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Metallomethanes

XV *. Vibrational spectra and force fields of the isoelectronic species tetrakis(methylmercurio)methane, $C(HgCH_3)_4$, and tetrakis(amminemercurio)methane cation, $[C(HgNH_3)_4]^{4+}$

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Abstract

The vibrational frequencies of the tetrakis(amminemercurio)methane cation, $[C(HgNH_3)_4]^{4+}$ (**1**), in both aqueous ammonia buffer solutions and in solid $[C(HgNH_3)_4](PF_6)_4$ have been used in an all-atom normal coordinate analysis for **1**. A similar analysis has been carried out for the isoelectronic tetrakis(methylmercurio)methane, $C(HgCH_3)_4$ (**2**). **1** and **2** respectively exhibit the highest (2.016 N/cm) and lowest (1.509 N/cm) valence force constants K(C–Hg) in the central CHg_4 entity so far observed for tetramercuriomethanes. The force constants for the peripheral $Hg–NH_3$ and $Hg–CH_3$ bonds in **1** and **2** are 2.461 N/cm and 2.183 N/cm, respectively. Both the electronic properties of the peripheral ligands and the total charge on the molecule are shown to influence the force constants. The potential energy distributions indicate that the valence vibrations of the N–H/C–H and $Hg–NH_3$/$Hg–CH_3$ bonds in **1** and **2**, and the breathing vibrations of the central CHg_4 units are almost independent of all other vibrations, which in turn are more or less strongly coupled.

Introduction

Several studies of vibrational spectra of neutral tetrakis(anionomercurio)methanes, $C(HgX)_4$, with subsequent estimations of force constants of the C–Hg bonds

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* For part XIV see ref. 1.

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in the central CHg_4 units revealed a pronounced dependence of the C–Hg bond strengths on the electronegativity or ionization potential of the peripheral ligands X, respectively [2–4]. Of special interest is the comparison of force constants in isoelectronic species expected to have similar bonding characteristics. To date the only appropriate comparable pair is $C(HgCH_3)_4$ and $[C(HgNH_3)_4]^{4+}$, for which the force fields, including all atoms, are reported here [5]; the results of a normal coordinate treatment of $C(HgCH_3)_4$ with point masses for the methyl groups have previously been presented [6].

Experimental

Tetrakis(methylmercurio)methane, $C(HgCH_3)_4$, was prepared by reaction of tetrakis(dimethoxyboryl)methane [7,8] with methylmercury acetate and lithium methoxide in absolute tetrahydrofuran under dry N_2, and characterized by elemental analysis (C, H and Hg), and by mass spectrometry [9].

Hofmann's base was prepared from mercury(II) oxide, potassium hydroxide, and ethanol in a procedure [10], modified as described in ref. 11. Solutions of tetrakis(amminemercurio)methane, $[C(HgNH_3)_4]^{4+}$, for Raman spectrometry were prepared by saturation of NH_4F/conc. aqueous NH_3 and NH_4NO_3/NH_3 buffers at room temperature with Hofmann's base; solutions of the perdeuterated species were prepared similarly with ND_4NO_3/ND_3 buffer.

Tetrakis(amminemercurio)methane hexafluorophosphate, $[C(HgNH_3)_4](PF_6)_4$, was obtained by gradual evaporation of a solution of Hofmann's base in NH_4PF_6/NH_3 buffer, and removing the residual NH_4PF_6 from any product fractions which contained it (as indicated by Raman spectroscopy) by washing with i-propanol. The dried product is very soluble in water. (Found: C, 0.92; H, 0.95; N, 3.79; Hg, 54.5. $CH_{12}F_{24}Hg_4N_4P_4$ calc: C, 0.82; H, 0.83; N, 3.83; Hg, 54.87%.)

The Raman spectra of both the buffer solutions and the solid were obtained by excitation with Spectra Physics lasers 165 (Ar^+, 514.5 nm) and 164 (Kr^+, 647.1 nm) and recorded with the Cary 82 spectrometer.

