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Studies on Metal Gluconic Acid Complexes

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ABSTRACT

The presence of organic complexants, such as gluconic acid, in an intermediate-level radioactive-waste (ILW) repository may have a detrimental effect on the sorption of radionuclides, by forming organic complexes in solution. In order to assess this, stability constants are required for the complexes formed with radionuclides at high pH. This study reports the stability constants for the reactions of metals with gluconic acid (Gl). The metals studied were Cd, Ce, Co, Eu, Fe(II), Fe(III), Ho and U(VI) at pH 13.3; and Ce, Co and U(VI) at pH 7. The constants were measured by the Schubert (ion-exchange) or solubility product methods. Stoichiometries of the complexes were also determined. At pH 7 each complex was of the form M_1Gl_1 , with $\log \beta$ values suggestive of salt formation. The M^{2+} $\log \beta$ values were between 13 and 20. For M^{3+} , there was less consistency. The M_2Gl_1 complexes (Ho & Ce) had values of 49.8 and 43.9, whereas the M_1Gl_1 type (Fe(III) & Eu) range from 24 to 38. The constants have enabled speciation calculations to be performed showing the effect of gluconic acid on the metal's solubility. Solubility is predicted to increase in the presence of gluconic acid from pH 9 to 13.5, suggesting that gluconic acid may have an impact on radionuclide behaviour. The largest increases in solubility are for Cd, Co, Eu, Ho and Ni, the smallest is with U(VI).

INTRODUCTION

The Nirex Phased Geological Repository Concept involves the use of a cementitious backfill to provide a chemical barrier to radionuclide migration from the near field [1]. The backfill chemically conditions the porewater to provide a high pH under which the solubility of many radionuclides is low. The backfill also provides a large surface area for radionuclide sorption. The presence of organic complexants may increase the solubility and decrease the sorption of radionuclides by forming soluble organic complexes [2], thereby increasing their mobility in the near field and alkaline-disturbed zones. Gluconic acid, $CO_2H(CHOH)_4CH_2OH$, is a polyhydroxylated carboxylic acid with potentially labile hydroxyl protons that can be displaced during metal complexation at high pH. Its possible presence in a cementitious ILW repository as a cement additive has been reported elsewhere [3]. Stability constants are required for the reactions of radionuclides with gluconic acid at high pH, in order to calculate the effect on radionuclide migration. To date the NiGl [4] constant has been reported. The work reported here adds constants for Cd, Ce, Co, Eu, Fe(II), Fe(III), Ho, U(IV) and U(VI) at pH 13.3; and Ce, Co and U(VI) at pH 7. Some of these elements will have radionuclides that will be present in the repository, and some are useful analogue or "model" elements for important radionuclides. All constants except for U(VI) at high pH were measured by the Schubert method [4]. The solubility product method [2] was used for measuring the constant for U(VI) at pH 13.3. The stoichiometries of the complexes, and the number of OH^- ions involved in the reactions, were determined using Bjerrum plots, conductometric titrations and spectrophotometric methods [4].

The constants were derived using the Schubert expression (equation 1) [5]:

$$\log\left(\frac{D_0}{D} - 1\right)A = \log \beta + z \log [Gl] \quad (1)$$

D describes the distribution of metal between resin $[M_{res}]$ and solution phase $[M_{sol}]$ in the presence of ligand, and D_0 in the absence of ligand [4]. The side-reaction coefficient (A term) is defined as discussed by Maes *et al.* [5] for complexes containing one cation ($n = 1$). However, if $n = 2$ a different expression is obtained (equation 3) [4]:

$$\beta = \frac{A^2 D_0}{[M_{sol}][Gl]^z[OH]^y D} \left(\frac{D_0}{D} - 1\right) \quad (2)$$

