CN)_4 \cdot dioxane$ compound (in powder form) was excited using the 514.5 nm line of a Spectra-Physics Model 2016- Ar^+ ion laser and recorded on a Jobin Yvon U1000 spectrometer which was calibrated using CCl_4 bands. It should be noted that because of its dark colour, Raman spectra could not be recorded for the $CoL_2Ni(CN)_4 \cdot dioxane$ compound.

3. Results and Discussion

The IR and Raman spectra of the Ni-Ni-L-dio clathrate are given in Figures 1 and 2, respectively. The assignments and the wavenumbers of the vibrational bands of 4-*tert*-butylpyridine observed in the IR and Raman spectra of the Ni-Ni-L-dio and Co-Ni-L-dio clathrates are listed in Table I, together with the liquid 4-*tert*-butylpyridine wavenumbers and the infrared values of the ligand in the Ni-Ni-L host complex [7] for comparison.

As is clear from Table I, the vibrational bands of 4-*tert*-butylpyridine observed in the IR spectra of the Ni-Ni-L complex and of the Ni-Ni-L-dio clathrate are found to be the same in frequency.

The 4-*tert*-butylpyridine vibrational modes observed in the IR and Raman spectra of the compounds studied show all the characteristics of a coordinated ligand, e.g. several modes of the coordinated ligand (except the butyl part of the ligand) have upward shifts in frequency compared to those in the free molecule and the shifts are metal dependent. Similar shifts are observed in the pyridine complexes [8] and explained as the coupling of the internal modes of the aromatic molecule with the M—N vibrations. Thus we have obtained direct evidence from the vibrational spectra of M-Ni-L-dio that 4-*tert*-butylpyridine molecules coordinated to metal [M = Ni or Co].

All the vibrational frequencies of the dioxane guest molecules in the IR spectra of M-Ni-L-dio clathrates correspond closely in frequency and intensity to those in the IR spectra of $M(NH_3)_2Ni(CN)_4 \cdot 2C_4H_8O_2$ (M = Ni or Cd) clathrates [9]. It is

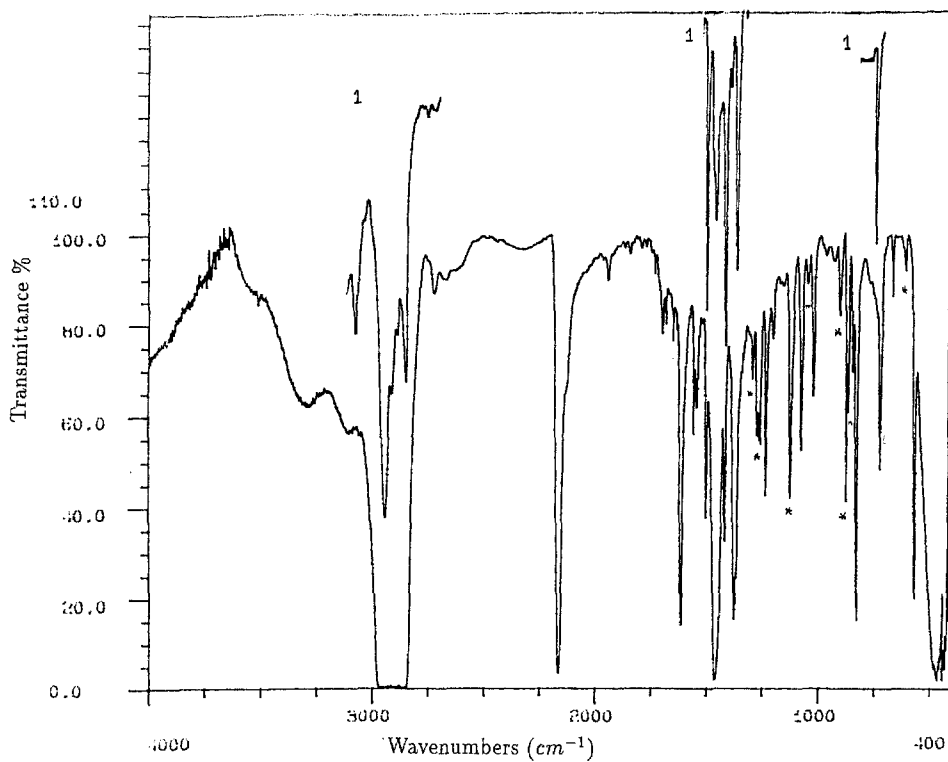


Figure 1. IR spectrum of the Ni-Ni-L-dio clathrate in Nujol mull. (1 in KBr). Dioxane bands marked *.

