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Raman spectroscopic determination of formation constant of uranyl hydrolysis species $(UO_2)_2(OH)_2^{2+}$

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Abstract

Raman spectra of uranyl species in 10^{-2} M uranium(VI) perchlorate solutions were measured in pH range 2.88–3.46. The bands of ν_1 symmetrical stretching vibration were observed at 872 and 853 cm^{-1} which were attributed to UO_2^{2+} and $(UO_2)_2(OH)_2^{2+}$, respectively. Under the coexistence of $(UO_2)_2(OH)_2^{2+}$, concentration of UO_2^{2+} was accurately determined using the Raman intensity. The formation constant of $(UO_2)_2(OH)_2^{2+}$ was estimated, and this constant was discussed with the values determined by other methods. The validity of this method was discussed in conjunction with the covalent-bond character of U=O.

Keywords: Raman spectrometry; Uranyl, hydrolysis product; Formation constant; Polarizability

1. Introduction

A monomeric hydrolyzed species of uranyl, UO_2OH^+, at a total concentration of uranium greater than 10^{-4} M, has been reported to have the strong tendency for dimerization [1,2]. The dimerized hydrolysis species had been identified as $U_2O_5^{2+}$ or $(UO_2)_2OH^{3+}$, but more recent data indicated that the species should be dihydroxyl-bridged $(UO_2)_2(OH)_2^{2+}$ [3].

The equilibrium constant between UO_2^{2+} and $(UO_2)_2(OH)_2^{2+}$ [1,4,5] has been investigated by titration method [6–16], calorimetric analysis [17], solubility measurement [18], absorption spectrometry [9,16,19–22] or time-resolved fluorescence spectroscopy [20], etc. Under the coexistence of similar uranyl complexes, every method has a difficulty of measuring equilibrium concentrations independently.

The stretching frequency of U=O bonds is known to decrease with complexation, which have received considerable attention [3,23–27]. By using the frequency shift of U=O bonds in Raman spectra through dimerization, we can deal with UO_2^{2+} and the dinuclear species $(UO_2)_2(OH)_2^{2+}$ independently. In the present study, we measured the Raman spectra of the solutions containing 10^{-2} M uranium(VI) at pH around 3. Under the condition, the quantitative measurement of UO_2^{2+} was examined by laser Raman spectrometry. The formation constant of uranyl hydrolysis species $(UO_2)_2(OH)_2^{2+}$ was determined, and this constant was discussed with the values determined by other methods. To our knowledge, this paper presents the first trial for the determination of the formation constant of $(UO_2)_2(OH)_2^{2+}$ by laser Raman spectrometry.

2. Experimental details

Uranium(VI) solutions (10^{-2} M) of various pH, whose ionic strength were all kept at 1 M by $NaClO_4$, were prepared. The pH was adjusted with either $HClO_4$ or NaOH. The solutions were filtered by a membrane with 3000 nominal molecular weight limit (NMWL) (Millipore, Microcon YM-3). It corresponds to ca. 2 nm in average pore size. The membrane was pre-rinsed to remove trace amount of glycerin before usage. The pH of the filtrate was measured, and a 2-ml aliquot of each solution was transferred into a quartz cell for Raman spectrometry. The quartz cell was sealed with a stopcock.

Due to the naturally occurring evaporation during the centrifugation, the concentration of uranium was determined by absorption spectrometry (Shimadzu, UV-3100PC). Before the measurement, the samples were acidified by adding $HClO_4$ for a quantitative conversion of uranium into UO_2^{2+}, and the absorption at 414 nm was measured. The change of the ionic strength was corrected.

Raman spectra were obtained by an excitation using the 514.5-nm line of Ar^+ laser (NEC, GLS3280 and

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GLG3280). The laser power at the sample was 300 mW. The Raman scattering was collected at 90° to the incident beam. The Raman spectra were recorded by a Jasco NR-1100 spectrophotometer at 0.1-cm^{-1} intervals. The scanning rate was 60 cm^{-1}/min. One hundred scans for one sample in the range from 800 to 900 cm^{-1} were averaged to obtain the final spectrum. The measurements were performed at ambient temperature of 293–295 K, and no evidence of warming was observed.