EXPERIMENTAL

Deionised water from a Barnstead NANOpure ultrapure system and AR reagents were used throughout. Radionuclides (^{109}Cd , ^{141}Ce , ^{57}Co , ^{59}Fe , ^{152}Eu , ^{233}U) were obtained from Amersham. BioRad 50W-X2 cation exchange resin was used in the measurements. pH was measured with an Orion 720A glass electrode. Spectrophotometric absorbances were measured using 1 cm silica cells in a Philips PU8730 UV/Vis spectrophotometer. A Jenway 4310 meter was used to measure conductivity. β -emitting isotopes were counted by liquid scintillation counting in Ecoscint using a Canberra Packard TRI-Carb 2750TR/LL. Γ -emitters were counted on a Packard Cobra II Auto-Gamma. Ho was measured by ICP-MS with PFA nebuliser on a VG PQ ExCell instrument.

Full details of all methods for the measurement of stoichiometry, except the precipitate absorption method, are given in Warwick *et al.* [4]. For the precipitate absorption method, solutions containing Co (0.01 mol dm^{-3}), excess NaGl (0.05 mol dm^{-3}), and varying amounts of NaOH to give OH⁻:Co mole ratios up to 4:1 were adjusted with 0.1 mol dm^{-3} KNO₃ to give constant ionic strength and equilibrated for 1 week under N₂, to prevent auto-oxidation. Absorbances were measured at 281 nm.

In the Schubert method, 5 measurements were made for each point at 25 °C in 20 cm³ polypropylene vials containing 1000 and 100 mg resin for di- and trivalent cations respectively. 15 cm³ aliquots of Na gluconate solution, pH adjusted with NaOH, were spiked with ^{107}Cd , ^{131}Ce , ^{57}Co , ^{152}Eu , ^{59}Fe or ^{233}U giving a metal concentration between 10^{-8} and $10^{-9} \text{ mol dm}^{-3}$, and equilibrated in a shaker bath for 72 hours. One set of vials was used to check for wall sorption. 1 cm³ of supernatant liquid was withdrawn, through a 0.45 μm filter, and the activity measured. Full details of the solubility product approach are given in Warwick *et al.* [6].

RESULTS

Bjerrum plots

Full details are given for Cd, and curves are shown for Cd, Ce and Co (Fig. 1). Data for all metals were interpreted similarly. Cadmium gluconate (Cd-Gl) appeared to form 3 complexes. Below pH 7.9, a colourless soluble complex was formed. Above 7.9, a white precipitate occurred, which partially dissolved above pH 11. There was no evidence for OH⁻ participation in the formation of the soluble complex, but there was evidence for a 1:2 (Cd:OH) ratio in the complex formed above pH 11, as shown by the inflexion in the plot.

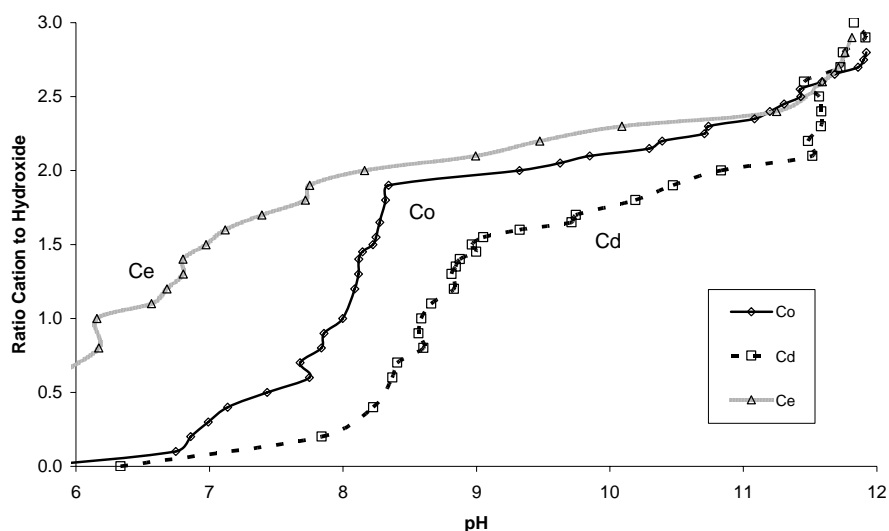


Figure 1. Bjerrum plots for Cd, Ce and Co.

