

**VIBRATIONAL SPECTROSCOPIC INVESTIGATION OF SOME HOFMANN
TYPE CLATHRATES: $M(4\text{-PHENYLPYRIDINE})_2Ni(CN)_4 \cdot 2G$
(M = Ni, Co AND Cd, G = 1,4-DIOXANE)**

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ABSTRACT. New Hofmann type clathrates in the form of $M(4\text{-Phpy})_2Ni(CN)_4 \cdot 2G$ (where 4-Phpy = 4-phenylpyridine, G = 1,4-dioxane and M = Ni, Co and Cd) have been prepared in powder form and their FT-IR and Raman spectra have been reported. The results suggest that these compounds are similar in structure to the Hofmann type clathrates and their structures consist of polymeric layers of $[M-Ni(CN)_4]_n$ with the 4-Phpy bound to the metal (M) atom.

KEY WORDS: Hofmann type clathrates, Vibrational spectra, 4-Phenylpyridine, 1,4-Dioxane

INTRODUCTION

Metal organic frameworks (MOF) consist of metal ions or clusters coordinated to often rigid organic molecules to form one-, two-, or three-dimensional structures that can be porous. MOF is also known as coordination polymer which is the term given in inorganic chemistry to a metal coordination compound where a ligand bridges between metal centres, where each metal centre binds to more than one ligand to create an infinite array of metal centres. It can be said that the Hofmann type compounds are the members of the metal organic frameworks or coordination polymers. One-, two- and three-dimensional CN-bridged metal complex structures made up of building blocks such as linear $[Ag(CN)_2]$, square planar $[Ni(CN)_4]^{2-}$ or tetrahedral $[Cd(CN)_4]^{2-}$, and of the complementary ligands such as ammonia, water, unidentate amine, bidentate α,ω -diaminoalkane, etc., are reviewed with an emphasis on their behaviour as hosts to afford clathrates inclusion compounds with guest molecules and as self-assemblies to form supramolecular structures with or without guest [1]. These metal complexes can act as adsorbents for gases, as molecular sieves, in sensing devices, as hosts for smaller guest molecules, in non-linear optics devices and as magnetic materials [1].

The Hofmann type clathrates are two component inclusion compounds consisting of a host lattice and a guest molecule which are associated without ordinary chemical union, but throughout complete enclosure of one set of molecules in a suitable structure formed by another [1, 2]. Their general formula is $M(II)L_2M'(II)(CN)_4 \cdot nG$ where, M is octahedrally coordinated metal: Mn, Fe, Co, Ni, Cu, Zn or Cd; M' is square-planar coordinated metal: Ni, Pd or Pt; L is a unidentate ligand molecule and n is the number of G (guest) molecules depending on the bulkiness of the ligand and the guest molecule [1-5]. The host framework consists of two dimensional polymeric layers composed of ML_2 cations and $M'(CN)_4$ anions. The M' atoms are coordinated to four C atoms of the CN groups in a square planar environment. M atoms are octahedrally surrounded by six N atoms, two of which are from ligands and the rest are from cyanide groups. The ligand molecules lie above and below the layers. This structure provides α -type cavity similar to rectangular box for the guest molecules.

For 4-Phpy, studies of the Hofmann type complexes, transition metal(II)-chloro complexes, isothiocyanate complexes and Hofmann- T_d type complexes exhibit the coordination properties

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of the 4-Phpy [6-8]. In the present work, three new $M(4\text{-Phpy})_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_4\text{H}_8\text{O}_2$ clathrates (abbreviated hereafter as M-4Phpy-Ni-D) have been synthesized using a non-aromatic guest molecule, where M = Ni, Co and Cd, for the first time and their FT-IR and Raman spectra have been investigated. It should be noted that several unsuccessful attempts have been made to synthesize similar clathrates with benzene and benzene derivatives as guest molecules.

EXPERIMENTAL

The M-4Phpy-Ni-D (M = Ni, Co and Cd) compounds were prepared as follows: firstly 1 mmol of $\text{K}_2\text{Ni}(\text{CN})_4$ (Acros, 98%, Belgium) was dissolved in distilled water, then slightly more than 2 mmols of 4-Phpy (Acros, 99%, Belgium) were added to this solution under stirring. After a short time, 3 mmols of 1,4-dioxane (Merck, 99%, Germany) was added to the prepared solution. Finally, 1 mmol of MCl_2 (Merck, 98%, Germany) dissolved in distilled water was added dropwise to the prepared mixture, again under stirring. The final mixture was left for stirring for a week at room temperature. The products obtained were filtered and washed with water, ethanol and ether successively and stored in a desiccator containing guest vapour.