3. Results and discussion

Fig. 1 shows the Raman spectra of uranyl perchlorate solutions which contain 0.14 M $HClO_4$ with the ionic strength kept at 1 M by $NaClO_4$. Under this condition, all the uranyl is present in the unhydrolyzed form. The band at 872 cm^{-1} was assigned previously to the ν_1 symmetrical stretching vibration of UO_2^{2+} [3,25], while the band at 935 cm^{-1} is known to be the ν_1 mode of ClO_4^-. Since the solutions have the same ionic strength, and hence the intensities at 935 cm^{-1} should be identical, the Raman spectra of UO_2^{2+} are drawn as the relative intensities to the band at 935 cm^{-1}.

The obtained Raman spectra in the range of pH 2.88–3.46 are shown in Fig. 2. With the increase of pH, there is an obvious growth of a band at 853 cm^{-1}. The appearance of this band is attributed to the increase of $(UO_2)_2(OH)_2^{2+}$ species [3,25]. Trinuclear species has been reported to have a band at 836–840 cm^{-1} [3,25], but it was not observed in the range of pH shown in Fig. 2. Thus, under the condition of the present study, only an equilibrium between UO_2^{2+} and $(UO_2)_2(OH)_2^{2+}$;

$$2UO_2^{2+} + 2H_2O \leftrightarrow (UO_2)_2(OH)_2^{2+} + 2H^+ \tag{1}$$

can be considered to govern the system.

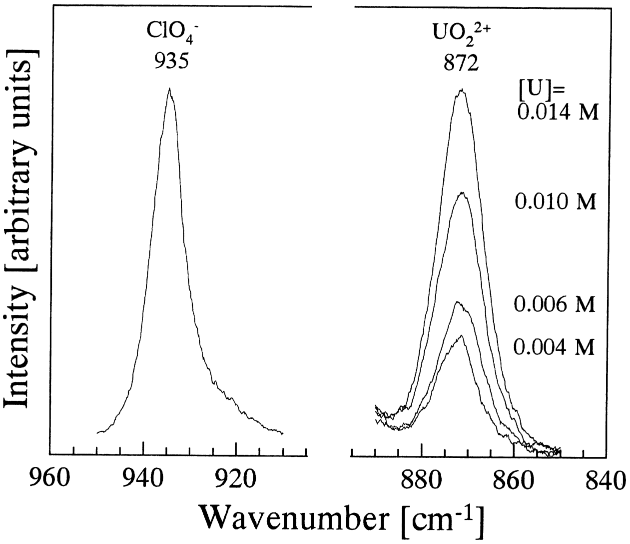

Fig. 1. Raman spectra of uranyl perchlorate solutions. The ν_1 symmetric stretching vibrations at 872 and 935 cm^{-1} correspond to unhydrolyzed mononuclear uranyl species and perchlorate ion, respectively. The Raman spectra of UO_2^{2+} are shown as the relative intensities to the band at 935 cm^{-1}. No filtration was performed for these solutions. Sixteen scans averaged for the spectra of UO_2^{2+}. Slit widths were 2 and 5 cm^{-1} for ClO_4^- and UO_2^{2+}, respectively.