Conductometric titrations

Plots for Co (Fig. 2) are described in detail. Plots for the other metals were similar. The conductance changes during the titration, as metal ions are added. A change in the gradient indicates the point at which the ions are in the same stoichiometric ratio to each other as in the complex. Metal ions added after this point are not complexed by gluconate. Each point is the mean of 3 measurements. Line B shows a Co:OH⁻ ratio of 1:2 in the complex (change in gradient at 10 cm³). Line C shows a Co:Gl ratio of 1:1 in the complex formed when there are 1.5 OH⁻ ions to every Co²⁺ present (significant gradient change from 1.40 to 1.57 at 10 cm³ with R² > 0.99).

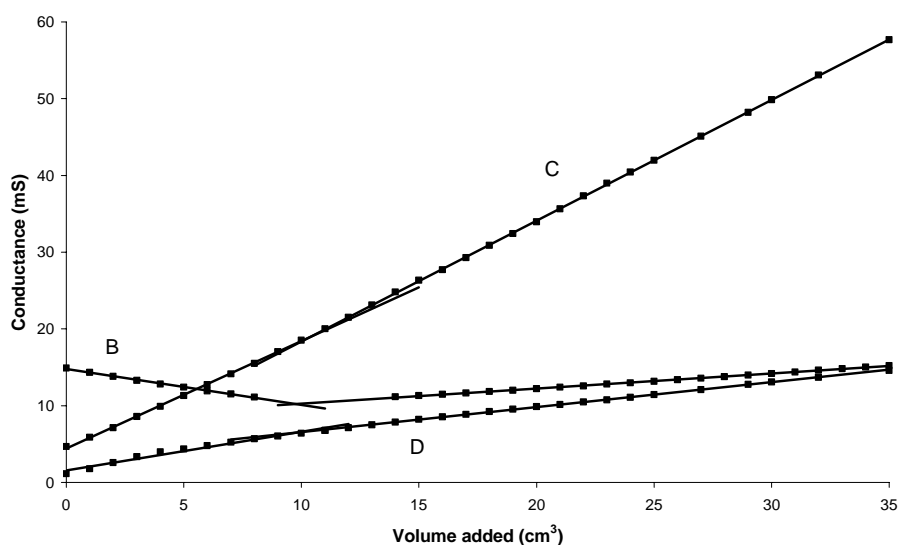


Figure 2. Conductometric titrations for cobalt gluconate.

Line D shows the formation of a complex with a Co:Gl ratio of 1:1, when there are two OH⁻ ions to every Co²⁺ ion (significant gradient change from 0.503 to 0.325 at 10 cm³ with R² > 0.99).

Spectrophotometric studies

Only Co showed an absorbance peak for the complex, sufficiently separate from the metal and its hydrolysis products to use spectrophotometric methods for analysis.

Precipitate absorbance method

Absorbances were measured at high pH. The minima showed the complex formed at high pH had a mole ratio of 1:2, and the one formed at intermediate pH a mole ratio of 2:3.

Measurement of stability constants by the Schubert method

Cadmium

The stability constants used to calculate the A term were $\log \beta$ (Cd(OH)₂) = 7.7, Cd(OH)₃⁻ = 10.3 and Cd(OH)₄²⁻ = 8.7 [7]. At pH 13.3, the stoichiometry of the complex was found to be CdGl(OH)₂. The derived value for the stability constant was $\log \beta = 14.2 \pm 0.2$. In other studies, Blomqvist *et al* [8] suggested the formation of Cd₂Gl₂²⁻ and Melton [9] postulated the precipitate as being Cd₃Gl₂(OH)₄.2H₂O. Pecsok [10] found Cd₂Gl₃(OH)₂⁴⁻ ($\log \beta = 10.2$) and Cd₂Gl(OH)₄⁻ ($\log \beta = 8.7$) between pH 13 and 14. None of these high pH species was found in this study, but the diversity of results suggests that this is a complicated system which requires more study. A summary of the stoichiometries and measured stability constants are shown in tables I to III, arranged by pH.