Results and discussion

Spectra and assignments

The Raman spectrum of a NH_4F/NH_3 buffer solution of Hofmann's base, showing the polarization state of the Raman bands, is presented in Fig. 1 as representative of those for solutions of the $[C(HgNH_3)_4]^{4+}$ ion in all the buffers. The relevant data for all three studied buffer solutions with assignments are listed in Table 1. First of all, the very intense totally polarized Raman band at 150 cm^{-1}, with a minor isotope shift, can be assigned unequivocally to the totally symmetric valence vibration of the central CHg_4 unit of the ion. The polarized and depolarized components, both showing a distinct isotope shift, of the strong band around 490 cm^{-1} are clearly the symmetric and degenerate valence vibrations of the four Hg–N bonds. Position, intensity and band profile of the degenerate valence vibration $\nu_d(CHg_4)$ are similar to those in other tetramercuriomethanes. The vibrations of the coordinated ammonia molecules are well known from data for other ammine complexes [12,13].

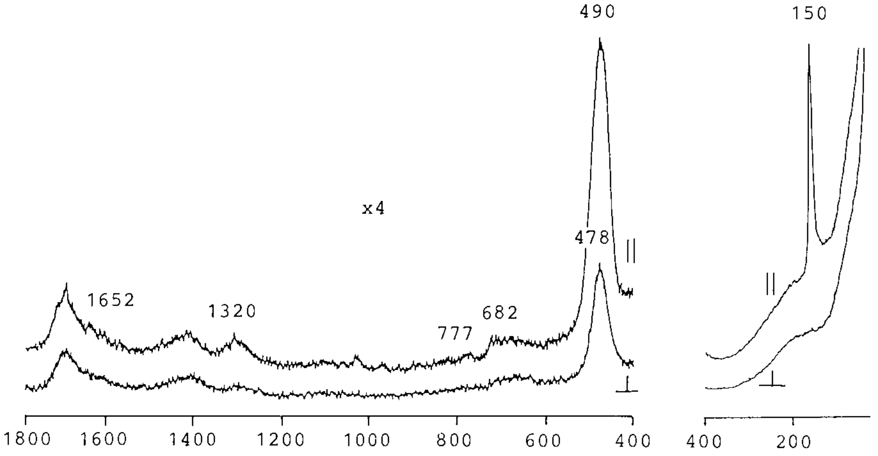

Fig. 1. Raman spectrum of a NH_4F/NH_3 buffer solution of $[C(HgNH_3)_4]^{4+}$ generated by dissolution of Hofmann's base in the buffer. The polarization states are indicated by ∥ and ⊥.

The Raman spectrum of solid $[C(HgNH_3)_4](PF_6)_4$ (Fig. 2, Table 2) shows the valence vibrations of the CHg_4 unit at almost the same frequencies as in solution. In addition, deformation modes of this unit, known for other tetramercuriomethanes, are visible as weak bands at 96 and 62 cm^{-1}, respectively. Other weak bands in the low frequency region (163 and 120 cm^{-1}) must be assigned to bending modes of the C–Hg–NH_3 groups. The ν(Hg–N) bands are strongly overlapped by $\nu_5(t_{2g})$ of the PF_6^- anion.

The vibrational spectra and assignments of tetrakis(methylmercurio)methane, $C(HgCH_3)_4$, have been discussed previously [6].

Force constant calculations

If tetrahedral symmetry is assumed for the species $C(HgCH_3)_4$ and

Table 1

Raman bands with assignments of $[C(HgNH_3)_4]^{4+}$ in various ammonia buffer solutions

Buffer [a]	NH_3/NH_4F	NH_3/NH_4NO_3	ND_3/ND_4NO_3	Approximate description and symmetry species of modes
	3395 dp,mw		2520 s	$\nu_d(NH_3)$, e, f_2
	3309 p,vs		2407 vs	$\nu_s(NH_3)$, a_1, f_2
	1652 dp,vw			$\delta_d(NH_3)$, e, f_2
	1320 p,mw		1000 mw	$\delta_s(NH_3)$, a_1, f_2
		833 w		
	777 p,vw	761 w		$\rho(NH_3)$, e, f_2
	682 dp,mw	690 dp,w		$\nu_d(CHg_4)$, f_2
	490 p,vs	486 p,s	453 s	$\nu_s(HgN)$, a_1
	478 dp,s	475 dp,m	445 s	$\nu_d(HgN)$, f_2
	150 p,vs	150 p,vs	149 vs	$\nu_s(CHg_4)$, a_1

[a] Raman bands of the buffer are omitted.

