Journal of Inclusion Phenomena and Molecular Recognition in Chemistry **28:** 259–267, 1997.

Vibrational Spectroscopic Studies on the Hofmann-dabn-Type Benzene Clathrates: M(1,4-diaminobutane)$Ni(CN)_4 \cdot 1.5C_6H_6$ (M = Mn, Fe, Co, Ni or Cd)

ERGÜN KASAP[*] and SÜLEYMAN ÖZCELÍK
Gazi Üniversitesi, Fen Edebiyat Fakültesi, Teknikokullar, 06500, Ankara, Turkey

(Received: 26 July 1996; in final form: 1 October 1996)

Abstract. IR spectra of M(1,4-diaminobutane)$Ni(CN)_4 \cdot 1.5C_6H_6$ (M = Mn, Fe, or Co), and IR and Raman spectra of M(1,4-diaminobutane)$Ni(CN)_4 \cdot 1.5C_6H_6$ (M = Ni or Cd) clathrates are reported. The spectral features suggest that the compounds are similar in structure to the Hofmann-dabn-type clathrates.

Key words: Clathrates, inclusion compounds, 1,4-diaminobutane, IR spectra, Raman spectra, benzene, tetracyano-nickelate.

1. Introduction

Recently several three-dimensional host lattices, Cd(α,ω-diaminoalkane) $Ni(CN)_4$, have been developed from the two-dimensional Hofmann-type host lattice, $Cd(NH_3)_2Ni(CN)_4$, by replacing the ammonia molecules by bidentate ligands with longer carbon chains, with the aim of extending the range of guest molecules which can be accommodated in the host lattices [1,2]. Bidentate α, ω-diamino alkane ligands with long carbon chains give three-dimensional host structures, and permit the inclusion of bulkier guest molecules, by bridging between the Cd atoms in the adjacent two-dimensional $[Cd—Ni(CN)_4]_\infty$ layers [1–3]. In previous studies, Iwamoto et al. reported the preparation of Cd(dabn)$Ni(CN)_4 \cdot x$G (dabn = 1,4-diaminobutane, x = 1–1.5; G = an aromatic guest molecule such as pyrrole, benzene, aniline, etc.) [2], and determined the crystal structures of Cd(dabn)$Ni(CN)_4 \cdot x$G clathrate compounds (x = 1, G = 2,5-xylidine [4], and N, N-dimethylaniline in the monoclinic ($P2_1/m$), x = 1, G = pyrrole in the monoclinic ($P2/m$) and x = 1.5, G = aniline or o-toluidine in the triclinic system ($P\bar{1}$) [5,6]) by single crystal X-ray diffraction methods. The crystal structure of Cd(dabn)$Ni(CN)_4 \cdot 1.5$ aniline is shown in Figure 1 [5]. These studies show that the compounds in this series are not isomorphous with each other, but they have a Hofmann-type structure and may be comparable to the Hofmann-type and analogous series which are isostructural [5, 7]

---

[*] Author for correspondence.

