

This article was downloaded by: [Renmin University of China]

On: 13 October 2013, At: 10:30

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gcoo20>

Synergistic extraction of copper(II) from sulfate medium with capric acid and tri-n-octylphosphine oxide in chloroform

F. Adjel^a & D. Barkat^a

^a Department of Industrial Chemistry, Faculty of Science and Technology, Biskra University, 07000 Biskra, Algeria

Published online: 24 Jan 2011.

To cite this article: F. Adjel & D. Barkat (2011) Synergistic extraction of copper(II) from sulfate medium with capric acid and tri-n-octylphosphine oxide in chloroform, *Journal of Coordination Chemistry*, 64:4, 574-582, DOI: [10.1080/00958972.2010.551400](https://doi.org/10.1080/00958972.2010.551400)

To link to this article: <http://dx.doi.org/10.1080/00958972.2010.551400>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <http://www.tandfonline.com/page/terms-and-conditions>

Synergistic extraction of copper(II) from sulfate medium with capric acid and tri-*n*-octylphosphine oxide in chloroform

F. ADJEL and D. BARKAT*

Department of Industrial Chemistry, Faculty of Science and Technology,
Biskra University, 07000 Biskra, Algeria

(Received 4 August 2010; in final form 16 November 2010)

The synergistic solvent extraction of copper(II) from 0.33 mol dm^{-3} Na_2SO_4 aqueous solutions with capric acid (HL) in the absence and presence of tri-*n*-octylphosphine oxide (TOPO) in chloroform at 25°C has been studied. The extracted species when capric acid was used alone is $\text{CuL}_2(\text{HL})_2$. In the presence of TOPO, the extracted complex is $\text{CuL}_2(\text{HL})_2(\text{TOPO})$. The TOPO–HL interaction strongly influences the synergistic extraction efficiency. The extraction constants were calculated.

Keywords: Solvent extraction; Copper(II); Capric acid; TOPO; Synergism

1. Introduction

Liquid–liquid extraction is one of the most useful techniques for selective removal and recovery of metal ions from aqueous solutions, applied in purification processes in numerous chemical and metallurgical industries [1–3]. Carboxylic acids have been studied as extractants for numerous metals and have been shown to exhibit good extraction and separation efficiency.

Copper(II) is extracted as a dimer $\text{Cu}_2\text{L}_4(\text{HL})_2$ in non-solvating solvents [4–14]. Because of the extensive solvation by alcohols and ketones, the monomeric and dimeric species are in equilibrium in these solvents [15, 16]. Synergism in solvent extraction systems has been investigated by many authors [17–24]. Mareva *et al.* [25] have successfully utilized a salicylic acid and tri-*n*-octylphosphine oxide (TOPO) mixture for the separation of uranium from rare earth, thorium, zirconium, and iron. Hirose *et al.* [26, 27] extracted copper(II) and zinc(II) with capric acid in benzene in the presence of pyridine (Py). The synergistic effect is interpreted by the formation of the following mixed ligand complexes in benzene: $\text{CuL}_2(\text{HL})_3\text{Py}$, $\text{CuL}_2(\text{HL})_2\text{Py}_2$, and $\text{Cu}_2\text{L}_4(\text{HL})\text{Py}$ for copper(II) and $\text{ZnL}_2(\text{HL})\text{Py}$, $\text{ZnL}_2(\text{HL})_3\text{Py}$ for zinc(II).

*Corresponding author. Email: barkat_djamel@yahoo.fr

In this study, the study of the synergistic extraction of copper(II) from sulfate medium with capric acid in the absence and presence of TOPO in chloroform was carried out. The object of this study was the determination of the stoichiometries of the extracted complexes and their extraction constants.

2. Experimental

2.1. Reagents

Capric acid (98%, Fluka) and TOPO ($\geq 97\%$, Fluka) were used as purchased. Chloroform was pre-equilibrated with aqueous solution which did not contain copper(II). The ionic strength of the aqueous medium was assumed to be unity ($[\text{Na}_2\text{SO}_4] = 0.33 \text{ mol dm}^{-3}$). The initial concentration of copper is $1.57 \times 10^{-3} \text{ mol dm}^{-3}$ (100 ppm).