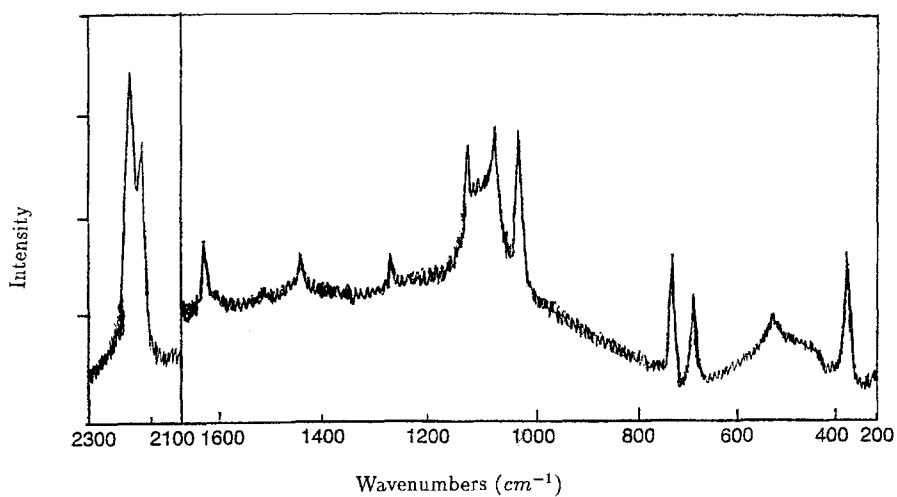


Figure 2. Raman spectrum of the Ni-Ni-L-dio clathrate.

Table I. The vibrational wavenumbers (cm^{-1}) of 4-*tert*-butylpyridine and dioxane in the M-Ni-L-dio clathrates.

| Assignments ^a | L = 4- <i>tert</i> - Butylpyridine ^a | | Ni-Ni-L ^a | Ni-Ni-L-dio | Ni-Ni-L-dio | Cu-Ni-L-dio |
|---------------------------------|--|---------|----------------------|-------------|-------------|-------------|
| | IR | Raman | IR | IR | Raman | IR |
| CH str. (py) | 3085 s | 3060 s | 3093 m | 3093 m | 3080 w | 3089 m |
| CH ₃ asym. str. (tb) | 2964 vs | 2967 m | 2967 s | 2967 s | 2974 w | 2967 s |
| CH ₃ sym. str. (tb) | 2869 s | 2867 m | 2869 m | 2865 m | — | 2871 m |
| δ (H ₂ O) | | | | 1700 w* | — | 1708 w* |
| Ring str. (py) | 1596 vs | 1596 m | 1618 vs | 1618 vs | 1612 w | 1614 m |
| Ring str. (py) | 1544 s | 1543 vs | 1556 w | 1556 w | — | 1556 w |
| | | | 1546 w | 1546 w | — | 1544 w |
| Ring str. (py) | 1494 s | 1495 vw | 1502 s | 1502 s | — | 1502 m |
| CH ₃ asym. def. (tb) | 1469 s | 1470 w | 1471 m | 1471 m | — | 1471 s |
| CH ₃ asym. def. (tb) | 1457 s | — | 1459 m | 1459 m | 1460 w | 1459 m |
| CH ₃ sym. def. (tb) | 1409 vs | 1408 vw | 1419 s | 1419 s | — | 1419 m |
| CH ₃ asym. def. (lb) | 1365 s | — | 1367 s | 1367 s | — | 1365 m |
| CH ₂ twist | | | | 1294 m* | — | 1294 s* |
| i.p. (CH) (py) | 1274 s | 1274 m | 1272 s | 1272 s | 1277 w | 1272 vs |
| CH ₂ twist | | | | 1265 s* | — | 1262 s* |
| i.p. (CH) (py) | 1224 m | 1224 m | 1234 s | 1234 s | — | 1234 w |
| CC str. (py) | 1203 m | 1202 w | 1203 m | 1203 m | — | 1201 m |
| CC str. (lb) | 1120 w | 1120 s | — | — | — | — |
| Ring str. | | | | 1124 s* | 1129 m | 1124 vs* |
| CH ₂ rock | | | | | | 1082 s* |
| i.p. (CH) (py) | 1074 s | 1074 m | 1076 s | 1076 s | 1080 m | 1075 s |
| Ring str. | | | | 1049 w* | — | 1048 s* |
| | | | | | | 1044 s* |
| Ring str. (py) | 995 vs | 996 vs | 1022 s | 1024 s | 1030 m | 1020 w |
| CH ₃ rock (tb) | 927 w | 931 w | 925 w | 925 w | — | — |
| CH ₃ rock (tb) | 869 vw | — | — | — | — | — |
| CH ₂ rock | | | | 906 m* | — | 905 s* |
| | | | | | | 897 s* |
| Ring str. | | | | 873 s* | — | 873 s* |
| | | | | 865 s* | — | 865 s* |
| py breathing | 842 s | 842 m | 846 m | 846 m | — | 844 vw |
| o.p. (CH) (py) | 821 vs | — | 829 vs | 829 vs | — | 830 m |
| o.p. (CH) (py) | 750 m | — | 754 vw | 754 vw | — | 752 m |
| o.p. ring def (py) | 711 s | — | 725 m | 725 m | 730 m | — |
| CC str. (tb) | 669 vs | 667 vw | 669 vw | 669 vw | 669 m | — |
| Ring bending | | | | 644 sh | — | 622 w |
| | | | | 611 w* | — | 611 m* |
| Skeletal str. (lb) | 569 vs | 572 w | 570 vs | 570 vs | — | 569 s |
| Rock (lb) | 534 m | 527 m | 541 m | 541 m | 548 m | 539 m |
| CCC def. (lb) | 392 m | — | 394 sh | 394 sh | — | 392 sh |
| CH ₃ torsion (tb) | 312 m | 314 m | 326 w | 327 w | — | 330 w |
| ν (M-N) | | | 267 w | 267 m | 262 m | 250 w |