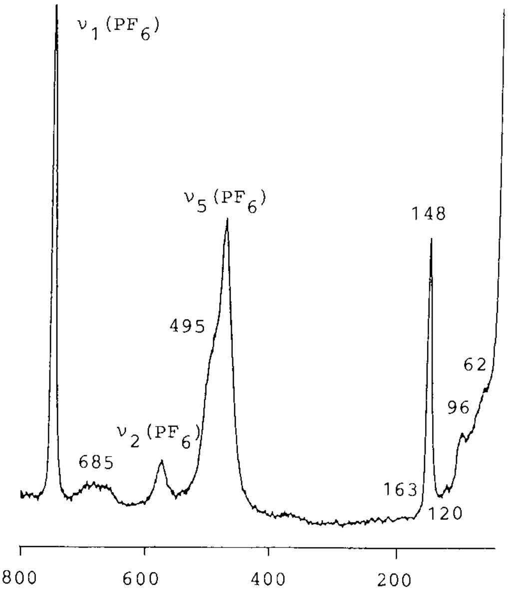

Fig. 2. Raman spectrum (section) of solid $[C(HgNH_3)_4](PF_6)_4$. The bands of the cation are indicated by their wave numbers.

$[C(HgNH_3)_4]^{4+}$, the vibrational modes are distributed into the irreducible representations of T_d as follows (cf. [6], spectral activities in parentheses):

$$\Gamma(T_d) = 4a_1(\mathrm{R}) + a_2(ia) + 5e(\mathrm{R}) + 5f_1(ia) + 9f_2(\mathrm{IR, R})$$

The four possible torsional modes of the ligands CH_3 and NH_3 span the representations $a_2 + f_1$, i.e. they are not observable, and for this and other reasons are not considered in the normal coordinate treatment.

Figure 3 shows the types of internal coordinates as a basis for the construction of the symmetry coordinates. Tetrahedral angles around carbon and nitrogen and linear bonding about mercury were assumed. In $C(HgCH_3)_4$ the lengths of the C–Hg, Hg–CH_3 and C–H bonds were taken as 209.6, 209.4 and 109.0 pm,

Table 2

Raman bands with assignments of solid $[C(HgNH_3)_4](PF_6)_4$

	Assignments
748 vs	$\nu_1(PF_6)$
685 mw,br	$\nu_d(CHg_4)$
577 mw	$\nu_2(PF_6)$
495 sh	$\nu_2(HgN)$ $\nu_d(HgN)$
477 s	$\nu_5(PF_6)$
163 vw	$\delta(CHgN)$, e
148 s	$\nu_s(CHg_4)$
129 vw	$\delta(CHgN)$, f_2
96 w	$\delta(CHg_4)$, f_2
62 vw	$\delta(CHg_4)$, e

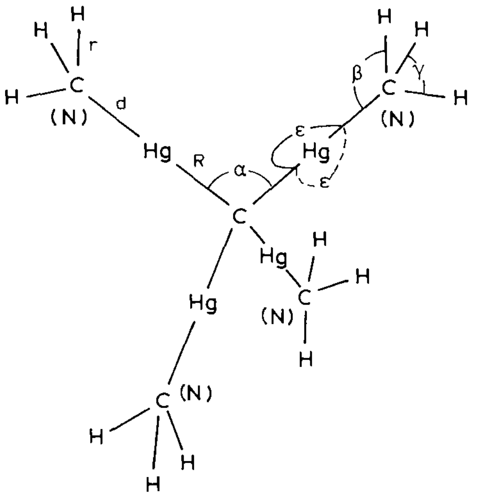

Fig. 3. Internal coordinates of the species $C(HgCH_3)_4$ and $[C(HgNH_3)_4]^{4+}$. Coordinates ϵ' refer to the C–Hg–C (or C–Hg–N) out-of-plane deformations.

respectively, and for $[C(HgNH_3)_4]^{4+}$ the lengths of the corresponding C–Hg, Hg–N and N–H bonds were taken as 207.0, 205.0 and 102.0 pm, respectively. These sets of data were taken respectively from structural data for other mercuriomethanes ([14,15] and references therein) and those for compounds with $Hg-NH_3$ groups [13]. Initial force constants were taken from earlier, somewhat simpler, calculations for $C(HgCH_3)_4$ [6], or were estimated roughly for $[C(HgNH_3)_4]^{4+}$ [5].