The compounds were analyzed for Ni, Co and Cd metals with Perkin Elmer 4300 DV ICP-OES (USA) and for C, H and N with Fisons EA-1108 elemental analyser (UK). The results of elemental analysis are given in Table 1. Infrared spectra of the clathrates were recorded in the region of $(4000\text{-}400)\text{ cm}^{-1}$ with Perkin-Elmer FTIR 2000 (USA) spectrometer at a resolution of 4 cm^{-1} . In order to provide better identifications for the vibrational bands of the clathrates prepared in this study, two different mulls (in nujol and hexachloro-1,3-butadiene) were used. In the MIR region of spectrum, bands of nujol were reported at 1377 cm^{-1} , 1461 cm^{-1} , 2858 cm^{-1} , 2925 cm^{-1} and of hexachloro-1,3-butadiene 655 cm^{-1} , 793 cm^{-1} , 852 cm^{-1} , 941 cm^{-1} , 981 cm^{-1} , 1170 cm^{-1} , 1564 cm^{-1} , 1610 cm^{-1} , respectively. The Raman spectra of the clathrates were recorded in the region of $(2750\text{-}1650)\text{ cm}^{-1}$ with Bruker Senterra Dispersive Raman Microscope (Germany) using the 532 nm line of a 3B diode laser. All the analyses of these compounds were carried out immediately to avoid any de-clathration.

Table 1. Elemental analysis of M-4Phpy-Ni-D (M = Ni, Co and Cd) clathrates.

Empirical formula of samples and $M_r(\text{g})$	Elemental analysis, found (calculated) (%)					
	C	H	N	Ni	Co	Cd
$\text{Ni}(\text{C}_{11}\text{H}_9\text{N})_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_4\text{H}_8\text{O}_2$	57.49	4.80	11.75	16.44	-	-
$M_r = 708.06$	(57.67)	(4.84)	(11.87)	(16.58)	-	-
$\text{Co}(\text{C}_{11}\text{H}_9\text{N})_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_4\text{H}_8\text{O}_2$	57.45	4.79	11.73	8.14	8.16	-
$M_r = 708.30$	(57.65)	(4.84)	(11.87)	(8.29)	(8.32)	-
$\text{Cd}(\text{C}_{11}\text{H}_9\text{N})_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_4\text{H}_8\text{O}_2$	53.44	4.46	10.92	7.53	-	14.55
$M_r = 761.78$	(53.61)	(4.50)	(11.03)	(7.70)	-	(14.76)

RESULTS AND DISCUSSION

The infrared and Raman spectra of M-4Phpy-Ni-D (M = Ni, Co and Cd) clathrates are compatible with each other. This indicates that the compounds have similar spectral features. The infrared and Raman spectra of the compounds are shown in Figures 1 and 2. The spectral analysis of each compound has been performed by taking into account the 4-Phpy ligand molecule, $\text{Ni}(\text{CN})_4$ ions and 1,4-dioxane guest molecule individually.

4-Phy vibrations

The molecular structure of 4-Phy was studied by Bayari *et al.* [6] and Zawada *et al.* [9]. The former study was reported in the (4000-400) cm^{-1} infrared range while the latter covered the IR range from 438 cm^{-1} to 1609 cm^{-1} . 4-Phy belongs to the C_{2v} point group and it has 57 fundamental modes of vibration. The vibrational bands consist of 39 planer bands with 20 of class A_1 and 19 of class B_1 , and 18 non-planer bands with 7 of class A_2 and 11 of class B_2 . All these vibrations are Raman active but only the vibrations of A_1 , B_1 and B_2 classes are infrared active. The assignments and the frequencies of the fundamental bands observed in the infrared spectra of the clathrates under study are given in Table 2, together with the wavenumbers of 4-Phy and some of its host structures for comparison.

