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Novel synthesis and vibrational analysis of (arene)osmium(II) complexes of the type $[(C_6H_3(CH_3)_3)OsH_2(L)]$

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Abstract

The dihydridoosmium(II) complexes $[(mes)OsH_2(L)]$ (mes = $C_6H_3(CH_3)_3$; L = CO, **4**; $CNCH_3$, **5**) have been prepared in nearly quantitative yields from $[(mes)OsCl_2(L)]$ (L = CO, **1**; $CNCH_3$, **2**) and Mg/Hg in THF in the presence of C_2H_5OH as a proton source. These complexes are suitable for studies of C–H activation by UV irradiation in solution. The FT-IR and Raman spectra of **4** and **5** have been recorded in the range between 400 and 3300 cm^{-1} and between 100 and 3300 cm^{-1}, respectively; a complete assignment of the observed vibrational modes is presented, supported by polarized Raman spectra. The Os–ligand vibrations of half sandwich complexes of this type have been determined for the first time. A normal coordinate analysis of the osmium-ligand modes has been performed by treating the ring ligand as a point mass. Force constants and potential energy distributions are given.

Introduction

Recently, the preparation of a variety of dihydridoruthenium(II) and dihydridoosmium(II) complexes of the general type $[(arene)MH_2(L)]$ (M = Ru,Os; L = PR_3 [1]; M = Os, L = CO [2–4]) has been described. Compared with the phosphane derivatives, the carbonyldihydridoosmium(II) compounds are photochemically more labile, and thus useful starting materials for C–H activation studies both in a matrix and in solution [2–6]. In the present paper we describe new synthetic routes to the dihydridoosmium(II) complexes $[(mes)OsH_2(L)]$ (mes = mesitylene, 1,3,5-trimethylbenzene; L = CO, $CNCH_3$). Furthermore, vibrational analysis and normal coordinate calculations of these complexes are presented for the first time, and the results are discussed in detail.

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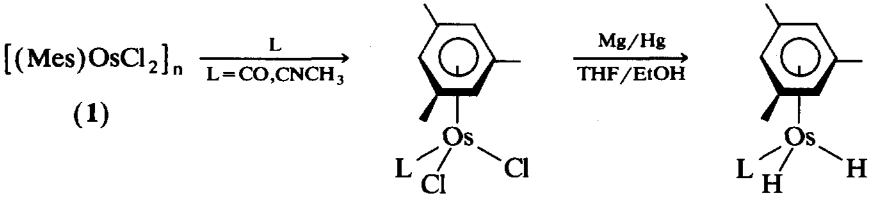
Results and discussion

The bridging halide complex [(mes)OsCl$_2$]$_n$ (**1**), which is either a polymer [2] or a dimer [7], reacts with CO [2] or CNCH$_3$ [8] to give the mononuclear compounds [(mes)OsCl$_2$(L)] (L = CO, **2**; CNCH$_3$, **3**). The dichloro-complexes are useful starting materials for the synthesis of dihydridoosmium(II) compounds. As recently described [2], [(mes)OsH$_2$(CO)] (**4**) is available from [(mes)OsCl$_2$(CO)] (**2**) with Na in liquid ammonia in the presence of ^{t}BuOH. However, this method gives a rather low yield of **4** (~ 50%), and the synthesis of the dihydridoisonitrile derivative is not possible.

A very successful new method, which gives nearly quantitative yields of both [(mes)OsH$_2$(CO)] (**4**) and [(mes)OsH$_2$(CNCH$_3$)] (**5**) involves the reaction of the dichloroosmium(II) complexes [(mes)OsCl$_2$(L)] (L = CO, **2**; CNCH$_3$, **3**) with Mg/Hg in THF and in the presence of ethanol as a proton source. (A similar halide/hydride exchange has been described for the synthesis of [(mes)OsH(CH$_3$)(CO)] from [(mes)OsI(CH$_3$)(CO)] with Na/Hg in THF/C$_2$H$_5$OH [2].)