* Bands of dioxane.

^a Wavenumbers and assignment are taken from Ref. 7.

i.p. = in plane, o.p. = out of plane, str. = stretch, sym. = symmetric, asym. = asymmetric vibrations, vw = very weak, w = weak, m = medium, s = strong, vs = very strong, sh = shoulder.

Table II. The vibrational wavenumbers (cm^{-1}) of the $\text{Ni}(\text{CN})_4$ group of M-Ni-L-dio clathrates and Ni-N i-L complex.

| Assignment | Ni-Ni-py ^a | Ni-Ni-L ^b | Ni-Ni-L-dio | Co-Ni-L-dio |
|-------------------------|-----------------------|----------------------|-------------|-------------|
| $A_{1g} \nu(\text{CN})$ | (2172) vs | (2181) s | (2183) vs | — |
| $B_{1g} \nu(\text{CN})$ | (2160) s | (2174) sh | (2175) s | — |
| $E_u \nu(\text{CN})$ | 2154 s | 2165 vs | 2167 vs | 2161 vs |
| HOT $\nu(\text{CN})$ | | 2130 sh | 2130 sh | |
| $E_u \delta(\text{CN})$ | 425 vs | 439 vs | 439 vs | 435 vs |

^{a,b} Taken from Refs. 8 and 7, respectively.

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

found that dioxane escapes slightly from dioxane-treated samples upon grinding or under reduced pressure without any change in the vibrational frequencies of the host structure.

The vibrational wavenumbers of the $\text{Ni}(\text{CN})_4$ group vibrations of the M-Ni-L-dio clathrates are given in Table II, along with the vibrational wavenumbers of the $\text{Ni}(\text{py})_2\text{Ni}(\text{CN})_4$ complex. The $\nu(\text{CN})$ and $\delta(\text{NiCN})$ vibrational wavenumbers are found to be similar to those of Hofmann-type clathrates [3] and the pyridine [8] complex, showing that the $\{\text{M-Ni}(\text{CN})_4\}_\infty$ layers have been preserved. Since we observed only one $\nu(\text{CN})(E_u)$ band in the IR spectra and the other two $\nu(\text{CN})(A_{1g}$ and $B_{1g})$ bands in the Raman spectra of the M-Ni-L-dio clathrates, we propose a square planar environment around the tetracyanonickelate ion.

We did not observe any differences in the $\text{Ni}(\text{CN})_4$ group vibrational modes of the M-Ni-L-dio clathrates in comparison to those of the corresponding M-Ni-L [7] complexes.

Acknowledgements

This study was funded by the Turkish Scientific and Technical Research Council (TUBITAK) through research Grant No. TBAG- 1301. We also thank Prof. Dr. Z. Kantarci for Raman spectra.

References

1. T. Miyoshi, T. Iwamoto, and Y. Sasaki: *Inorg. Chim. Acta* **1**, 120 (1967).
2. T. Iwamoto, T. Nakano, M. Morita, T. Miyoshi, T. Miyamoto, and Y. Sasaki: *Inorg. Chim. Acta* **2**, 313 (1968).
3. S. Akyüz, A.B. Dempster, and R.L. Morehouse: *Spectrochim. Acta* **30A**, 1989 (1974).
4. J.E.D. Davies, A.B. Dempster, and S. Suzuki: *Spectrochim. Acta* **30A**, 1183 (1974).
5. Ş. Ağustoslu, S. Akyüz, and J.E.D. Davies: *J. Mol. Struct.* **114**, 437 (1984).
6. S. Akyüz: *J. Incl. Phenom.* **3**, 403 (1985).
7. Ş. Yurdakul, and M. Bahat: *J. Mol. Struct.* (in press).
8. S. Akyüz, A.B. Dempster, R.L. Morehouse, and S. Suzuki: *J. Mol. Struct.* **17**, 105 (1973).
9. A.B. Dempster, R.L. Morehouse, and H. Uslu: *Spectrochim. Acta* **31A**, 1775 (1975).