Table I. Summary of stoichiometric results from acidic and near-neutral pH range.

Metal	Solution	pH	Bjerrum plot	Conductometric titrations (M:Gl)	Schubert slope (M:Gl)	Species formed ^a	Log β
Cd	Colourless	< 7.9	No OH	1:1	1:1	CdGl	
Ce	Colourless	< 7.6	No OH	1:1	1:1	CeGl	2.5 ± 0.8
Co	Pink/Purple	< 7.3	No OH		1:1	CoGl	1.0 ± 0.4
Eu	Colourless	< 6.1	No OH	1:1	1:1	EuGl	
Ho	Pink	< 6.4	No OH	1:1		HoGl	
Fe(II)	Yellow	< 6.7	No OH	1:1	1:1	FeGl	
Fe(III)	Green	< 3.2	No OH	1:1	1:1	FeGl	
U(VI)	Yellow	6-13.5	No OH	1:1		UO ₂ Gl	6.3 ± 0.4

Table II. Summary of stoichiometric results from high pH range.

Metal	Solution	pH	Bjerrum plot	Conductometric titrations		Schubert slope	Species formed ^a	Log β
				M:OH	M:GI			
Cd	White ppt	> 11	1:2	1:2	1:1		CdGl(OH) ₂	14.2±0.2
Ce	White ppt	> 7.6	1:2	1:2	2:1		Ce ₂ Gl(OH) ₄	43.9±0.6
Co	Purple	> 11.8	1:2	1:2	1:1		CoGl(OH) ₂	13.1±0.8
Eu	Colourless	> 7.7	1:4	1:4	1:1	1:1	EuGl(OH) ₄	24.3±0.3
Ho	Colourless	> 9	1:3	1:3	2:1		Ho ₂ Gl(OH) ₆	49.8±0.4
Fe(II)	Green	> 7.4	1:4	1:4	1:1		FeGl(OH) ₄	17.8±0.9
Fe(III)	Green	> 3.9	1:3	1:3	1:1	1:1	FeGl(OH) ₃	37.9±1.2
U(VI)	Yellow	6-13.5	No OH		1:1		UO ₂ Gl	19.9±2

a Charges omitted from species formed

Table III. Summary of stoichiometric results from intermediate pH range.

Metal	Description	pH	Precipitate absorbance method	Bjerrum plot	Conductometric titrations		Schubert slope	Species formed
					M:OH	M:OH		
Ratio			M:OH	M:OH	M:GI	M:OH	M:GI	
Cd	White ppt	7.9-11		1:2	1:1	1:2		CdGl(OH) ₂
Co	Pink ppt	7.3-11.8	2:3		1:1			Co ₂ Gl ₂ (OH)
Eu	White ppt	6.1-7.7		No OH				
Ho	White ppt	6.4-9		1:2	2:1			
Fe ²⁺	Green ppt	6.7-7.4		No OH				
Fe ³⁺	Green-Brown ppt	3.2-3.9		1:1	1:1		1:1	

Cerium

At pH 7, the complex was determined to be 1:1, i.e. CeGl. The derived value for the stability constant was $\log \beta = 2.5 \pm 0.8$. It was assumed that the significant species were Ce³⁺ and CeOH²⁺, for which $\log \beta = 4.9$ [7]. The Schubert plot for this complex also indicated a 1:1 Ce:Gl ratio. $\log \beta = 2.36$ was obtained for CeGl by Marcu *et al.* [11]. At pH 13.3, the complex was determined to be Ce₂Gl(OH)₄, which gave a value of $\log \beta = 43.9 \pm 0.6$. Calculation of the A term assumed that the significant species were Ce³⁺ and Ce(OH)⁴⁻ ($\log \beta = 16.4$ [12]).