A recently developed program [16] was used to calculate the G matrices and for refining the force constants. In both cases, all initial force constants, after transformation to symmetry force constants, were refined without constraints. Subsequently, the final internal force constants were obtained by solving the system of linear inhomogeneous equations, which define the symmetry force constants in terms of the internal force constants. These refined internal force constants of both species for comparison are listed in Table 3.

Wave numbers calculated from the final sets of force constants, observed wave numbers and potential energy distributions for $C(HgCH_3)_4$ and $[C(HgNH_3)_4]^{4+}$ are listed in Tables 4 and 5, respectively. The agreement between assigned observed and calculated wave numbers is generally very good, even in the low-wave number region, in the case of $[C(HgNH_3)_4]^{4+}$. It has been emphasized previously that the force constants of the C–Hg bonds in the central CHg_4 units of tetramercuriomethanes are strongly dependent on the electronic properties of the peripheral ligands X [2–4]. The species $C(HgCH_3)_4$ and $[C(HgNH_3)_4]^{4+}$ have now been shown to represent two extreme cases in that the valence force constants K(C–Hg) adopt the lowest (1.509 N/cm) and highest values (2.016 N/cm), respectively, observed for tetramercuriomethanes. The force constant for the cation is even slightly higher than that for tetrakis(fluoromercurio)methane $C(HgF)_4$ (2.002 N/cm) [4] *. As a consequence we have to assume that the K(C–Hg) values are not only

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* In ref. 4 the force constant K(Hg–X) for X = F (Table 1) should read 2.569 N/cm.

Table 3

Refined internal force constants (GVFF) for $[C(HgNH_3)_4]^{4+}$, $C(HgCH_3)_4$ and $Hg(CH_3)_2$ in units of 10^2 N/m for valence and stretch–stretch interaction force constants, 10^{-10} Nm/rad for bending and 10^{-8} N/rad for stretch–bend interaction force constants

Force constants	Coordinates involved	Common atom(s)	$[C(HgNH_3)_4]^{4+}$	$C(HgCH_3)_4$		$Hg(CH_3)_2$
				This work	Ref. 6	Ref. 18 [c]
Stretch						
K_r	r	–	6.102	4.629	–	4.739
K_R	R	–	2.016	1.509	1.582	2.379
K_d	d	–	2.461	2.183	2.160	2.379
Stretch–stretch						
F_r	r,r	N/C	−0.028	−0.011	–	0.016
F_R	R,R	C	0.301	0.257	0.255	–
F_d	d,d	–	−0.016	0.023	0.024	–
F_{Rd}	R,d	Hg	0.602	0.169	(0.031) [a]	0.031
F_{dr}	d,r	N/C	−0.126	−0.085	–	−0.075
Bend						
H_γ	γ	–	0.482	0.396	–	0.433
H_β	β	–	0.325	0.314	–	0.538
H_α	α	–	1.614	1.583	1.251	–
H_ϵ	ϵ	–	0.501	0.363	0.455	0.453
$H_{\epsilon'}$	ϵ'	–	0.501	0.363	0.455	0.453
Stretch–bend						
$F_{r\beta}$	r,β	N–H/C–H	−0.044	0.146	–	0.179
$F_{r\beta'}$	r,β	N–H/C–H	0.420	0.158	–	0.124
$F_{d\beta}$	d,β	Hg–N/Hg–C	−0.010	0.070	–	0.213
$F_{R\beta}$	R,β	Hg	−0.017	−0.043	–	0.032
$F_{R\alpha}$	R,α	C–Hg	0.286	0.286	(0.255) [a]	–
Bend–bend						
$F_{\beta\gamma}$	β,γ	N–H/C–H	−0.204	−0.137	–	−0.041
F_β	β,β	Hg–N/Hg–C	−0.294	−0.198	–	−0.110
F_α	α,α	C–Hg	0.352	0.501	0.272	–
$F_{\alpha\epsilon}$	α,ϵ	C–Hg	0.163	0.104	[b]	–

[a] Constrained. [b] Not considered. [c] The bending and stretch–bend interaction force constants of ref. 18 are weighted by the C–Hg bond distance of $Hg(CH_3)_2$ (209.4 pm) in case of necessity. Note that force constants in Table 7 of ref. 18 are uniformly weighted for the C–H bond length of dimethylmercury (109 pm).

influenced by the electronegativities and/or the ionization potentials of the ligands X, but also by the overall charge on the molecule. It is to be expected that in species with positive charges the molecular orbitals responsible for bonding are lowered in energy and contracted to yield better overlap and hence stronger bonds. Consequently, negative charges should lead to weaker bonds, and so, we are at present studying anionic mercuriomethanes, e.g. the topologically comparable anion $[C(HgSO_3)_4]^{4-}$ with K(C–Hg) 1.654 N/cm [17].