2.2. Extraction and analytical procedures

An aqueous copper solution (40 mL , $1.57 \times 10^{-3} \text{ mol dm}^{-3}$) was placed in a thermostated vessel at 25°C . To the solution, an equal volume of chloroform solution containing 5×10^{-3} to $4 \times 10^{-2} \text{ mol dm}^{-3}$ of capric acid or a mixture of $5 \times 10^{-3} \text{ mol dm}^{-3}$ of capric acid and 1.25×10^{-3} to $4 \times 10^{-2} \text{ mol dm}^{-3}$ of TOPO was added and shaken for 15 min. This time was sufficient since the equilibrium was reached rapidly; after equilibrium, both phases were allowed to stand for more than 30 min for a complete phase separation. The pH of the solution was adjusted to between 4.8 and 7 by adding a few drops of 0.1 mol dm^{-3} NaOH. The metal ion concentrations were determined in aqueous phase photometrically at 810 nm using a Philips UV-Vis SP6-36. The metal ion concentrations in the organic phase were calculated from the difference between the metal ion concentrations in the aqueous phase before and after extraction.

3. Results and discussion

3.1. General treatment of extraction equilibrium of copper(II) with capric acid

Capric acid exists as a dimer in solvents of low polarity such as toluene, benzene, chlorobenzene, dichloroethane, carbon tetrachloride, and alkanes [14]. The extraction of metal by a dimerized capric acid, $(\text{HL})_2$, in chloroform can be represented by the general equation:



where the subscripts aq and org correspond to the aqueous and organic phases, respectively, and j , degree of polymerization of the complex; $(\text{HL})_2$, extractant in dimeric form; n , cationic charge; and m , number of monomeric acids contained

in the complex. The extraction constant can be written as the following expression:

$$K_{\text{ex}} = \frac{[(\text{ML}_n(\text{HL})_m)_j]_{\text{org}} [\text{H}^+]^{nj}}{[\text{M}^{n+}]_{\text{aq}}^j [(\text{HL})_2]_{\text{org}}^{j(n+m)/2}} \quad (2)$$

The distribution coefficient D of the metal between the organic and aqueous phases may be expressed as follows:

$$\begin{aligned} D &= \frac{C_{\text{M}_{\text{org}}}}{C_{\text{M}_{\text{aq}}}} = \sum_j \sum_m j [\text{ML}_n(\text{HL})_m]_{\text{org}} / [\text{Cu}^{2+}] \alpha_{\text{M}} \\ &= \sum_j \sum_m \left(j K_{\text{ex}} [\text{M}^{n+}]_{\text{aq}}^{(j-1)} \alpha_{\text{M}}^{-1} [(\text{HL})_2]_{\text{org}}^{j(n+m)/2} [\text{H}^+]^{-nj} \right) \end{aligned} \quad (3)$$

where $C_{\text{M}_{\text{org}}}$, $C_{\text{M}_{\text{aq}}}$, and α_{M} are the total concentrations of the metal in the organic and aqueous phases, and the side reaction coefficient allowing for metal complexation in the aqueous phase, respectively. If only $(\text{ML}_n(\text{HL})_m)_j$ is responsible for the extraction system, equation (4) is derived from equation (3) as follows:

$$\log D = (j-1) \log [\text{M}^{n+}]_{\text{aq}} + j \frac{n+m}{2} \log [(\text{HL})_2]_{\text{org}} + (nj) \text{pH} - \log \alpha_{\text{Cu}} + \log j + \log K_{\text{ex}} \quad (4)$$