Cobalt

At pH 7, the stoichiometry of the complex was determined to be 1:1, i.e. CoGl, with a stability constant of $\log \beta = 1.0 \pm 0.4$. The A term was calculated on the assumption that the only significant species present was Co^{2+} . The Schubert plot also indicated that the M:L ratio was 1:1. At pH 13.3, the complex was found to be $\text{CoGl}(\text{OH})_2$. The derived value was $\log \beta = 13.1 \pm 0.8$. It was assumed that the significant species present was HCoO_2^- . The constant used was ($\log \beta = 9.20$ [12]). Pickering *et al.* have shown the presence of an anionic complex at high pH [13] with between 1.5 and 2 OH^- ions per Co involved in the complex. Various authors [14] [15] [16] also found a 1:1 Co:Gl stoichiometry. Ashton *et al.* postulated that the insoluble species formed at pH 7.5 were $\text{Co}_2\text{Gl}(\text{OH})_3 \cdot x\text{H}_2\text{O}$ and $\text{Co}_3\text{Gl}_2(\text{OH})_2 \cdot 2\text{H}_2\text{O}$. Above pH 9.5 there was an anionic species which was subject to rapid auto-oxidation.

Europium

At pH 13.3, the complex was found to be $\text{EuGl}(\text{OH})_4$. The derived value was $\log \beta = 24.3 \pm 0.3$, assuming that the significant species present was $\text{Eu}(\text{OH})_4^-$ ($\log \beta = 18.52$ [12]). The Schubert plot also showed an Eu:Gl ratio of 1:1.

Holmium

At pH 13.3, the stoichiometry was determined to be $\text{Ho}_2\text{Gl}(\text{OH})_6$. The derived value was $\log \beta = 49.8 \pm 0.4$ assuming that the significant species present was $\text{Ho}(\text{OH})_4^-$ ($\log \beta = 17.2$ [12]).

Iron(II)

At pH 13.3, the complex was determined to be $\text{FeGl}(\text{OH})_4$, which gave a $\log \beta$ value of 17.8 ± 0.9 . The A term was calculated on the assumption that the significant hydrolysis species present were $\text{Fe}(\text{OH})_3^-$ ($\log \beta = 13$) and $\text{Fe}(\text{OH})_4^{2-}$ ($\log \beta = 10$) [7].

Iron(III)

At pH 13.3, the complex was determined to be $\text{FeGl}(\text{OH})_3$, with $\log \beta = 37.9 \pm 1.2$. The A term was calculated assuming the only significant species present was $\text{Fe}(\text{OH})_4^-$ ($\log \beta = 34.4$ [7]). The Schubert plot showed an Fe(III):GL ratio of 1:1. In other studies of this system, $\text{FeGl}(\text{OH})_2^-$ and $\text{FeGl}(\text{OH})_4^{2-}$ ($\log \beta = 37.2$) were found at high pH [17], as well as $\text{Fe}_2\text{Gl}_2(\text{OH})^-$, $\text{Fe}_2\text{Gl}_2(\text{OH})_3^-$, FeGl^- and $\text{FeGl}(\text{OH})_2^-$ [18]. Zay *et al.* [19] observed FeGl ($\log \beta = 9.63$) and Fe_2Gl ($\log \beta = 9.63$). Kaminski [20] measured the constants for $\text{FeGl}(\text{OH})_2^-$ ($\log \beta = 5.7$), and also observed $\text{FeGl}(\text{OH})_2^{2-}$ and $\text{FeGl}(\text{OH})_3^{3-}$. Nagy *et al.* [21] found the species $\text{Fe}_2\text{Gl}_2(\text{OH})_4(\text{H}_2\text{O})_2\text{Na}_2$ at pH 10 to 12.