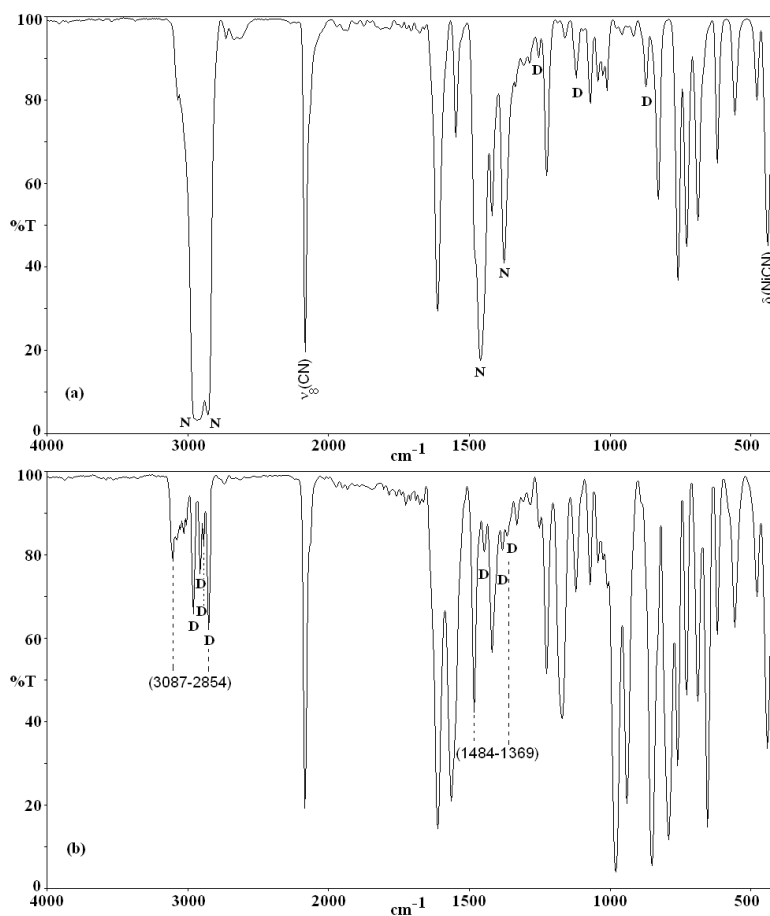


Figure 1. IR spectra of Ni-4Phy-Ni-D clathrate in nujol (a) and in hexachloro-1,3-butadiene (b). N: bands of nujol, D: bands of 1,4-dioxane.

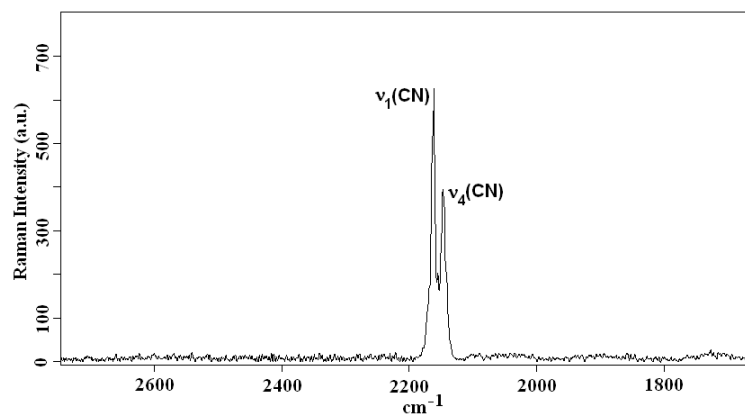


Figure 2. Raman spectrum of Cd-4Phy-Ni-D clathrate.

As can be seen in Table 2, the shifts for the vibrational modes of the A_1 class are more noticeable pointing out that the vibrational modes have been perturbed strongly by complexing. The strong ring stretching band at 1588 cm^{-1} has shifted around 24 cm^{-1} as an intense band for the compounds. Another strong ring breathing mode at 1001 cm^{-1} has showed an upward shift of about 12 cm^{-1} . In the lower frequency region, a shift taking place for the strong ring bending band at 608 cm^{-1} is around 11 cm^{-1} for the compounds. The strong ring bending mode at 438 cm^{-1} has shifted towards higher wavenumbers of about 43 cm^{-1} . The observed shifts of the vibrational frequencies are consistent with previously reported Hofmann type complexes of 4-Phpy [6]. These shifts in frequencies have been explained in terms of coupling of the internal vibration of 4-Phpy molecule with M-N vibrations [3-6, 10-12].