With a predetermined capric acid concentration in the organic phase, the relationship

$$\log D + \log [\text{M}^{n+}]_{\text{aq}} = f(\log [\text{M}^{n+}]_{\text{aq}} + n\text{pH}) \quad (5)$$

should give a straight line of slope j . On the other hand, at a predetermined metal concentration in the aqueous phase, the relationship

$$\log D - (j-1) \log [\text{M}^{n+}]_{\text{aq}} - (nj) \text{pH} = f(\log [(\text{HL})_2]_{\text{org}}) \quad (6)$$

should yield a straight line of slope $\frac{j+n}{2}$ which intersects the axis at

$$(\log K_{\text{ex}} + \log \alpha_{\text{M}} + \log j)$$

Equation (4) shows that the function $\log D = f(\text{pH})$ at a constant $[(\text{HL})_2]_{\text{org}}$ should yield a straight line with a slope of n only when j and α_{M} are equal to unity.

3.2. Extraction of copper(II) with capric acid alone

The stoichiometries of the extracted species were determined by analyzing the experimental data. Conventional slope analysis was used.

The experimental results are arranged according to equation (4). Figure 1 shows the results obtained for extraction of copper(II) with solutions of various capric acid concentrations. The degree of extraction of Cu(II) increases with increase in pH and capric acid concentration. Plots of $\log D$ versus pH for various concentration of capric acid are straight lines with slope equal to 2 ($n=2$). This suggests full neutralization of copper(II) valence leading to the release of two protons as given by equation (7). The data in figure 1 also reveal no dependence of copper distribution upon the aqueous

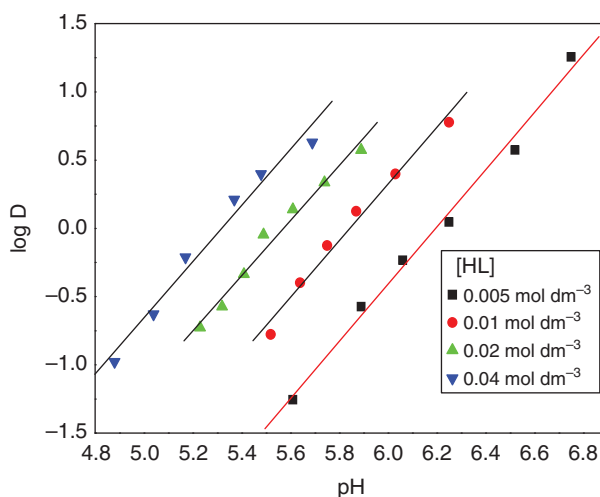
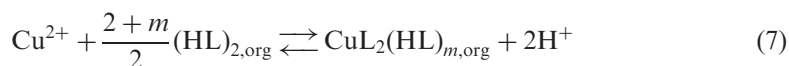


Figure 1. Effect of pH on the extraction of copper(II) with capric acid in chloroform.

copper concentration, thereby confirming the monomeric nature of the extracted complex ($j=1$, $\alpha_{\text{Cu}}=1$).



Under these experimental conditions, the concentration of metal in organic phase is negligible compared to the concentration of extractant; therefore, concentration of dimer was calculated as $[(\text{HL})_2] = [\text{HL}]/2$.

According to equation (4), the number of capric acid molecules involved in the monomeric species can be determined from the slope of plots of $(\log D)$ against $\log[(\text{HL})_2]_{\text{org}}$ at constant pH. Plots of $\log D$ versus $\log[(\text{HL})_2]_{\text{org}}$ at constant pH were also linear with a slope of $(2+m)/2=2$, i.e., $m=2$, as shown in figure 2. This suggests that two molecules of dimeric capric acid take part in the extraction of one ion of copper. This means that only $\text{CuL}_2(\text{HL})_2$ is extracted into chloroform. The same type of extracted species was reported for the extraction of copper(II) with cyclopentyl acetic acid [28] and α -bromostearic acid [29] in benzene.

It is likely that a carboxylic acid dimer is bidentate in the monomeric extracted species as in the extraction of copper with di-(2-ethylhexyl)-phosphoric acid [30]. The complex formed has a structure of an adduct, in which particular places in the coordination sphere of copper are occupied by four molecules of the extractant. At the same time, two of them, as acid anions, form polarized covalent bonds, and the other two, as non-dissociated molecules coordinating *via* the carbonyl oxygen (figure 3).