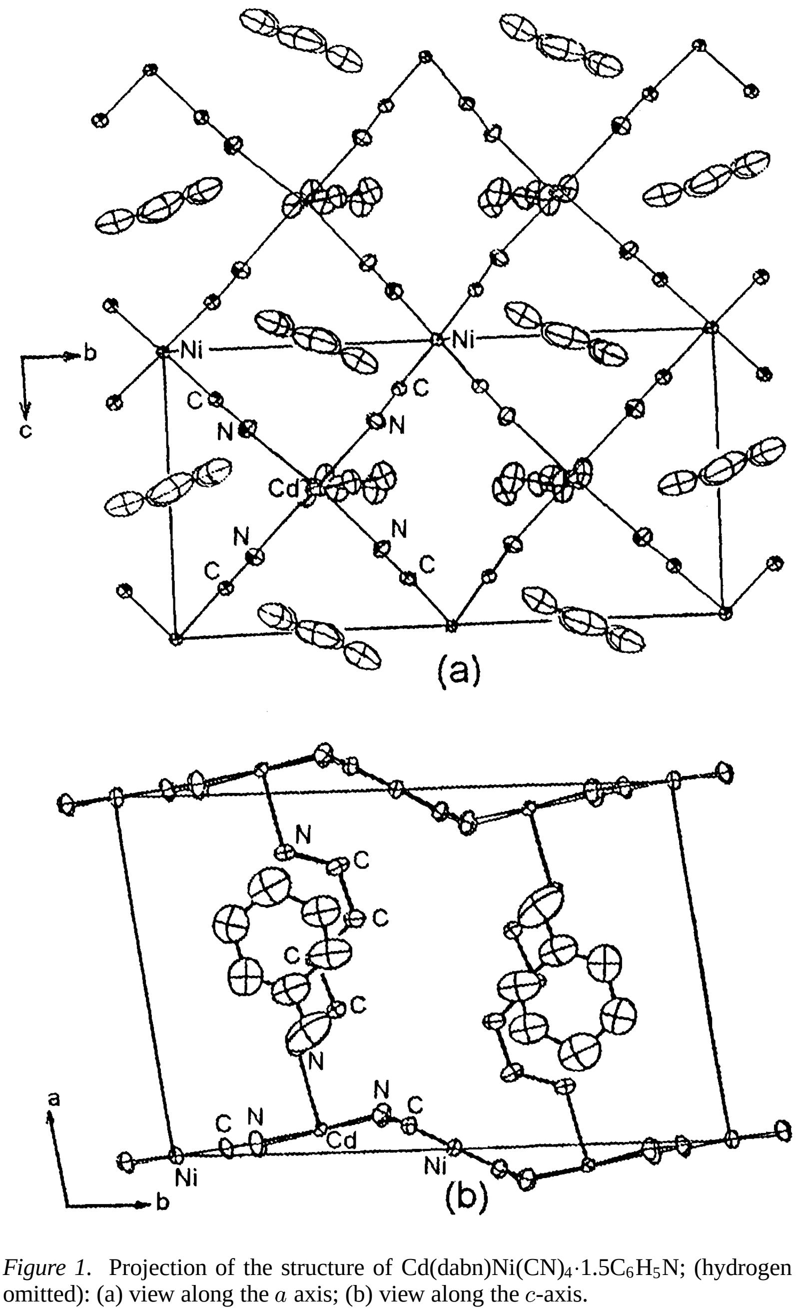

Figure 1. Projection of the structure of $Cd(dabn)Ni(CN)_4 \cdot 1.5C_6H_5N$; (hydrogen atoms are omitted): (a) view along the a axis; (b) view along the c-axis.

We have extended these studies and prepared $M(dabn)Ni(CN)_4 \cdot 1.5C_6H_6$ (M = Mn, Fe, Co or Ni) compounds for the first time. The IR spectra of $M(dabn)Ni(CN)_4 \cdot 1.5C_6H_6$ (M = Mn, Fe, Co, Ni or Cd) (abbreviated henceforth as M-Ni-Bz), and the Raman spectra of M(dabn)Ni$(CN)_4$·1.5C_6H_6 (M = Ni or Cd) compounds are reported. The IR spectrum of the Cd(dabn)Ni$(CN)_4$·1.5 aniline clathrate is also reported for comparison. The Raman spectra of compounds (M = Mn, Fe or Co) could not be obtained by using the 488 or 515 nm laser line. A previous paper by Iwamoto *et al.* gives very limited vibrational data with tentative assignments for the Cd(dabn)Ni$(CN)_4$·1.5C_6H_6 compounds [2, 3]. We give in detail the IR wavenumbers of the dabn molecule related to its denticity and to the presence of the different transition metals.

2. Experimental

2.1. PREPARATION

All chemicals used were reagent grade (Merck) and used without further purification.

The compounds M(dabn)Ni$(CN)_4$ · 1.5C_6H_6 (M = Mn, Fe, Co, Ni or Cd) were prepared by adding slightly more than one millimole of 1,4-diaminobutane to one millimole of $K_2Ni(CN)_4$ and one millimole of MCl_2 solution in water saturated with benzene. The precipitate was filtered, washed with water, ethanol and ether, successively, and kept in a desiccator containing molecular sieve and saturated benzene vapour.

2.2. ANALYTICAL RESULTS

The freshly prepared compounds were analyzed for M (M = Mn, Fe, Co, Ni or Cd) by AAS (Philips, PU 9200), and C, H and N by a LECO CHNS-932 analyzer with the following results (found %/calculated%):

$Mn(C_4H_{12}N_2)Ni(CN)_4$·1.5C_6H_6: Mn, 12.04/12.99; Ni, 13.54/13.88; C, 47.93/48.27; H, 4.76/5.00; N, 19.71/19.86.

$Fe(C_4H_{12}N_2)Ni(CN)_4$ · 1.5C_6H_6: Fe, 13.12/13.17; Ni, 13.33/13.85; C, 47.42/48.16; H, 4.86/4.99; N, 19.49/19.82.