As has been pointed out previously, the central C–Hg bonds in $C(HgCH_3)_4$ are weaker than the peripheral $Hg–CH_3$ bonds [6], and these findings, with minor alterations, are confirmed in the present all-atom calculation.

Table 4

Observed and calculated vibrational frequencies (cm^{-1}) and potential energy distribution (%) for $C(HgCH_3)_4$

Frequencies		PED in % [b]
obs. [a]	calc.	
2951	2951.0	100 $\nu_d(CH_3)$
2874	2874.0	95 $\nu_s(CH_3)$
1380	1380.9	67 $\delta_d(CH_3)+14\ \rho(CH_3)$
1167	1167.0	104 $\delta_s(CH_3)+11\ \nu_s(CH_3)$
736	736.6	42 $\delta_d(CH_3)+96\ \rho(CH_3)$
602	601.8	64 $\nu_d(CHg_4)+74\ \delta(CHg_4)$
517	517.5	95 $\nu_s(HgMe)$
505	504.6	97 $\nu_d(HgMe)$
137	141.1	100 $\delta(CHgMe)$
137	133.7	100 $\nu_s(CHg_4)$
109	105.9	107 $\delta(CHgMe)$
91	85.7	46 $\delta(CHgMe)+11\ \nu_d(CHg_4)+22\ \delta(CHg_4)$
47	50.6	100 $\delta(CHg_4)$

[a] Averaged values from IR and Raman spectra of the solid; cf. [6]. [b] Only contributions by the involved internal coordinates greater than 10% are considered.

It is interesting to compare the force constants of $C(HgCH_3)_4$ with the corresponding data for $Hg(CH_3)_2$ [18] shown in the last column of Table 3. All stretching force constants fall remarkably on going from $Hg(CH_3)_2$ to $C(HgCH_3)_4$. Since the C–Hg bond distances in the two molecules probably differ less than the force constants, the differences in the latter can be explained in terms of some non-bonded $Hg \cdots Hg$ interaction in $C(HgCH_3)_4$. Corresponding interaction and deformation force constants in the two molecules largely agree, but the relative

Table 5

Observed and calculated vibrational frequencies (cm^{-1}) and potential energy distribution (%) for $[C(HgNH_3)_4]^{4+}$

Frequencies		PED in % [b]
obs. [a]	calc.	
3395	3395.0	98 $\nu_d(NH_3)$
3309	3308.0	92 $\nu_s(NH_3)$
1653	1653.3	65 $\delta_d(NH_3)+14\ \rho(NH_3)$
1320	1320.3	107 $\delta_s(NH_3)+19\ \nu_s(NH_3)$
780	783.0	110 $\rho(NH_3)+52\ \delta_d(NH_3)$
690	687.9	62 $\nu_d(CHg_4)+55\ \delta(CHg_4)$
490	496.0	100 $\nu_s(HgN)$
477	479.8	101 $\nu_d(HgN)+17\ \nu_d(CHg_4)+11\ \delta(CHg_4)$
163	162.0	100 $\delta(CHgN)$
149	149.0	104 $\nu_s(CHg_4)$
120	119.0	71 $\delta(CHgN)+23\ \nu_d(CHg)_4+15\ \delta(CHg_4)$
96	93.6	34 $\delta(CHg_4)+26\ \delta(CHgN)+15\ \nu_d(CHg_4)$
62	63.2	97 $\delta(CHg_4)$

[a] Averaged values from buffer solutions (Table 1) and solid $[C(HgNH_3)_4](PF_6)_4$ (Table 2). [b] Only contributions of > 10% by the internal coordinates involved are considered.

magnitude of H_γ and H_β for the tetramercuriomethanes $[C(HgNH_3)_4]^{4+}$ and $C(HgCH_3)_4$ is the reverse of that for $Hg(CH_3)_2$ ($H\gamma < H_\beta$). The distinct difference found for the F_{Rd} and $F_{d\beta}$ interaction terms can be explained in terms of the more complex vibrational forms in $C(HgCH_3)_4$. Overall the force field determined for $C(HgCH_3)_4$ without using isotopic substitution (CD_3) shows a reasonable agreement with the force field for $Hg(CH_3)_2$ determined with higher accuracy by using frequencies of both $Hg(CH_3)_2$ and $Hg(CD_3)_2$.