Uranium (VI)

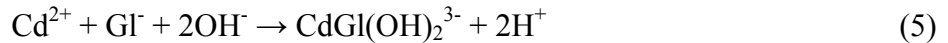
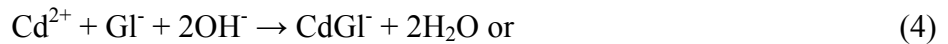
At near-neutral pH the complex was determined to be UO_2Gl . The measured stability constant was $\log \beta = 6.3 \pm 0.4$. The A term was calculated assuming the significant species present were; UO_2OH^+ ($\log \beta = 7.7$ [7] and $\text{UO}_2(\text{OH})_2$ (17.25 [12]). Sawyer [22] measured the constant for the complex $\text{UO}_2\text{Gl}(\text{OH})_2$ ($\log \beta = 6.25$).

The solubility product method for measuring stability constants

The solubility of Na₂U₂O₇(am) at pH 13.3 in Gl-free samples was measured to obtain a value for the solubility product. A value of $\log K_{sp} = -57.5$ was obtained. The A term was calculated assuming that the significant species were UO₂(OH)₄²⁻ and UO₂(OH)₃⁻ ($\log \beta = 22.2$ for both [7]). Determination of a stability constant, using the method of Warwick *et al.* [6] gave $\log \beta = 19.9 \pm 2$ for U(VI)-Gl.

CONCLUSIONS

Each complex formed at near-neutral pH was of the form M₁Gl₁, with $\log \beta$ values in a range suggestive of salt formation, except the oxycation UO₂²⁺ for which $\log \beta = 6.3$. In all cases, except U(VI), OH⁻ ions have been involved in the formation of complexes at high pH. It is not clear whether the OH group was coordinated to the cation in addition to the gluconate, or if chelate complexes were formed with the consequent elimination of hydrogen ions from the ligand, e.g. the equation for the formation of the Cd complex at high pH could be (equations 4 and 5):



More work is required to determine which of these possibilities is applicable to each complex [6]. However, for the purposes of consistency in this paper the stoichiometry of the complexes has been written as though the OH groups are co-ordinated to the metal. At pH 13.3 the divalent cation constants were in the region $\log \beta = 13$ to 20, with 2 OH⁻ ions being involved in their formation, apart, again, from U(VI). For the trivalent cations, there appears to be less consistency in the results. The M₂L complexes (Ce and Ho) have $\log \beta$ values of 43.9 and 49.8, whereas the ML type range from 24.3 (Eu) to 37.9 (Fe(III)). This may be due to the different number of OH⁻ ions involved in their formation. These constants have enabled speciation calculations to be performed using the speciation programme JCHESS [12], showing the effect of gluconate on the solubility of the metals. Of particular interest is the effect in the near field and the alkaline-disturbed-zone. To show this a solubility enhancement factor was determined; defined as:

$$\text{Enhancement Factor} = \frac{\text{metal solubility in presence of gluconic acid}}{\text{metal solubility in absence of gluconic acid}} \quad (6)$$

Figure 3 shows the variation of enhancement factor against pH for all di- and trivalent cations for which high pH $\log \beta$ values are known. For most radionuclides used in this study solubility increases between pH 9 and 13.5, indicating that gluconate may have a major impact on the behaviour of radionuclides in the near field of a cementitious repository. The largest increases, between 10³ and 10⁶, are for Cd, Co, Eu, Ho and Ni. The increase for most metals falls at higher pH as hydrolysis products become more significant. The smallest effect is on U(VI). The data determined in this study will help to develop the understanding of the effects of gluconic acid and similar complexants on the migration of radionuclides.