$Co(C_4H_{12}N_2)Ni(CN)_4$ · 1.5C_6H_6: Co, 13.71/13.80; Ni, 13.82/13.75; C, 46.99/47.81; H, 4.72/4.96; N, 19.59/19.68.

$Ni(C_4H_{12}N_2)Ni(CN)_4$ · 1.5C_6H_6: Ni, 27.55/27.51; C, 46.99/47.84; H, 4.83/4.96; N, 19.78/19.69.

$Cd(C_4H_{12}N_2)Ni(CN)_4$ · 1.5C_6H_6: Cd, 23.35/23.39; Ni, 12.16/12.22; C, 42.26/42.49; H, 4.38/4.40; N, 17.51/17.49.

2.3. SPECTRA

IR spectra of the compounds were recorded in the range 4000 to 400 cm^{-1} on a Mattson 1000 FTIR spectrometer and the 400 to 200 cm^{-1} range on a Perkin-Elmer 1330 spectrometer, which were calibrated using polystyrene film and indene solution. The samples were prepared as mulls in nujol and hexachlorobutadiene between CsI windows and as KBr discs. The Raman spectra of the Ni-Ni-Bz and Cd-Ni-Bz compounds (in powder form) in a home-made spinning cell were 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 against the laser plasma emission lines.

3. Results and Discussion

The IR spectra of the compounds M-Ni-Bz (M = Mn, Fe, Co, Ni or Cd), are very similar. The similarities between the IR and Raman spectral features of the compounds suggest that they also have similar structural features. These in turn suggest that the degree of the interactions of the benzene, dabn ligand and $Ni(CN)_4$ species with their surroundings are almost the same for each compound. It will be most convenient to divide the vibrations into three groups arising from the 1,4-diaminobutane ligands, from the $Ni(CN)_4$ units and from the benzene moieties, respectively. The vibrational wavenumbers of the bands in the spectra of these species are tabulated in Tables I–III, respectively, together with some relevant spectral data for comparison.

3.1. VIBRATIONS OF 1,4-DIAMINOBUTANE

The assignments and the wavenumbers of the vibrational bands of the dabn molecule observed in the spectra of the compounds under study are given in Table I, together with the spectral data for the dabn molecule in the liquid phase and in solution in CCl_4 on which the assignments are based. The vibrational wavenumbers of the $Cd(dabn)Ni(CN)_4\cdot$ 1.5 aniline clathrate is also given in Table I for comparison.

The bands observed in the 3300–3280 cm^{-1} range (Table I) are assigned to the NH_2 symmetric and asymmetric stretching frequencies which are lower than the corresponding values of the free dabn molecule and characteristic of bonded —NH_2 groups. The absence of splitting of these bands indicate that the ligand molecules are bonded in a bidentate manner. Based on the present spectral data it is not possible to give an account on the conformation of the dabn ligand in our compounds. However, some implication may be deduced from the structure of $Cd(dabn)Ni(CN)_4\cdot xG$: the dabn ligand bridging adjacent cyanometal complex sheets is in a $trans$ conformation similar to those reported previously for $Cd(dabn)Ni(CN)_4 \cdot x$G (x = 1–1.5, G = pyrrole, aniline, N,N-dimethyaniline, 2,5-xylidine, o-toluidine) [4,5,6].

As seen in Table I, four bands are assigned to two kinds of CH_2 groups (one for asymmetric CH stretching and one for symmetric CH stretching) in two different environments.

Table I. The vibrational wavenumbers (cm^{-1}) of 1,4-diaminobutane in the M-Ni-Bz compounds.