The dihydrido complexes **4** and **5** are photochemically reactive and able to activate C–H bonds either in solution [3,5] or in a matrix [4]. In competition with the C–H bond activation, there is loss of the mesitylene ligand. Because of this, theoretical studies were performed by Combariza et al. [9] in order to indicate how the selectivity between these two reactions could be controlled. The aim of the present study was to find a means of selectively exciting certain vibrational modes to optimize the reaction conditions and favour the C–H activation products. For this purpose, information about force constants and bond properties, based on a vibrational analysis of the compounds, is of great importance. Until now, few vibrational data for osmium complexes have been reported [10–13]. The initial results of the present work on vibrational spectra were communicated previously [14]. In the vibrational analysis of **4** and **5** given in this paper, we emphasize the osmium-ligand modes. To facilitate the calculations, the mesitylene ligand was considered as a point mass. A normal coordinate analysis involving the whole ring ligand is in progress [15]. The ring ligand of these complexes is coordinated to the central atom without distortion of its geometry. The symmetry of the ring ligand is changed from D_{3h} to C_{3v} if the rest of the molecule is considered as a point mass. Additional modes, *i.e.* the Os–ring stretch and the degenerated Os–ring tilt



(1)

L = CO (2)
L = CNCH$_3$ (3)

L = CO (4)
L = CNCH$_3$ (5)

Scheme 1.

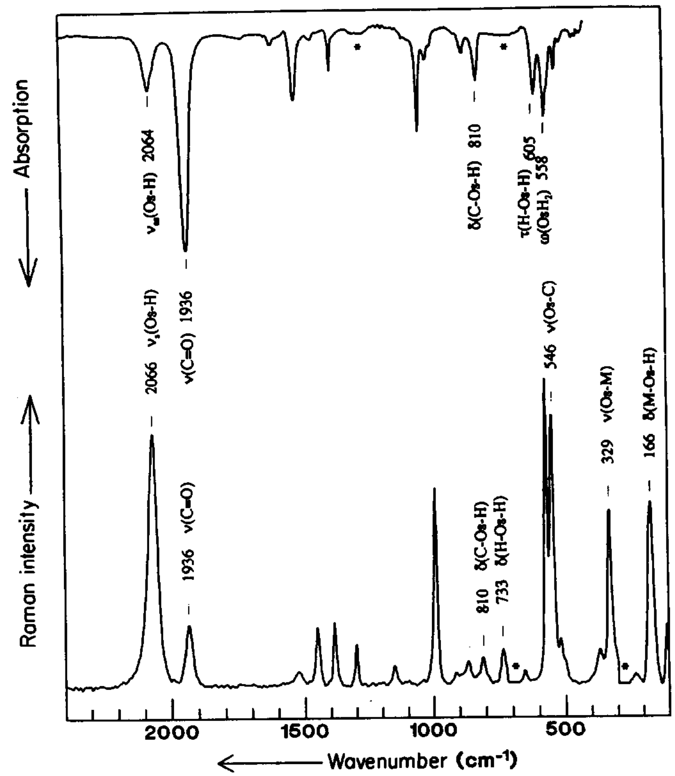


Fig. 1. Part of the survey FT-IR and Raman spectra of [(mes)OsH$_2$(CO)] (4) in CH$_2$Cl$_2$. FT-IR: resolution $s = 4$ cm^{-1}; number of scans $n = 32$. Raman: excitation wavelength = 676.4 nm; laser power $P = 100$ mW; slit width $s = 3$ cm^{-1}; concentration $c = 0.24$ mol/l; temperature $T = 300$ K; * marks the positions of solvent compensation.

vibrations, are described below. In principle, we discuss the vibrational spectra by separating the molecular vibrations into internal ring vibrations and Os-ligand vibrations. The internal ring vibrations are not considered here, but are discussed elsewhere [15]. The vibrational analysis allows us to extend our research to photochemical C–H activation in a matrix in order to determine the nature of the photoreaction by irradiation with selective wavelengths.

Figures 1 and 2 show the Raman and FT-IR spectra of **4** and **5**, respectively. In Tables 1 and 2 are listed the observed Raman and IR frequencies, together with the calculated frequencies and potential energy distributions for the two compounds. With the ring ligand considered as a point mass, compounds **4** and **5** can be regarded as molecules with C_s symmetry. Consequently, only modes of the species A′ and A″ are considered. Due to the heavy central atom, no vibrational coupling should occur between the ν(Os–H) and the other ν(Os-ligand) vibrations. The OsH$_2$ moiety thus can be treated on the basis that local C_{2v} symmetry gives rise to a polarized and a depolarized stretching vibration of species A$_1$ and B$_2$, respectively.