The logarithmic value of K_{ex} of copper(II) can, therefore, be calculated for each experimental point ($\log K_{\text{ex}} = -7.53$).

For the logarithmic extraction equilibrium constant of copper(II) with capric acid, values of -11.61 and -11.36 have been reported for carbon tetrachloride–aqueous perchlorate solution system and benzene–aqueous perchlorate solution system [31], respectively.

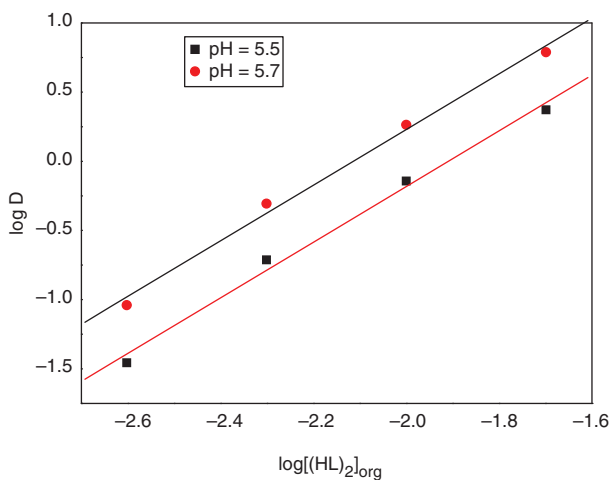


Figure 2. Determination of the number of capric acids involved in the extracted complex.

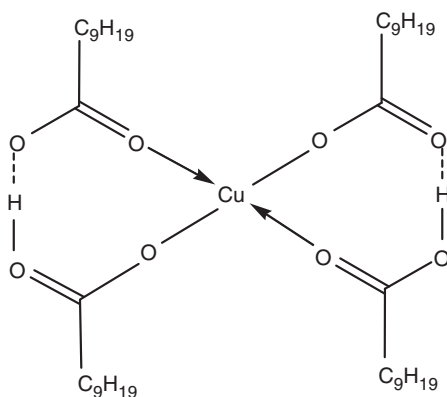


Figure 3. Structure of the complex of copper ion with capric acid.

The experimental conditions in this study, chloroform–aqueous sulfate solution system, is different from those reported above and dimeric species are responsible for the extraction in higher concentration of capric acid in the organic phase.

3.3. Synergistic extraction of copper(II) with capric acid and TOPO

In the synergic extraction of copper(II) with a mixture of capric acid (HL) and TOPO, the extraction equilibrium and the synergistic extraction constant, K_{ex} , can be expressed by



$$K_{\text{ex}} = \frac{[\text{CuL}_2(\text{HL})_2(\text{TOPO})_{s,\text{org}}][\text{H}^+]^2}{[\text{Cu}^{2+}]_{\text{aq}}[(\text{HL})_2]^2[\text{TOPO}]^s} \quad (9)$$

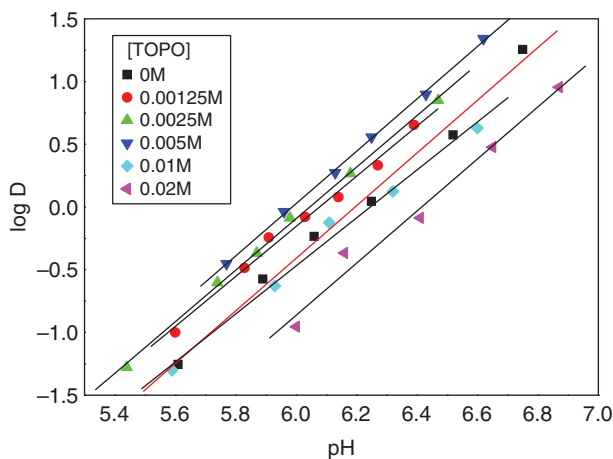


Figure 4. Synergistic effect of TOPO in the extraction of copper with capric acid in chloroform.