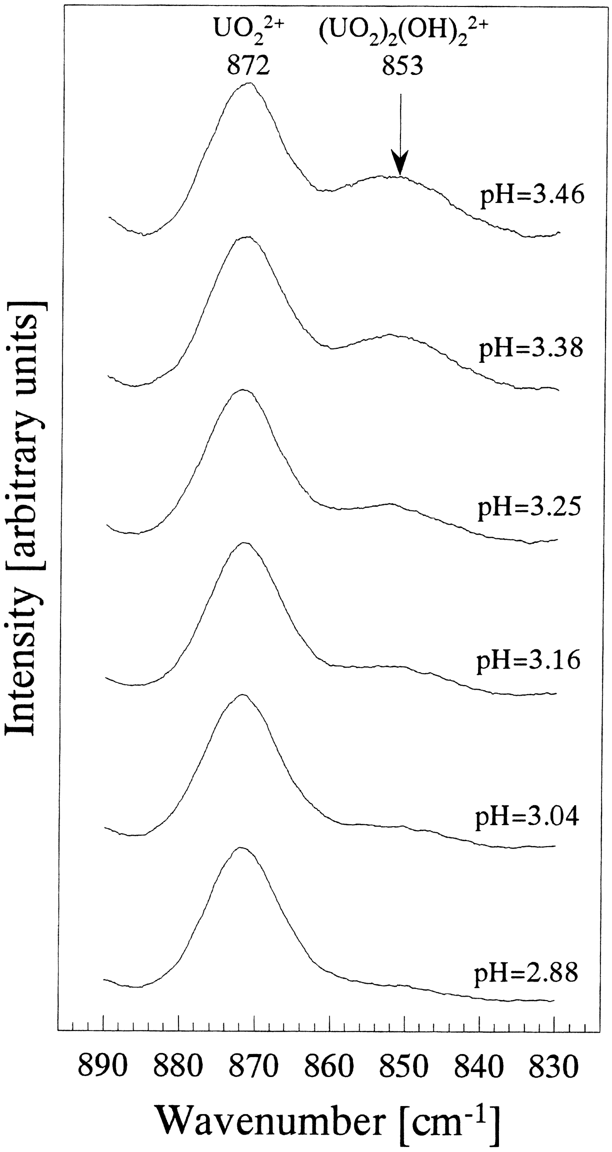

Fig. 2. Raman spectra of the solutions with different pH. The ν_1 uranyl symmetric stretching vibration at 853 cm^{-1} corresponds to hydrolyzed dinuclear uranyl species. The spectra are drawn as the intensities at 872 cm^{-1} to be unity. Slit width was 5 cm^{-1}.

Each spectrum in Fig. 2 can be resolved into four components: (a) baseline, (b) tailing of the ν_1 mode of ClO_4^- at 935 cm^{-1}, (c) ν_1 mode of UO_2^{2+} at 872 cm^{-1} and (d) ν_1 mode of $(UO_2)_2(OH)_2^{2+}$ at 853 cm^{-1}. The Raman spectrum of the pH 3.46 solution is illustrated in Fig. 3. In the range over 830 cm^{-1}, the linear part can be considered to be the baseline. The baseline was defined as a linear

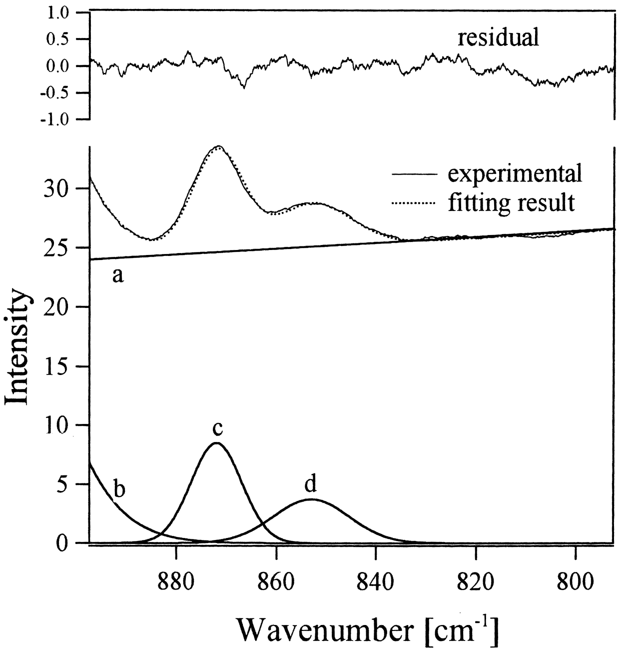

Fig. 3. Raman spectrum of the pH 3.46 solution. The spectrum is resolved into four components: (a) baseline, (b) tailing of the ν_1 mode of ClO_4^- at 935 cm^{-1}, (c) ν_1 mode of UO_2^{2+} at 872 cm^{-1} and (d) ν_1 mode of $(UO_2)_2(OH)_2^{2+}$ at 853 cm^{-1}.