Assignment[a]	Liquid dabn[b]	Cd-Ni-An[c]	Mn-Ni-Bz	Fe-Ni-Bz	Co-Ni-Bz	Ni-Ni-Bz	Cd-Ni-Bz
$\nu(NH_2)$, A	3346s	3348s	3356s	3355s	3354s	3356s	3350s
$\nu(NH_2)$, B	3280s	3383s	3292s	3293s	3291s	3294s	3284s
$\nu(CH_2)$, A	–	2952s	2930m	2953s	2953s	2950s	2954s
$\nu(CH_2)$, A	2926vs	2915m	2920m	2917s	2914s	2912m	2917s
$\nu(CH_2)$, B	–	2882m	2881w	2880m	2887s	2879m	2885m
$\nu(CH_2)$, B	2853vs	2850s	2828s	2851m	2854s	2830s	2854s
$\delta(NH_2)$, B	1606s	1590s	1589w	1586w	1591m	1587w	1587m
$\delta(CH_2)$, B	1497mw	1461m	1460m	1461m	1462m	1460m	1462m
$\rho_w(CH_2)$, B	1390mw	1377w	1378w	1378w	1378vw	1377w	1377w
$\rho_w(CH_2)$, B	1353vw	1365vw	1364vw	1365w	1364vw	1366vw	1366vw
$\rho_t(CH_2)$, A	1309vw	1313vw	–	1315vw	–	1315vw	1313vw
$\rho_t(NH_2)$, A	1145vw	1166vw	1169vw	1169vw	1167vw	1170w	–
$\nu(CN)$, B	1070w	1065w	1069vw	1069w	–	1068vw	1068w
$\nu(CN)$, B	–	1051w	1055w	1054mw	1055mw	1057m	1050w
$\rho_w(NH_2)$, B	954w	1001m	1008m	1009mw	1002mw	1010m	1010mw
$\rho_w(NH_2)$, B	–	941vw	–	944vw	944vw	945vw	933vw
$\rho_r(CH_2)+\rho_w(NH_2)$	878m,br	914vw	912w	910w	910vw	910vw	
$\rho_r(CH_2)$, A	863m,br	–	–	–	–	–	–
$\rho_r(CH_2)$, A	738w	741vw	–	743w	743vw	742vw	741w

[a] Taken From Ref.[17].

[b] Solution in CCl_4.

[c] Cd(1,4-diaminobutane)$Ni(CN)_4 \cdot 1.5$ aniline.

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

3.2. $Ni(CN)_4$ GROUP VIBRATIONS

In assigning the bands attributable to the $Ni(CN)_4$ ion in the spectra of our compounds we refer to the work of McCullough *et al.* who presented vibrational data for the $Ni(CN)_4^{2-}$ ion in $Na_2Ni(CN)_4$ [8]. The structural studies on these salts have shown that the $Ni(CN)_4^{2-}$ ion is not coordinated to the cations [8]. Therefore, it can be treated as an isolated unit and thus used as a reference to observe the effect on the vibrations when coordination takes place to the metals M. The vibrational data for $Ni(CN)_4$ groups in the compounds studied are given in Table II together with the vibrational wavenumbers of $K_2Ni(CN)_4$. Table II also lists the wavenumbers of the IR spectra of the $Ni(CN)_4$ group in the benzene clathrates $Cd(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$ [9] and $Cd(en)Ni(CN)_4 \cdot 2C_6H_6$ [10] for comparison.

The assigned wavenumbers for the $Ni(CN)_4$ group in the compounds studied appear to be much higher than those for isolated $Ni(CN)_4$ units (Table II). Such frequency shifts have been observed for other Hofmann-type clathrates, $M(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$ (M = Mn, Fe, Ni, Cu, Zn or Cd) [9], and Hofmann-type host complexes $M(pyridine)_2Ni(CN)_4$ (M = Mn, Co, Fe, Ni, Cu, Zn and Cd) [11], in which both ends of the CN group are coordinated and explained as the mechanical coupling of the internal modes of $Ni(CN)_4$ with the metal (Ni—NC) vibrations [9].

The characteristic frequencies of the $Ni(CN)_4$ group are found to be similar to those of the Hofmann-type clathrates [9] and Hofmann-type pyridine complexes [11], suggesting that coordination about the Ni atom is square planar and the $[Cd—Ni(CN)_4]_\infty$ layers have been preserved.

3.3. VIBRATIONS OF BENZENE

The assignments and the wavenumbers of the bands arising from the benzene observed in the IR spectra of Mn-Ni-Bz, Fe-Ni-Bz and Co-Ni-Bz, and IR and Raman spectra of Ni-Ni-Bz and Cd-Ni-Bz compounds are given in Table III, together with the wavenumbers of benzene in the liquid phase [13] and in some clathrates [14,15] on which the assignments are based. The most outstanding spectral features are the following.

IR and Raman bands in the spectra of the compounds (Table III), are noncoincident, suggesting that the selection rules for the benzene molecule under its intrinsic symmetry (D_{6h}) are preserved.