The ν(Os–H), the ν(C=O) and the ν(C=N) stretching vibrations are observed in the region between 1800 cm^{-1} and 2300 cm^{-1}. The ν(C=O) band of **4** is at 1936

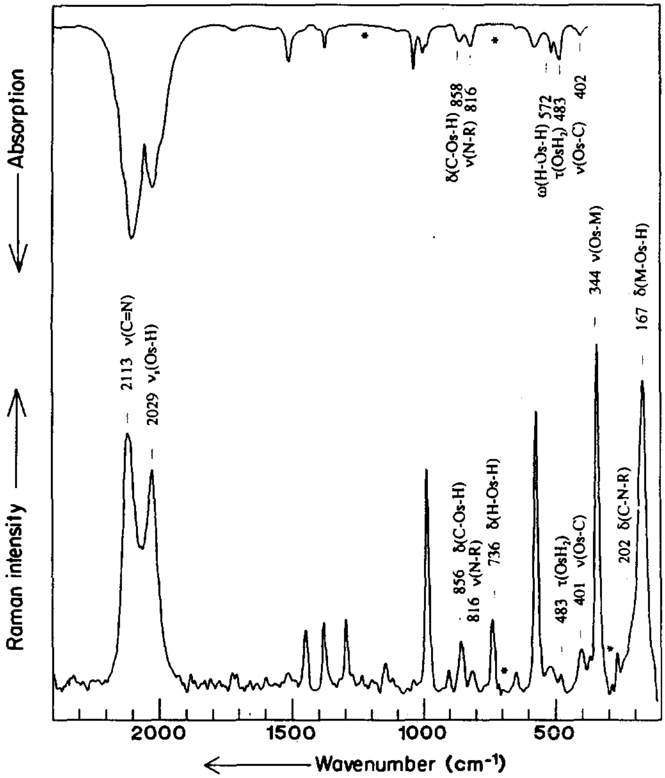


Fig. 2. Part of the survey FT-IR and Raman spectra of [(mes)OsH$_2$(CNMe)] (5) in CH$_2$Cl$_2$. FT-IR: resolution $s = 4$ cm^{-1}; number of scans $n = 32$. Raman: excitation wavelength = 676.4 nm; laser power $P = 100$ mW; slit width $s = 3$ cm^{-1}; concentration $c = 0.24$ mol/l; temperature $T = 300$ K; * marks the positions of solvent compensation.

Table 1

Observed Raman, IR, and calculated frequencies for [(mes)OsH$_2$(CO)] (4) and potential energy distribution (PED) (for internal coordinates see Fig. 4.); M, mesitylene as a point mass; vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder

Raman (cm^{-1})	IR (cm^{-1})	Calculated	Assignment	PED (%)
2066vs	2066w,sh	2066	ν_s(Os–H)	100s_1
2062w,sh	2064m	2062	ν_{as}(Os–H)	100s_1
1936m	1936vs	1936	ν(C≡O)	87s_3 + 13s_2
810w	810w	810	δ(C–Os–H)	$60\theta + 29\epsilon$
733w		733	δ(H–Os–H)	$81\alpha + 9\beta + 5\theta$
	605m	605	τ(H–Os–H)	$74\epsilon + 26\beta$
	558m	559	ω(OsH$_2$)	$40\epsilon + 31\theta + 25\beta$
546vs	546vw	546	ν(Os–C)	76s_2 + 13s_3
329s		330	ν(Os–M)	77s_4 + 8s_2 + $6\epsilon + 5\beta$
166s		168	δ(M–Os–H)	$92\beta + 7\epsilon$
137m,sh		132	δ(M–Os–C)	$47\gamma + 23\beta$

Table 2

Observed Raman, IR, and calculated frequencies for [(mes)OsH$_2$(CNMe)] (**5**) and potential energy distribution (PED) (for internal coordinates see Fig. 5); M, mesitylene as a point mass; R, CH$_3$ as a point mass; vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder

Raman (cm^{-1})	IR (cm^{-1})	Calculated (cm^{-1})	Assignment	PED (%)
2113s	2110vs	2113	ν(C=N)	$87s_3+9s_2$
2029s		2026	ν_s(Os–H)	$100s_1$
2021w	2022s	2022	ν_{as}(Os–H)	$100s_1$
856m	858w	856	δ(C–Os–H)	$57\theta+14\epsilon+13s_5+6s_2$
816w	816w	816	ν(N–R)	$54s_5+27s_2+11\theta$
736m		736	δ(H–Os–H)	$81\alpha+12\beta$
	572w	574	ω(H–Os–H)	$35\epsilon+22\alpha+21\theta+17\beta$
483w	483w	483	τ(OsH$_2$)	$67\epsilon+33\beta$
401w,sh	402vw	402	ν(Os–C)	$39s_2+26s_4+21s_5+11s_3$
344vs		347	ν(Os–M)	$72s_4+14s_2+7s_5$
202w,sh		202	δ(C–N–R)	$48\Omega+23\gamma+10\beta+5s_2$
167s		151	δ(M–Os–H)	$88\beta+12\epsilon$
		96	δ(M–Os–C)	$47\Omega+17\theta+17\gamma+5\beta+5\gamma$