As well as the strong shifts, another spectral feature caused by coordination is the small frequency shifts resulting from the environmental changes of 4-Phpy [3-6, 10-12]. Hence the observed small frequency shifts for the B_1 and B_2 classes of the ligand molecule are resulting from the environmental changes caused by 4-Phpy on coordination.

Ni(CN)₄ group vibrations

Ni(CN)_4 ion consists of 9 atoms, so it has 21 normal mode frequencies and belongs to the D_{4h} point group. Within this point group, we can distinguish between 15 in plane and 6 out of plane normal modes. In plane modes belong to the symmetry species A_{1g} , A_{2g} , B_{1g} , B_{2g} and E_u . The A_{1g} , B_{1g} and B_{2g} modes are Raman active whereas the E_u modes are IR active. The A_{2g} modes are neither IR nor Raman active. The A_{1u} , B_{1u} , A_{2u} , B_{2u} and E_g modes are identified as out of plane normal modes. Among them only the A_{2u} and E_g modes are IR and Raman active, respectively. The remaining modes display no IR and Raman activity.

Assignments of the bands for Ni(CN)_4 ion in the spectra of the present compounds have been carried out by means of vibrational data of Ni(CN)_4 ion in $\text{Na}_2\text{Ni(CN)}_4$ reported by McCullough *et al.* [13]. Since the ion is not coordinated to cations, it can be treated as an isolated unit. Therefore, it has been used as a reference for finding out whether coordination to the M is taking place. The vibrational data for Ni(CN)_4 groups in our clathrates are given in Table 3 along with McCullough *et al.*'s data. The wavenumbers of the infrared and Raman spectra [6] of Ni(CN)_4 group in the host structures of 4-Phpy are also listed in Table 3.

Table 2. The vibrational wavenumbers (cm^{-1}) of 4-Phpy in the M-4Phpy-Ni-D (M = Ni, Co and Cd) clathrates.

Assignment ^a	Solid 4-Phpy ^a	Ni-4Phpy-Ni ^a	Cd-4Phpy-Ni ^a	M-4Phpy-Ni-D		
				Ni	Co	Cd
A₁						
$\nu(\text{CH})$	3083 w	3085 w	3085 w	3087 m ^b	3086 m ^b	3087 m ^b
$\nu(\text{CH})$	3038 w	3041 w	-	3054 w ^b	3054 w ^b	-
$\nu(\text{CH})$	3028 w	3030 w	3031 w	3030 w ^b	3031 w ^b	3030 w ^b
ν_{ring}	1588 s	1613 vs	1611 vs	1613 vs	1613 vs	1611 vs
ν_{ring}	1484 s	1476 vs	1476 vs	1484 vs ^b	1485 vs ^b	1484 vs ^b
$\delta(\text{CH})$	1410 ms	1424 m	1422 vs	1421 s	1422 s	1420 s
$\nu_{\text{ring}} + \delta(\text{CH})$	1279 w	1290 w	1288 w	1284 w	1287 m	1284 w
$\delta(\text{CH})$	1233 s	1226 vs	1218 vs	1226 vs	1226 vs	1225 vs
ν_{ring}	1042 s	1045 s	1044 s	1044 m	1042 m	1044 m
Ring breathing	1001 s	1013 vs	1011 vs	1013 s	1013 s	1012 s
δ_{ring}	832 vs	830 vs	830 vs	830 vs	830 vs	831 vs
$\delta_{\text{ring}} + \nu_{\text{ring}}$	762 vs	759 vs	758 vs	760 vs	760 vs	761 vs
δ_{ring}	608 s	621 vs	619 vs	620 vs	619 vs	618 vs
δ_{ring}	438 s	482 ms	482 ms	480 s	482 s	482 s
B₂						
$\nu(\text{CH})$	-	3075 w	3073 w	3074 w ^b	3074 w ^b	3073 w ^b
$\nu(\text{CH})$	3008 w	3016 mw	3013 w	3012 w ^b	3011 w ^b	3010 w ^b
ν_{ring}	1543 s	1551 s	1549 s	1549 s	1548 s	1547 vs
ν_{ring}	1341 mw	-	1331 m	1335 w	1336 w	1336 w
ν_{ring}	1314 mw	1307 mw	1308 mw	1307 w	1307 w	1310 w
$\delta(\text{CH})$	1190 m	1182 w	1181 w	1186 w	1186 w	1187 w
$\delta(\text{CH})$	1163 m	1159 m	1159 m	1161 m	1161 m	1160 m
$\delta(\text{CH})$	1104 ms	1100 m	1100 m	1102 w	-	-
ν_{ring}	1073 s	1075 s	1073 s	1072 s	1070 s	1073 s
$\delta(\text{CH})$	1017 mw	1026 s	1025 s	1027 m	-	-
δ_{ring}	561 s	558 s	557 s	558 s	557 s	560 s
B₁						
$\gamma(\text{CH})$	-	978 mw	978 mw	974 vw	-	-
$\gamma(\text{CH})$	965 w	959 mw	959 mw	959 w	-	960 w
$\gamma(\text{CH})$	918 m	919 m	918 m	918 w	918 m	919 m
$\gamma(\text{CH})$	731 s	731 s	731 s	729 vs	729 vs	732 s
γ_{ring}	687 vs	691 vs	691 vs	689 vs	688 vs	692 vs