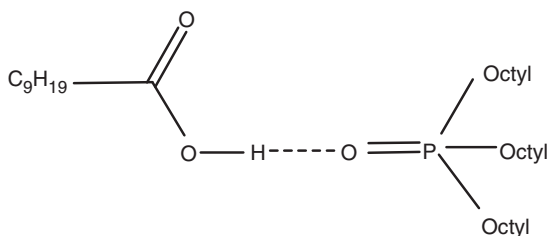


Figure 5. Structure of the associated molecule of capric acid with TOPO.

Equation (9) shows that plots of $\log D$ against pH at constant $[(HL)_2]$ and constant $[TOPO]$ should consist of straight lines with slope 2. Typical plots for the extraction of copper(II) from 0.33 mol dm^{-3} sodium sulfate solution by the mixture of capric acid and TOPO in chloroform are shown in figure 4. The slopes obtained (1.85–2.00) confirm the expected second-order dependence of metal distribution upon pH.

A different situation is observed for the synergistic extraction of copper(II). As illustrated in figure 4, the addition of TOPO causes an enhanced extraction of copper(II) for TOPO concentration $\leq 0.005 \text{ mol dm}^{-3}$, showing that TOPO gives a synergistic effect for these concentrations. Further increase in the amount of TOPO in the organic phase results in a decrease in the extraction of copper(II).

The antagonistic effect may be explained in terms of decrease of the effective concentration of capric acid due to association between TOPO and capric acid in the organic phase; formation of such associated molecules is possible because the oxygen from TOPO is able to form hydrogen bonds with capric acid (figure 5).

The number of TOPO molecules involved in the extracted species can be determined from the slope of the graph $\log D$ against $\log[TOPO]_{\text{org}}$ at constant pH and $[(HL)_2]$. As figure 6 shows, the plot yielded a straight line with a slope of unity. Thus, the number of TOPO involved in the extracted complex is one, suggesting a complex extraction of type $\text{CuL}_2(\text{HL})_2(\text{TOPO})_{\text{org}}$.

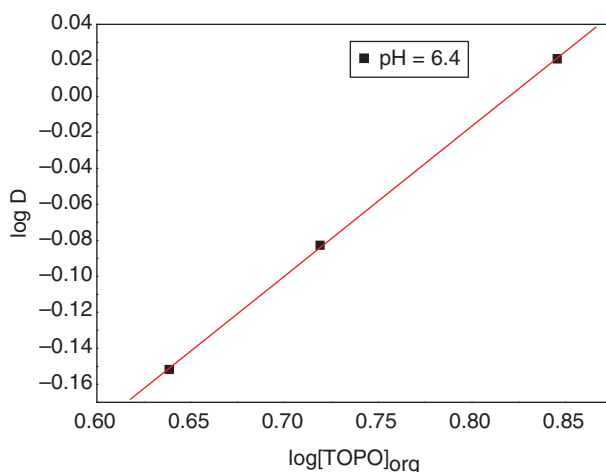


Figure 6. Determination of the number of TOPO's involved in the extracted species.

From the above results, the equation for the synergistic extraction equilibrium of copper(II) is considered to be



The synergistic extraction equilibrium was obtained from figure 5 as $\log K_{\text{ex,syn}} = -4.63$.

According to the structural study [32], copper(II) carboxylates are characterized by distorted octahedral structure involving two bidentate dimeric capric acid (HL_2^-). Thus, copper(II) caprate in chloroform is considered to have a similar structure with two water molecules at an axial position. The formation of $\text{CuL}_2(\text{HL})_2(\text{TOPO})_{\text{org}}$ is due to the replacement by TOPO of one water molecule at an axial position of the monomeric copper(II) caprate (figure 7). Hirose *et al.* [26] reported the incorporation of one or two molecules of pyridine in the copper(II) species extracted in the pyridine–capric acid system. Also, in a study on the extraction of copper(II) with butyric and α -bromobutyric acids in the presence of pyridine or quinoline, the extracted species was found to contain two molecules of the amine per copper atom [33].