cm^{-1}, and shows strong IR absorption and medium Raman intensity. The strong Raman band at 2066 cm^{-1} is assigned to the symmetric ν(Os–H) stretching mode and cannot be seen in the IR spectrum. The corresponding anti-symmetric mode is hidden beyond the symmetric Raman band but can be detected in the polarized Raman spectrum ($I_\perp$) as well as in the FT-IR spectra at 2062 cm^{-1}. The ν(Os–H) and the ν(C=N) modes are superposed in the case of compound **5**. The ν(C=N) stretching mode gives rise to a strong polarized band at 2113 cm^{-1}. The symmetric and anti-symmetric ν(Os–H) frequencies are lower at 2026 cm^{-1} and 2020 cm^{-1}, respectively. This is a consequence of higher electron donor ability of the isonitrile ligand.

We carried out a deconvolution of the polarized and depolarized spectra of **4** and **5** in this region by a curve fitting routine for a more precise determination of the position and the intensity of the superposed bands. The single bands were fitted to a Voigt profile, which is a convolution of a Gaussian and Lorentzian function with about 20% Lorentzian character.

The ν(Os–C) band of compound **4** gives rise to a strong polarized Raman band at 546 cm^{-1}. In comparison with the CO ligand in **4**, the CNMe ligand in **5** appears to experience a smaller π-back-donation from the osmium atom. Along with the mass effect, this causes a decrease in the Os–C bond order and a shift of the ν(Os–C) band to lower frequencies. Furthermore, a decrease of the intensity corresponding to the increase of the Os–C bond polarity is expected. In fact, the position of the corresponding vibration of **5** is lowered to 404 cm^{-1} and the observed band is of weak intensity.

A typical pattern of the half sandwich complex for the metal–ring stretching modes is detected at 329 cm^{-1} and 368 cm^{-1} for **4** and at 344 cm^{-1} and 376 cm^{-1} for **5**, respectively. Despite the increased electron density on the central atom in **5**, there is an increased bond strength between the metal and the ring which causes a small shift of 15 cm^{-1} of the ν(Os–ring) mode to higher wavenumbers in comparison to that for **4**. This observation may be attributed to a higher back-donation from the metal atom into unoccupied orbitals of the ring.

Table 3

Bond lengths and bond angles in **4** and **5** used as input for the normal coordinate analysis: M, mesitylene as point mass; R, CH_3 group as point mass

	4/5
Bond angle	
(M–Os–H)	135.1
(M–Os–C)	134.8
(H–Os–H)	90.1
(Os–C–O)/(Os–C–N)	177.5
Bond lengths (Å)	
Os–H	1.856
Os–C	1.836
Os–M	1.681
C–O	1.169
C–N	1.166
N–R	1.534

The various Os-ligand deformation modes are found in the region between 100 cm^{-1} and 900 cm^{-1}. They are also listed in Tables 1 and 2. The assignment of these modes is supported by the normal coordinate calculation described below and by comparison with data for other metal hydrides [16–18].

For the normal coordinate calculations, we used a geometry of the molecule adapted from X-ray structural data for similar species [6,8,19,20]. Errors in bond angles of up to 10% arising from this approximation were shown to be negligible [21]. Thus, the bond angles and bond lengths of corresponding bonds in **4** and **5** can be regarded as identical. The methyl group of the isonitrile ligand was treated as a point mass. The bond angles and bond lengths used are listed in Table 3, and the defined normal coordinates are given in Figs. 3 and 4. It was necessary for the calculation program also to include Os–C–X (X = O, N) and C–N–Me torsion modes which are inactive both in Raman and IR spectroscopy. Since there is no possibility of determining the frequencies of these modes, the values for the force constants were set to about 0 mdyn/Å. The calculated frequencies of the modes are compiled in Tables 1 and 2 together with the observed frequencies mentioned above. These tables also show the potential energy distribution for each normal mode. There is good agreement between the experimental and the calculated frequencies. Deviations of up to *ca.* 5 cm^{-1} were found only in the low frequency

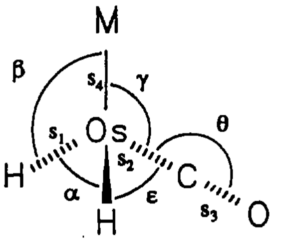


Fig. 3. Point mass model of compound **4** with defined internal coordinates.