^aTaken from Ref. [6]. ^bIn hexachloro-1,3-butadiene. vs: very strong, s: strong, m: medium, w: weak.

Table 3. The vibrational wavenumbers (cm^{-1}) of $\text{Ni}(\text{CN})_4$ group in the M-4Phpy-Ni-D (M = Ni, Co and Cd) clathrates.

Assignment ^a	$\text{Na}_2\text{Ni}(\text{CN})_4^{\text{a}}$	Ni-4Phpy-Ni ^b	Cd-4Phpy-Ni ^b	M-4Phpy-Ni-D		
				Ni	Co	Cd
$\nu_1(\text{CN}), A_{1g}$	(2149)	-	(2169) vs	(2185) vs	(2182) vs	(2162) vs
$\nu_4(\text{CN}), B_{1g}$	(2141)	-	(2156) s	(2172) s	(2170) s	(2148) s
$\nu_8(\text{CN}), E_u$	2132	2185 vs	2151 vs	2169 vs	2160 vs	2144 vs
$\delta(\text{NiCN}), E_u$	433	431 vs	426 vs	442 vs	439 vs	422 vs

^{a, b} Taken from Ref. [13] and [6], respectively. The bands observed in the Raman spectra are given in parentheses. vs: very strong, s: strong.

The assigned infrared and Raman wavenumbers for Ni(CN)₄ group in the compounds studied appear to be much higher than those for isolated Ni(CN)₄ units (Table 3, Figures 1, 2). Such frequency shifts have been observed for other Hofmann type [3-5] and Hofmann type dioxane [10-12] clathrates and are attributed to the mechanical coupling of the internal modes of Ni(CN)₄ with the M–NC vibrations. The characteristic frequencies of Ni(CN)₄ group are found to be similar to those of the Hofmann type clathrates suggesting that coordination around the Ni atom is square planar, and that IM-Ni(CN)₄ layers have been preserved.

1,4-Dioxane vibrations

1,4-Dioxane molecule consists of 14 atoms, so it has 36 normal mode frequencies and belongs to the C_{2h} point group. Vibrational modes of this molecule belong to the symmetry species A_g, A_u, B_g and B_u. The 9A_u/9B_u and 10A_g/8B_g modes are IR and Raman active, respectively.

Vibrational studies show that 1,4-dioxane has a chair conformation with a centre of symmetry in the gas and liquid phases [14], in the metal halide complexes [15] and in the Hofmann type dioxane clathrates [16]. The assignments and frequencies of the vibrational bands for 1,4-dioxane of clathrates are given in Table 4 along with the frequencies of 1,4-dioxane in the liquid phase [14]. The vibrational frequencies of 1,4-dioxane in the IR spectra of clathrates closely correspond in frequency to those in the IR spectrum of liquid dioxane and to the Hofmann type dioxane clathrates reported previously [11, 12, 16]. It can be said that 1,4-dioxane molecules in the clathrates are most likely in a chair conformation [11, 12, 16]. According to chemical results, the number of guest molecules in the present compounds is two (n = 2). This result has also been observed for other Hofmann type dioxane clathrates [11, 12].

Table 4. The vibrational wavenumbers (cm⁻¹) of 1,4-dioxane in the M-4Phpy-Ni-D (M = Ni, Co and Cd) clathrates.