Figure 8 shows some results that allow a comparison of the results obtained in this study with those reported with respect to extraction by N-(2-hydroxybenzylidene)aniline (N2HBA) [34] and di(2-ethylhexyl) phosphoric acid (D2EHPA) [1]. For an equal concentration of the extractants, the extractability of D2EHPA was found to be more efficacious than N2HBA and than capric acid with respect to the extraction of copper(II) from sulfate solutions.

It is well known [35] that the extraction constant for an acidic extraction is a function of the partition constant and $\text{p}K_a$ of the extractant, the overall formation constant of the extractible complex, and its partition constant. Since $\text{p}K_a(\text{D2EHPA}) = 1.8$ [36], $\text{p}K_a(\text{capric acid}) = 4.9$ [37], and $\text{p}K_a(\text{N2HBA}) = 9.5$ [38], this factor favors a better extraction with N2HBA than with capric acid and D2EHPA. In the case of capric acid, which is a better extractant (figure 8), the extraction of copper(II) is not improved as

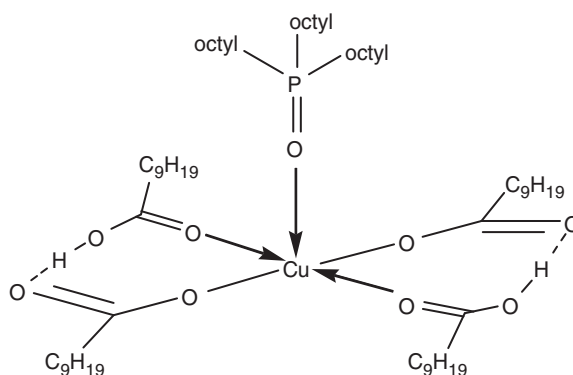


Figure 7. Structure of the complex of copper ion with capric acid and TOPO.

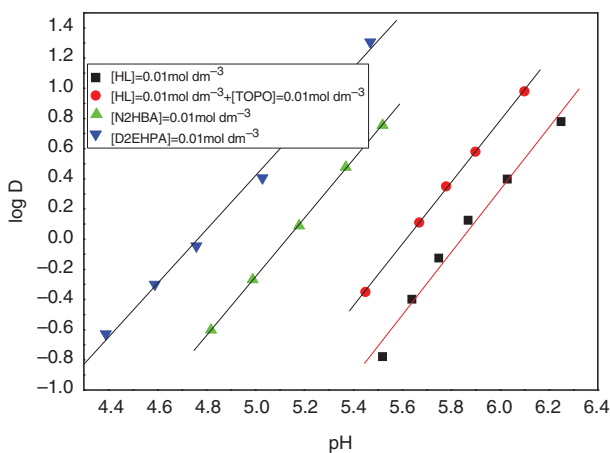


Figure 8. Extraction of copper(II) with capric acid (HL) in the absence and presence of TOPO, compared with the extraction by D2EHPA [1] and N2HBA [32].

with N2HBA, probably due to the dimerization of capric acid in the organic phase. However, the addition of TOPO in the organic phase has the advantage to improve the extraction of copper(II) by capric acid (figure 8).

4. Conclusion

The solvent extraction of copper(II) from sulfate medium with capric acid (HL) in the absence and presence of TOPO in chloroform was studied and the following information was obtained.

- In the absence of the synergic agent TOPO, the extracted species is $\text{CuL}_2(\text{HL})_2$. This agrees with the published results for the extraction of copper(II) with cyclopentylacetic acid [28] and α -bromostearic acid [29] in benzene.

- In the presence of TOPO, the extraction is improved for TOPO concentration $\leq 0.005 \text{ mol dm}^{-3}$. It was found that one molecule of synergistic agent is adducted to the extracted species of the corresponding non-synergistic system, which is in general agreement with the literature [26].
- The TOPO–HL interaction has been taken into account to explain the antagonism effect.
- Comparison between capric acid in the absence and presence of TOPO and the reported extractants D2EHPA [1] and N2HBA [34] revealed that the extraction of copper(II) varies according to the sequence: D2EHPA > N2HBA > capric acid + TOPO > capric acid.