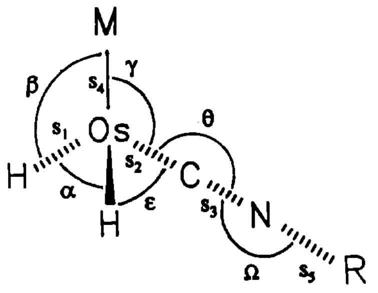


Fig. 4. Point mass model of compound **5** with defined internal coordinates.

region. Most of the calculated frequencies coincide almost exactly with those observed. We also found that there is no vibrational coupling of the ν(Os–H) modes with any other modes; this confirms the assumption of local C_{2v} symmetry for the H–Os–H moiety.

Comparison of the potential energy distributions (PED) of the ν(Os–ring) vibration for **4** and **5** reveals a decrease in the percentage of the pure osmium–ring

Table 4

Internal coordinates and force constants for compounds 4 and 5

Internal coordinate	Force constants (mdyn/Å)	
	[(mes)OsH$_2$(CO)] (4)	[(mes)OsH$_2$(CNMe)] (5)
s_1	2.5166	2.4211
s_2	4.7780	4.7745
s_3	12.9580	14.2706
s_4	5.8204	5.7311
s_5		2.8036
α	1.4424	1.3759
β	0.7551	0.7020
γ	0.5812	0.5868
ϵ	1.3700	0.9404
θ	1.6440	1.4984
Ω		0.1281
s_2s_4	−0.4101	0.0488
s_2s_3	−0.3913	−0.5064
$s_2\gamma$	−0.1228	−0.3547
$s_2\epsilon$	0.2042	0.1355
$s_4\beta$	−0.5182	0.3006
$s_3\theta$	0.1644	−0.0255
$s_2\theta$	0.4884	0.5173
$s_5\Omega$		0.0658
s_5s_3		−0.0900
$\gamma\epsilon$	−0.0335	−0.2086
$\alpha\epsilon$	−0.2556	−0.0940
$\epsilon\epsilon$	−0.2008	0.0002
$\gamma\beta$	0.1224	0.0996
$\beta\beta$	0.3377	0.3422
$\beta\gamma$		−0.1414
t_1	0.0000	0.0000
t_2		0.0000

stretching vibration s_4 (see Tables 1 and 2). The large mesitylene ligand contains 77% of the internal coordinate s_4 for **4** whereas in **5**, this value is reduced to 72%. Although the Os–C force constants (s_2) of **4** and **5** are nearly identical (see Table 4), the large shift of the ν(Os–C) mode in compound **5** from 546 cm^{-1} to 404 cm^{-1} is nicely confirmed by the normal coordinate analysis. Apparently, there is an additional mode mixing with the N–Me internal coordinate s_5 and the ring–metal internal coordinate s_4.

Conclusion

A novel synthesis of (arene)osmium(II) complexes of the type [(mes)OsH_2(L)] (L = CO, CNMe) has been devised. A comprehensive vibrational analysis has been carried out by means of Raman and FT-IR spectroscopy and by a normal coordinate analysis. The latter has been performed for the osmium-ligand modes of both complexes. The resulting force constants and potential energy distributions are reported and discussed. The results are regarded as a basis for further investigations on C–H activation in a matrix and for theoretical calculations relevant to the reaction mechanism.

Experimental

Preparation of [(mes)OsH$_2$(CO)] (4)

A suspension of 100 mg of **2** (0.24 mmol) and Mg/Hg (2 g Hg, 10 mmol; 25 mg Mg, 1 mmol) in 10 ml of THF/C_2H_5OH (50:1) was stirred for 1 h at room temperature. The solution was filtered and the residue washed with 20 ml THF. The filtrates were combined and dried *in vacuo*. The crude product was extracted with 20 ml of benzene/hexane (2:1), the extracts were filtered, and the combined filtrates were dried *in vacuo*. Recrystallization from hexane at 25°C to −78°C gave a microcrystalline white powder (77 mg, 94%).