line, which originates from the point at 792.5 cm^{-1}. The slope of baseline was analyzed as a parameter. The other components (b), (c) and (d) were analyzed by fitting to Gaussian functions. Four components were analyzed simultaneously. The integral of the Gaussian curve (c) within 2σ from the 872 cm^{-1} was recognized as the Raman intensity of UO_2^{2+} (I_{872}, hereafter). I_{853} was obtained for $(UO_2)_2(OH)_2^{2+}$. The Raman intensity of ClO_4^-, I_{935}, was defined as the integral of the raw spectrum over 923–947 cm^{-1}. As shown in Fig. 3, good baseline was obtained by using the filtration, which results in the accurate analysis of the Raman spectra of UO_2^{2+} and $(UO_2)_2(OH)_2^{2+}$.

The total intensity of a Raman line after averaging over all orientations of the particle, is given by [28],

$$I_{m,n} = \frac{2^3\pi}{3^2c^4} I_0 \omega^4 \sum_{\rho\sigma} |(\alpha_{\rho\sigma})_{m,n}|^2 \qquad (2)$$

where I_0 is the intensity of the incident light, ω is the frequency of the scattered light ($\omega = 2\pi\nu$), $\alpha_{\rho\sigma}$ is the (ρ,σ)th component of the polarizability tensor, m is the initial state, and n is the final state. Experimentally, the Raman intensity is written as,

$$I_{\exp} \propto I_{m,n} T(\nu) A(\nu) C \qquad (3)$$

where $T(\nu)$ and $A(\nu)$ are the transmission rates of the scattered light through the spectrophotometer and the sample, respectively. C is the concentration of the sample. In the present study, the absorption due to the sample is negligible small. Generally, quantitative analysis using laser Raman spectrometry is performed by the internal standard. From Eqs. (2) and (3), the relative intensity, I/I_{ref}, can be written as,

$$\frac{I}{I_{\mathrm{ref}}} = \frac{T(\nu)\nu^4\alpha^2}{T(\nu_{\mathrm{ref}})\nu_{\mathrm{ref}}^4\alpha_{\mathrm{ref}}^2 C_{\mathrm{ref}}} C \qquad (4)$$

where the subscript 'ref' means reference. In this equation, the first term, $T(\nu)/T(\nu_{\mathrm{ref}})$, gives a constant value for a given condition. Thus, under the coexistence of a reference substance with a standardized concentration C_{ref}, the relative intensity is proportional to the concentration of the sample.

For the data given in Fig. 1, I_{872} was obtained in the same manner adapted to the data of Fig. 3, and the obtained I_{872}/I_{935} was linearly correlated to $[UO_2^{2+}]$ which was determined by the absorption spectrometry. A correlation satisfactory factor of $R = 0.998$ was obtained for this calibration line. The absolute concentrations of UO_2^{2+} in Fig. 2 were determined using this calibration line and I_{872}/I_{935}. The obtained concentrations are given in Table 1. It is clear that the fraction of UO_2^{2+} in the solution decreases with the increase of pH. Since the pseudo-colloid larger than 2 nm in diameter was removed by filtration and the trinuclear species is evidently negligible small, the difference between $[U(VI)]_{\mathrm{total}}$ and $[UO_2^{2+}]$ can be expected to give the estimated concentration of $(UO_2)_2(OH)_2^{2+}$. By this treatment, the formation constant of $(UO_2)_2(OH)_2^{2+}$ defined for the equilibrium reaction Eq. (1) was evaluated as $\log K_{2,2} = -5.62 \pm 0.23$. The uncertainty of the constant was estimated as 3σ The pH was converted to $\log[H^+]$ by the Gran plot analysis [29]. The extended Debye–Hückel expression [4], $\log K_{2,2} + 2D$, was calculated and shown in Fig. 4 as a function of the ionic strength. The literature values of $\log K_{2,2} + 2D$ obtained by other methods are also shown in Fig. 4 for comparison; the available literature data [6–17,19–22] under the condition of $NaClO_4$ medium are used. In Fig. 4, $\log K_{2,2}$ by the above treatment appears to be slightly higher than the trend of literature values, though their uncertainty ranges overlap. This suggests the possibility of overestimation of the