Assignment ^a	Liquid dioxane ^a	M-4Phpy-Ni-D		
		Ni	Co	Cd
V ₁₁ stretching	2963	2962 vs ^b	2962 vs ^b	2961 vs ^b
V ₁₃ +v ₂₂	2917	2915 s ^b	2915 s ^b	2914 s ^b
V ₃ +v ₃₀	2887	2889 m ^b	2888 m ^b	2887 m ^b
V ₁₂ CH ₂ stretching	2852	2854 vs ^b	2855 vs ^b	2853 vs ^b
V ₁₃ CH ₂ scissoring	1445	1448 m ^b	1449 m ^b	1447 m ^b
V ₃₁ CH ₂ wagging	1375	1383 m ^b	1384 m ^b	1381 m ^b
V ₁₄ CH ₂ wagging	1366	1368 w ^b	1369 w ^b	1366 w ^b
V ₁₅ CH ₂ twisting	1256	1255 m	1255 m	1254 m
V ₁₆ ring stretching	1121	1122 s	1121 s	1119 s
V ₁₇ CH ₂ rocking	1083	1072 s ^c	1070 s ^c	1073 s ^c
V ₃₃ ring stretching	1048	1044 m ^c	1042 m ^c	1044 m ^c
V ₁₈	873	874 s	876 s	873 s
V ₃₅	614	620 vs ^c	619 vs ^c	618 vs ^c

^aTaken from Ref. [14]. ^bIn hexachloro-1,3-butadiene. ^cObscured by 4-Phpy bands. vs: very strong, s: strong, m: medium, w: weak.

CONCLUSIONS

The vibrational spectroscopic study of three new Hofmann type dioxane clathrates has shown that they have similar structures consisting of infinite two-dimensional polymeric layers formed with Ni(CN)₄ ions bridged by M(4-Phpy)₂ (M = Ni, Co and Cd) cations. According to the results, the host-guest interactions in obtained clathrates are weak and the trapped 1,4-dioxane

guest molecules have kept their free forms. In conclusion, the compounds presented in this study are also examples of the Hofmann type dioxane clathrates.

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REFERENCES

1. Iwamoto, T. *J. Incl. Phenom.* **1996**, 24, 61.
2. Ruiz, E.; Alvarez, S.; Hoffmann, R.; Bernstein, J. *J. Am. Chem. Soc.* **1994**, 116, 8207.
3. Parlak, C.; Alver, Ö.; Şenyel, M. *J. Mol. Struct.* **2009**, 919, 41.
4. Şenyel, M.; Sertbakan, T.R.; Kürkçüoğlu, G.S.; Kasap, E.; Kantarcı, Z. *J. Incl. Phenom.* **2001**, 39, 175.
5. Kürkçüoğlu, G.S.; Kantarcı, Z.; Coşkun, R.; Şenyel, M. *J. Incl. Phenom.* **2003**, 45, 129.
6. Bayarı, S.; Topaçlı, A.; Aydınli, A. *Spect. Lett.* **1994**, 27, 1083.
7. Bayarı, S.; Topaçlı, A.; Salih, B. *J. Mol. Struct.* **1999**, 482, 165.
8. Parlak, C.; Şentürk, Ş.; Şenyel, M. *Z. Naturforsch A* **2005**, 60, 629.
9. Zawada, K.; Bukowska, J.; Calvo, M.; Jackowska, K. *Electrochim. Acta* **2001**, 46, 2671.
10. Sungur, A.; Akyüz, S.; Davies, J.E.D. *J. Incl. Phenom.* **1987**, 5, 491.
11. Dempster, A.B.; Uslu, H. *Spectrochim. Acta A* **1978**, 34, 71.
12. Tufan, Y.; Karacan, N.; Davies, J.E.D. *J. Incl. Phenom.* **1999**, 33, 149.
13. McCullough, R.L.; Jones, L.H.; Croby, G.A. *Spectrochim. Acta* **1960**, 16, 929.
14. Ellestad, O.H.; Klabo, P.; Hagen, G. *Spectrochim. Acta A* **1971**, 27, 1025.
15. Fowles, G.W.A.; Rice, D.A.; Walton, R.A. *Spectrochim. Acta A* **1970**, 26, 143.
16. Kendi, E.; Ülkü, D. *Z. Kristallogr.* **1976**, 144, 91.