The crude product may also be purified by sublimation *in vacuo* (50°C, 5×10^{-5} mbar). For analytical, IR and ^{1}H-NMR data see ref. 2. ^{13}C NMR (C_6D_6, 100 MHz): δ 185.5 (CO), 103.3 ($C$$CH_3$ from $C_6H_3(CH_3)_3$), 82.9 (CH from $C_6H_3(CH_3)_3$), 21.0 (CCH_3 from $C_6H_3(CH_3)_3$).

Preparation of [(mes)OsH$_2$(CNCH$_3$)] (5)

The preparation of **5** was carried out as described for **4** but from 95 mg of **3** (0.22 mmol). After recrystallization from hexane at 25°C to −78°C or sublimation (50°C, 5×10^{-5} mbar), **5** was obtained as a pale yellow microcrystalline powder (73 mg, 94%); m.p. of **5** 130°C (dec.).

Anal. Found: C, 37.77; H, 5.05; N, 3.91. $C_{11}H_{17}NOs$ calc.: C, 37.38; H, 4.85; N, 3.96%. MS (70 eV): m/z 355 (7, M^+), 353 (15, $M^+ - H_2$), 314 (2, $M^+ - CNCH_3$), 312 (5, (mes)Os^+). IR (CH_2Cl_2): ν(CN) 2110 cm^{-1}, ν(OsH) 2022 cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz): δ 4.90 (s, 3H, $C_6\mathit{H}_3(CH_3)_3$); 2.50 (s, 3H, $CNC\mathit{H}_3$); 2.32 (s, 9H, $C_6H_3(C\mathit{H}_3)_3$); −10.30 (s, 2H, $Os\mathit{H}_2$). ^{13}C NMR (C_6D_6, 100 MHz): δ 149.0 ($\mathit{C}NCH_3$); 97.2 ($\mathit{C}CH_3$ from $C_6H_3(CH_3)_3$); 77.3 ($\mathit{C}H$ from $C_6H_3(CH_3)_3$); 28.6 ($CN\mathit{C}H_3$); 21.6 ($C\mathit{C}H_3$ from $C_6H_3(CH_3)_3$).

Materials and methods

All reactions were carried out under argon by Schlenk tube techniques. The starting materials $[(mes)OsCl_2]_n$ (**1**) [2] and $[(mes)OsCl_2(L)]$ (L = CO, **2** [2]; $CNCH_3$, **3** [8]) were prepared as previously described. ^1H and ^{13}C NMR spectra were recorded on a Bruker WM 400 and the mass spectra were recorded on a Varian MAT CH7 instrument.

Raman spectra were recorded in a conventional 90° scattering arrangement. Solvent compensation was carried out by the spinning cell technique using two compartments [22]. The 676.4 nm line of a Spectra Physics model 2025 krypton ion laser was used as the exciting source. The energy received by the samples was about 100 mW. In order to obtain the polarized and depolarized scattering intensity, the polarization of the incident laser light was rotated with a double Fresnel rhomb in parallel and perpendicular directions with respect to the analyzer which was placed in front of the entrance slit of the spectrometer. The scattered light was collected by a 1:0.7 photo objective ($f = 50$ mm), analyzed with a Spex model 1404 double monochromator and detected either by a cooled Burle model C31034-02A photomultiplier and a photon counting AT system or by a Photometrics RDS 200 CCD Raman detection system. The recording and treatment of the spectra were carried out by specially developed Raman software [23,24]. Plasma lines of the laser tube were filtered out by use of a modified Anaspec prism filter. The spectral resolution was chosen between 1 and 3 cm^{-1}. The spectral intensity was corrected by calibration with a tungsten broad band lamp. The concentration of the solution was 0.2 mol/l.

The FT-IR spectra were recorded with a Bruker model IFF-25 FT-IR spectrometer with Spectrafile^{plus} Software. The solutions were contained in KBr cells of 0.25 mm pathlength that had been purged with argon prior to filling. The resolution was 4 cm^{-1}.

The normal coordinate calculations were performed by use of the FG matrix method of Wilson [25] and of the programs OCMP-067 [26] for calculations and VIA [27] for display. The calculated frequencies, the refined force constants and the potential energy distribution were generated from a trial set of Cartesian coordinates, atom masses, internal coördinates, and approximate force constants. The calculations were carried out on a SPARC/2 workstation and displayed on a personal computer.

Acknowledgments

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