The CH out-of-plane mode (A_{2u}) in the IR spectra of the compounds appears as a singlet (Table III). A similar single band was observed in the infrared spectra of the Hofmann-type clathrates, $M(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$ (M = Mn, Fe, Ni, Cu, Zn or Cd) [10], and T_d-type clathrates, $Cd(4,4'\text{-bipyridyl})M'(CN)_4 \cdot 2C_6H_6$ (M′ = Cd, Hg) [16]. This vibrational mode splits into a doublet for $Cd(pyrazine)M'(CN)_4 \cdot C_6H_6$ (M′ = Cd, Hg) [17] and a triplet for $M(NH_3)_2M'(CN)_4 \cdot 2C_6H_6$ (M = Mn, Cd; M′ = Cd, Hg) [13]. This splitting is explained by the strong host–guest interactions [17].

Table II. The vibrational wavenumbers (cm^{-1}) of the cyanide group for the M-Ni-Bz compounds

Assignment	$Na_2Ni(CN)_4^a$	Cd-Ni-Bz[b,c]	Cd-Ni-Bz[d,e]	Cd-Ni-An[f]	Mn-Ni-Bz	Fe-Ni-Bz	Co-Ni-Bz	Ni-Ni-Bz	Cd-Ni-Bz
ν_1(CN) A_{1g}	2149	–	–	–	–	–	–	(2175vs)[f]	(2171vs)
ν_4(CN) B_{1g}	2141	–	–	–	–	–	–	(2162s)	(2160s)
ν_8(CN) E_u	2132	2156vs	2149s	2166vs	2165vs	2168vs	2164	2169vs	2168vs
	2128		–	–	–	–	–	–	–
Hot band?	–	2130w	–	2124vw	2116vw	2129vw	2127vw	2129vw	2127vw
$\nu(^{13}CN)$	2087	2115w	–	–	–	–	–	–	–
ν_9(NiC) E_u	543	554m,br	585s	574m	556m,br	578s	554s	579s	573s
π(NiC) A_{2u}	448	446w	466s	458vw	457vw	457vw	453vw	457vw	458vw
δ(NiCN) E_u	433	425vs	432s	439s	439s	440s	437s	440s	438s
	421	–	430s	–	–	–	–	–	–

[a] Taken From Ref. [8].
[b] $Cd(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$.
[c] Taken From Ref. [9].
[d] $Cd(en)Ni(CN)_4 \cdot 2C_6H_6$.
[e] Taken From Ref.[10].
[f] The bands observed in the Raman spectra are given in parentheses.
v = very, s = strong, m = medium, w = weak, br = broad.

Table III. The vibrational wavenumbers (cm^{-1}) of benzene in the M-Ni-Bz compounds.

Assignment[a]	Liquid Benzene[b]	Cd-Cd-Bz[d,e]	Cd-Cd-Bz[f,g]	Mn-Ni-Bz	Fe-Ni-Bz	Co-Ni-Bz	Ni-Ni-Bz	Cd-Ni-Bz
ν_8	(3166)[c]	–	–	–	–	–	–	–
ν_{20} E_{1u}	3073	3080m	3085m	3085w	3083m	3084m	3082m	3086m
$\nu_8+\nu_{19}$	3075	3064m	3066m	3065w	3064m	3063m	3064m	3066m
ν_{13} B_{1u}	3048	3028s	3028s	3026m	3025m	3026m	3026m	3029m
ν_2 A_{1g}	–	3062vw	3062vw	–	3064vw	–	3063vw	3066w
	(3062)	(3060m)	(3060s)	–	–	–	–	–
ν_7 E_{2g}	–	3042vw	3042vw	–	–	–	–	–
	(3050)	(3040w)	(3044s)	–	–	–	–	–
$\nu_5+\nu_{17}$ E_{1u}	1955	–	1960w	1971w	1969w	1968vw	1969w	1968vw
ν_8 E_{2g}	(1586)	(1580w)	(1584m)	–	–	–	–	–
$\nu_{10}+\nu_{17}$	1815	–	1818w	1834w	1833w	1834w	1832w	1837w
ν_{19} E_{1u}	1479	1477m	1477s	1477m	1479m	1477w	1478m	1477s
ν_{14} B_{2u}	1309	–	1309w	–	1309vw	1310vw	1314w	1312w
ν_9 E_{2g}	(1177)	–	1176vw	1170vw	1171w	1170vw	1170w	1172w
		(1174m)	(1176w)	–	–	–	–	–
ν_{15} B_{2u}	1149	1145sh	1147vw	1142vw	1142vw	1141vw	1142vw	1148w
ν_{18} E_{1u}	1036	1032w	1033m	1035w	1035w	1035w	1034w	1036w
ν_1 A_{1g}	(991)	(989vs)	(992vs)	–	–	–	(989vs)	(992vs)
ν_5 B_{2g}	989	–	–	–	–	–	–	–
ν_{17} E_{2u}	966	–	–	–	–	–	–	–
ν_{10} E_{1g}	(850)	(854w)	853vw	–	–	–	–	–
ν_{11} A_{2u}	670	698s	695sh	–	–	–	–	–
	–	686vs	683vs	692vs	692vs	692vs	691vs	693vs
			676sh	–	–	–	–	–
ν_6 E_{2g}	–	–	604vw	–	–	–	–	–
	(607)	(604m)	(605w)	–	–	–	–	–