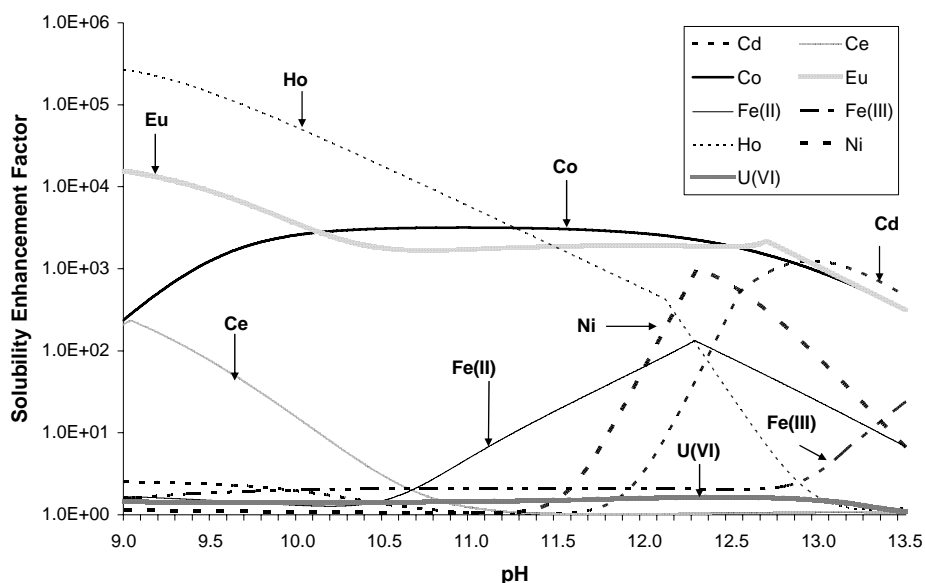


Figure 3. Variation of solubility enhancement factor with pH

REFERENCES

- [1] United Kingdom Nirex Ltd, *Nirex Report N/074*, (2003)
- [2] X. Bourbon and P. Toulhoat, *Radiochim. Acta*, **74**, 319 (1996)
- [3] J. Tits, E. Wieland, M. H. Bradbury and J-P. Dobler, *J. Conf. Abst.* **5(2)**, 1009 (2000)
- [4] P. Warwick, N. Evans, A. Hall, and S. Vines, *Radiochim. Acta* **91**, 233 (2003)
- [5] A. Maes, J. De Brabandere and A. Cremers, *Radiochim. Acta* **44/45**, 51 (1988)
- [6] P. Warwick, N. Evans, A. Hall, and S. Vines, *Radiochim. Acta* **92**, 897 (2004)
- [7] A. Martell and R. Smith, *Critical Stability Constants, Vol 3*, Plenum, New York, (1989)
- [8] K. Blomqvist and E. Still, *Anal. Chem.*, **57**, 749 (1985)
- [9] G. A. Melson and W. F. Pickering, *Aust. J. Chem.*, **21**, 2889, (1968)
- [10] R. L. Pecsok, *J. Am. Chem. Soc.*, **77**, 1489 (1955)
- [11] G. Marcu and G. Murgu, *Rev. Roum. Chim.*, **12**, 957 (1967)
- [12] J. Van der Lee, École des Mines de Paris, Fontainebleau, France (2002).
- [13] W. F. Pickering and J. Miller, *J. Proc. Roy. Soc. N.S. Wales*, **92**, 73 (1958)
- [14] F. B. Martinez and G. B. Miguez, *Z. Anal. Chem.*, **253**, 353 (1971)
- [15] J. F. Ashton and W. F. Pickering, *Aust. J. Chem.*, **23**, 1367 (1970)
- [16] L. I. Katzin and E. Gulyas, *J. Am. Chem. Soc.*, **92:5**, 1211 (1970)
- [17] R. L. Pecsok and J. Sandera, *J. Am. Chem. Soc.*, **77**, 1489 (1955)
- [18] J. Gonzalez-Velasco, J. Ortega and J. Sancho, *J. Inorg. Nucl. Chem.*, **38**, 889 (1976)
- [19] I. Zay, F. Gaizer and K. Burger, *Inorg. Chim. Acta*, **80**, L9 (1983)
- [20] W. Kaminski, *Roczniki Chemii Ann. Soc. Chim. Polonorum*, **46**, 339, (1972)
- [21] L. Nagy, K. Burger, J. Kürti, M. A. Mostafa, and I. Kiricsi, *Inorg. Chim. Acta*, 124 (1986)
- [22] D. T. Sawyer and R. J. Kula, *Inorg. Chem.*, **1(2)**, 303 (1962)