Table 1
Concentrations[a] of UO_2^{2+}

pH	$[U(VI)]_{\mathrm{total}}$ (10^{-2} M)	$[UO_2^{2+}]$ (10^{-2} M)	Fraction (%)	$\log K_{2,2}$
2.88	1.20	1.13	94.2	−5.71
3.04	1.14	1.05	92.1	−5.87
3.16	1.07	0.896	83.7	−5.64
3.25	1.16	0.814	70.2	−5.47
3.38	1.20	0.811	67.6	−5.69
3.46	1.07	0.557	52.1	−5.35
				−5.62±0.23

[a] Values were corrected for the naturally occurring evaporation. $[(UO_2)_2(OH)_2^{2+}]$ was defined as $([U(VI)]_{\mathrm{total}} - [UO_2^{2+}])$.

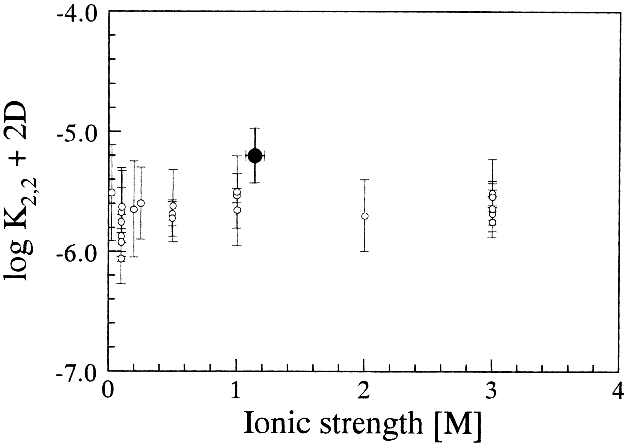

Fig. 4. Log $K_{2,2}+2D$ versus ionic strength. The solid circle shows $\log K_{2,2}+2D$ determined in the present study. The errors are 3σ. The open circles show those obtained by other methods under the condition of $NaClO_4$ medium [6–17,19–22]. The values of $\log K_{2,2}$ used correspond to those given in the original papers. Errors are 3σ or the appropriate errors estimated in the literature [5].

concentration of $(UO_2)_2(OH)_2^{2+}$. This might be attributed to the presence of a trace amount of other uranyl species that has less Raman activity.

If the concentration of $(UO_2)_2(OH)_2^{2+}$ can be directly determined in terms of I_{853}, $\log K_{2,2}$ can be obtained more accurately. From Eq. (4), the ratio of I_{872} and I_{853} is given,

$$\frac{I_{872}}{I_{853}}=\frac{T(\nu_M)\ \nu_M^4\alpha_M^2C_M}{T(\nu_D)\ \nu_D^4\alpha_D^2\ 2C_D} \tag{5}$$

where subscripts M and D represent UO_2^{2+} and $(UO_2)_2(OH)_2^{2+}$, respectively. $T(\nu_M)/T(\nu_D)$ should be unity, and $(\nu_D/\nu_M)^4$ can be calculated to be 0.996. For the same concentrations of uranium in UO_2^{2+} and $(UO_2)_2(OH)_2^{2+}$, the correlation between the Raman intensities can be given as,

$$I_{872}=0.448(\alpha_M/\alpha_D)^2\,I_{853} \tag{6}$$

If α_M/α_D is theoretically obtained, I_{853} can be converted into I_{872}, and hence the concentration of $(UO_2)_2(OH)_2^{2+}$ can be determined using the calibration line obtained for $[UO_2^{2+}]$. As a first-order approximation, we can regard that the bending angle of O=U=O bond is not influenced by the dimerization. On this assumption, i.e., $\alpha_M=\alpha_D$, the formation constant $\log K_{2,2}=-5.47\pm0.09$ is estimated. The uncertainty of the constant was estimated as 3σ. It is noteworthy that the error accompanied with this estimation is much smaller than that shown in Fig. 4.