Finally, the force constant for the Hg–N bond in $[C(HgNH_3)_4]^{4+}$ has a rather high value (2.461 N/cm) compared with, e.g., the value for $[Hg(NH_3)_2]Cl_2$ (2.06 N/cm) [19]. However, in the latter case the bond strength and force constant may be lowered by coordination of the chloride ions to the mercury atom, whereas for $[C(HgNH_3)_4](PF_6)_4$ any influence on the bonding in the cation by interaction with the counter-ion can be ruled out. To the best of our knowledge no potential constants for other compounds with $Hg–NH_3$ groups are available for comparison.

Inspection of the deformation force constants (Table 3) reveals that $C(HgCH_3)_4$ is generally somewhat more susceptible to deformations than $[C(HgNH_3)_4]^{4+}$.

A comparison of the potential energy distributions in $C(HgCH_3)_4$ (Table 4) and $[C(HgNH_3)_4]^{4+}$ (Table 5) reveals very similar patterns in both species. Thus, the valence vibrations of the C–H/N–H and $Hg–CH_3$/$Hg–NH_3$ bonds and the totally symmetric valence vibrations of the CHg_4 cores are highly characteristic, i.e. they are almost decoupled from all other vibrations, whereas the vibrations of the CHg_4 cores at 690 and 602 cm^{-1}, respectively, contain comparable contributions of degenerate valence and deformation vibrations. Among the deformation modes the linear bending of the $C–Hg–CH_3$/$C–Hg–NH_3$ and deformation of the CHg_4 sub-units, both of symmetry species *e*, seem to be almost pure. All other vibrations exhibit predominant deformation character, but with contributions from various internal coordinates.

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References

1 D.K. Breitinger and W. Kress, J. Mol. Struct., 143 (1986) 155.
2 D.K. Breitinger, W. Morell and K. Grabetz, Z. Naturforsch. B, 34 (1979) 390.
3 J. Mink, Z. Meić, M. Gál and B. Korpar-Čolig, J. Organomet. Chem., 256 (1983) 203.
4 J. Mink, D.K. Breitinger, Z. Meić and M. Gál, J. Mol. Struct., 115 (1984) 435.
5 R. Neufert, Doctoral Thesis, Erlangen, 1985.
6 J. Mink, D.K. Breitinger and W. Kress, J. Organomet. Chem., 301 (1986) 1.
7 D.S. Matteson in Gmelin, Handb. der Anorg. Chemie, Ergänzungswerk zur 8. Aufl., Bd. 48, Teil 16, Springer, Berlin, 1977, S. 34 ff.
8 R. Köster in Houben-Weyl, Methoden der organischen Chemie, Organoborchemie I, 4. Aufl., Thieme, Stuttgart, 1982, S. 749.
9 W. Kress, Doctoral Thesis, Erlangen, 1983.
10 D.K. Breitinger in J.J. Eisch and R.B. King (Eds.), Organometallic Syntheses, Vol. 3, Elsevier, New York-Amsterdam, 1986, p. 436.

11 A. Weiss and A. Weiss, Z. Anorg. Allg. Chem., 282 (1955) 324.
12 K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 4th edit., Wiley, New York-Chichester, 1986, p. 191 ff.
13 K.H. Schmidt and A. Müller, Coord. Chem. Rev., 19 (1976) 41.
14 D.K. Breitinger, G. Petrikowski, G. Liehr and R. Sendelbeck, Z. Naturforsch. B, 38 (1983) 357.
15 D. Grdenić, B. Kamenar, B. Korpar-Čolig, M. Sikirica and G. Jovanovski, Cryst. Struct. Comm., 11 (1982) 565.
16 J. Mink and L.M. Mink, Computer Program System for Vibrational Analysis of Molecules, Erlangen, 1983.
17 U. Krumphanzl, Doctoral Thesis, Erlangen, in preparation.
18 J. Mink and B. Gellai, J. Organomet. Chem., 66 (1974) 1.
19 C. Téllez and G. Díaz, J. Mol. Struct., 77 (1981) 213.