[a] Taken From Ref. [13]. [b] IR bands are taken from Ref. [18], and Raman bands are taken from ref. [19]. [c] The Raman bands are given in parentheses.
[d] $Cd(NH_3)_2Cd(CN)_4{\cdot}2C_6H_6$. [e] Taken From Ref. [12]. [f] $Cd(en)Cd(CN)_4{\cdot}2C_6H_6$. [g] Taken From Ref.[13].
v = very, s = strong, m = medium, w = weak, br = broad.

The host-guest interactions in the clathrates under study are not expected to lead to splitting, because of the larger cavities due to the dabn ligands.

It should be noted that (Section 2.2) in our clathrates the number of guest benzene molecules is 1.5. A similar number has been measured in $Cd(dabn)Ni(CN)_4 \cdot 1.5G$ (G = aniline [5], G = *o*-toluidine [6]). Therefore, the decrease of x from 2 in Hofmann-type [12] and Hofmann-Td type clathrates [14] to 1.5 in the present series is due to the fact that one of the four cavity units is occupied by the dabn ligands, and the other three cavity units are occupied by the benzene molecules [5, 6].

Acknowledgements

The authors wish to thank Dr. Ziya Kantarcı for very useful comments and to the Gazi University Research Fund for purchase of the Jobin Yvon U1000 Raman spectrometer.

References

1. J.E.D. Davies and A.M. Maver: *J. Mol. Struct.* **102**, 203 (1983).
2. T. Hasegawa, S. Nishikiori and T. Iwamoto: *J. Incl. Phenom.* **1**, 365 (1984).
3. T. Iwamoto, S. Nishikiori and T. Hasegawa: *J. Incl. Phenom.* **5**, 225 (1987).
4. S. Nishikiori and T. Iwamoto: *J. Incl. Phenom.* **2**, 341 (1985).
5. S. Nishikiori and T. Iwamoto: *Inorg. Chem.* **25**, 788 (1986).
6. S. Nishikiori, T. Hasegawa and T. Iwamoto: *J. Incl. Phenom.* **11**, 137 (1991).
7. T. Iwamoto, ‘The Hofmann-type and Related Inclusion Compounds’, in J.L. Atwood, J.E.D. Davies, and D.D. MacNicol (Eds.), *Inclusion Compounds*, v. 1, Academic Press, London (1984), pp. 29–57.
8. R.L. McCullough, L.H. Jones, and G.A. Crosby: *Spectrochim. Acta.* **16**, 929 (1960).
9. S. Akyüz, A.B. Dempster, and L. Morehouse: *Spectrochim. Acta* **30A**, 1989 (1974).
10. T. Iwamoto: *Inorg. Chim. Acta* **2**, 269 (1968).
11. S. Akyüz, A.B. Dempster, L. Morehouse, and S. Suzuki: *J. Mol. Struct.* **17**, 105 (1973).
12. E. Kasap and Z. Kantarcı: *J. Incl. Phenom.* **20**, 33 (1995).
13. E. Kasap and Z. Kantarcı: *J. Incl. Phenom.* **23**, 1 (1995).
14. E.B. Wilson: *Phys. Rev.* **45**, 706 (1934).
15. S. Bayarı, Z. Kantarcı, and S. Akyüz: *J. Incl. Phenom.* **17**, 291 (1994).
16. N. Ekici, Z. Kantarcı, and S. Akyüz: *J. Incl. Phenom.* **10**, 9 (1991).
17. M.G. Giorgini, M.R. Pelletti, G. Paliani, and R.S. Cataliotti: *J. Raman Spectrosc.* **14**, 16 (1983).
18. P.C. Painter and J.L. Koening: *Spectrochim. Acta* **33A**, 103 (1977).
19. J.E.D. Davies, A.B. Dempster, and S. Suzuki: *Spectrochim. Acta* **30**, 1183 (1974).