The empirical equations, $\nu_1=21+0.89\nu_3$ and $r=1.08\kappa^{-1/3}+1.17$ [30,31], enable us to calculate the force constant κ and the axial length r of U=O bond from the Raman shifts 872 and 853 cm^{-1}: $\kappa_M=7.39$ mdyne/Å, $\kappa_D=7.07$ mdyne/Å, $r_M=1.72$ Å and $r_D=1.73$ Å. These data prove that the covalent character of U=O bond is different between UO_2^{2+} and $(UO_2)_2(OH)_2^{2+}$. These data suggest that the polarizability of U=O of $(UO_2)_2(OH)_2^{2+}$ is greater than that of UO_2^{2+}, thus $\alpha_D>\alpha_M$. Thus, the formation constant $\log K_{2,2}=-5.47$ obtained on assumption of $\alpha_M=\alpha_D$ requires correction to lower direction. The dependence of $\log K_{2,2}+2D$ on α_D/α_M as a variable apparent parameter is given in Fig. 5. It is clear that $\log K_{2,2}+2D$ decrease with the increase of α_D/α_M. Further theoretical consideration is needed to evaluate both α_M and α_D, but it is understood that α_D/α_M in the range 1.1–1.5 gives sufficient agreement with the literature values of $\log K_{2,2}+2D$.

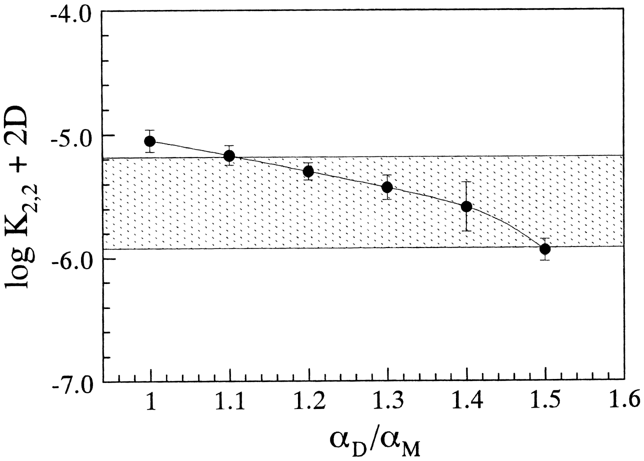

Fig. 5. Log $K_{2,2}+2D$ on polarizabilities. The errors are 3σ. The band shows literature data [13,19] for 1 M $NaClO_4$ medium.

4. Conclusions

Raman spectra of uranyl species in 10^{-2} M uranium(VI) perchlorate solutions were measured in pH range 2.88–3.46. The bands of ν_1 symmetrical stretching vibration were observed at 872 and 853 cm^{-1} which were attributed to UO_2^{2+} and $(UO_2)_2(OH)_2^{2+}$, respectively. Under the coexistence of $(UO_2)_2(OH)_2^{2+}$, absolute concentration of UO_2^{2+} was determined using the Raman intensity. The concentration of $(UO_2)_2(OH)_2^{2+}$ was estimated by different two assumptions; by which, the formation constant of $(UO_2)_2(OH)_2^{2+}$ was estimated to be $\log K_{2,2}=-5.62\pm0.23$ or -5.47 ± 0.09. A possibility was presented; if the polarizabilty can be theoretically obtained, the concentration of $(UO_2)_2(OH)_2^{2+}$ can also be determined using the Raman intensity, and hence $\log K_{2,2}$ can be accurately determined.

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References

[1] C.F. Baes Jr., R.F. Mesmer, in: The Hydrolysis of Cations, Wiley, New York, 1976.
[2] M.S. Caceci cian, G.R. Choppin, Radiochim. Acta 33 (1983) 207.
[3] L.M. Toth, G.M. Begun, J. Phys. Chem. 85 (1981) 547.
[4] C. Tsymbal, CEA-R-3476, C.E.A., Saclay, 1969.
[5] I. Grenthe, J. Fuger, R.J.M. Konings, R.J. Lemire, A.B. Muller, C. Nguyen-Trung, H. Wanner, in: Chemical Thermodynamics of Uranium, NEA-TDB, OECD, North-Holland, Amsterdam, 1992.
[6] K. Schlyter, Trans. R. Inst. Technol. Stockholm 195 (1962).
[7] H.S. Dunsmore, S. Hietanen, L.G. Sillén, Acta Chem. Scand. 17 (1963) 2644.
[8] S. Hietanen, B.R.L. Row, L.G. Sillén, Acta Chem. Scand. 17 (1963) 2735.
[9] M. Bartusek, L. Sommer, Z. Phys. Chem. 226 (1964) 309.
[10] M. Maeda, T. Amaya, H. Ohtaki, H. Kakihana, Bull. Chem Soc. Jpn. 45 (1972) 2464.
[11] L.H.J. Lajunen, S. Parhi, Finn. Chem. Lett. (1979) 143.
[12] L. Ciavatta, D. Ferri, M. Grimaldi, R. Palombari, F. Salvatore, J. Inorg. Nucl. Chem. 41 (1979) 1175.
[13] A. Vainiotalo, O. Mäkitie, Finn. Chem. Lett. (1981) 102.
[14] L. Maya, Inorg. Chem. 21 (1982) 2895.
[15] I. Grenthe, B. Lagerman, Acta Chem. Scand. 45 (1991) 122.
[16] P. Lubal, J. Havel, Chem. Papers 51 (1997) 213.
[17] R. Arneck, K. Schlyter, Acta Chem. Scand. 22 (1968) 1331.
[18] U. Kramer-Schnabel, H. Bischoff, R.H. Xi, G. Marx, Radiochim. Acta 56 (1992) 183.
[19] R.M. Rush, J.S. Johnson, J. Phys. Chem. 67 (1963) 821.
[20] G. Meinrath, Y. Kato, Z. Yoshida, J. Radioanal. Nucl. Chem. 174 (1993) 299.
[21] G. Meinrath, M. Schweinberger, Radiochim. Acta 75 (1996) 205.
[22] G. Meinrath, Radiochim. Acta 77 (1997) 221.
[23] M. Gál, P.L. Goggin, J. Mink, J. Mol. Struct. 114 (1984) 459.
[24] M.H. Brooker, C.-H. Huang, J. Sylwestrowicz, J. Inorg. Nucl. Chem. 42 (1980) 1431.
[25] M. Asano, J.A. Koningstein, Can. J. Chem. 60 (1982) 2207.
[26] A. Burneau, M. Tazi, G. Bouzat, Talanta 39 (1992) 743.
[27] P.G. Allen, J.J. Bucher, D.L. Clark, N.M. Edelstein, S.A. Ekberg, J.W. Gohdes, E.A. Hudson, N. Kaltsoyannis, W.W. Lukens, M.P. Neu, P.D. Palmer, T. Reich, D.K. Shuh, C.D. Tait, B.D. Zwick, Inorg. Chem. 34 (1995) 4797.
[28] J. Tang, A.C. Albrecht, in: H.A. Szymanski (Ed.), Developments in the Theories of Vibrational Raman Intensities, Raman Spectroscopy, Vol. 2, Plenum, New York, 1970.
[29] G. Gran, Analyst 77 (1952) 661.
[30] L.H. Jones, Spectrochim. Acta 11 (1959) 409.
[31] S.P. McGlynn, J.K. Smith, W.C. Neely, J. Phys. Chem. 35 (1961) 105.