References

- [1] F. Ghebghoub, D. Barkat. *J. Coord. Chem.*, **62**, 1449 (2009).
- [2] D. Barkat, Z. Derriche, A. Tyeb. *Turk. J. Chem.*, **25**, 381 (2001).
- [3] D. Barkat, M. Kameche. *Phys. Chem. Liq.*, **45**, 289 (2007).
- [4] A. Bartecki, W. Apostoluk. *J. Inorg. Nucl. Chem.*, **40**, 109 (1978).
- [5] A.W. Fletcher, D.S. Flett. *J. Appl. Chem.*, **14**, 250 (1964).
- [6] D.P. Graddon. *Nature (London)*, **186**, 715 (1960).
- [7] E. Grzegorzolka, Z. Chodowska, G. Maciejko. *Chem. Anal. (Warsaw)*, **24**, 1019 (1979).
- [8] W.J. Haffenden, G.J. Lawson. *J. Inorg. Nucl. Chem.*, **29**, 1133 (1967).
- [9] K. Inoue, H. Amano, I. Nakamori. *Hydrometallurgy*, **8**, 309 (1982).
- [10] K. Inoue, H. Amano, Y. Yayama, I. Nakamori. *J. Chem. Eng. Jpn.*, **13**, 281 (1980).
- [11] M.J. Jaycock, A.D. Jones, C. Robinson. *J. Inorg. Nucl. Chem.*, **36**, 887 (1974).
- [12] I. Kojima, M. Uchida, M. Tanaka. *J. Inorg. Nucl. Chem.*, **32**, 1333 (1970).
- [13] M. Tanaka, T. Niinomi. *J. Inorg. Nucl. Chem.*, **27**, 431 (1965).
- [14] H. Yamada, M. Tanaka. *J. Inorg. Nucl. Chem.*, **38**, 1501 (1976).
- [15] H. Yamada, R. Kitazaki, I. Kakimi. *Bull. Chem. Soc. Jpn.*, **56**, 3302 (1983).
- [16] H. Yamada, K. Takahashi, Y. Fujii, M. Mizuta. *Bull. Chem. Soc. Jpn.*, **57**, 2847 (1984).
- [17] N.P. Rudenko, N.V. Avilina, I.N. Kremenskaya. *Zh. Neorg. Khim.*, **11**, 947 (1966).
- [18] N.P. Rudenko, V.M. Dziomko, I.N. Kremenskaya. *Radiokhimiya*, **7**, 492 (1965).
- [19] D.S. Flett. *Trans. Natl. Res. Inst. Met. Jpn.*, **9**, 215 (1967).
- [20] D.S. Flett, S. Titmuss. *J. Inorg. Nucl. Chem.*, **31**, 2612 (1969).
- [21] D.S. Flett, D.W. West. *J. Inorg. Nucl. Chem.*, **29**, 1365 (1967).
- [22] J. Hála, L. Sotulářová. *J. Inorg. Nucl. Chem.*, **31**, 2247 (1969).
- [23] N.S. Poluektov, S.B. Meshkova, S.V. Beltyukova, E.I. Tselik. *Zh. Anal. Khim.*, **27**, 1721 (1972).
- [24] M. Konstantinova, St. Mareva, N. Jordanov. *Anal. Chim. Acta*, **68**, 237 (1974).
- [25] St. Mareva, N. Jordanov, M. Konstantinova. *Anal. Chim. Acta*, **59**, 319 (1972).
- [26] K. Hirose, N. Matsumoto, M. Tanaka. *J. Inorg. Nucl. Chem.*, **39**, 2261 (1977).
- [27] K. Hirose, M. Tanaka. *J. Inorg. Nucl. Chem.*, **40**, 1153 (1977).
- [28] C. Rozyckia. *Chem. Anal. (Warsaw)*, **26**, 37 (1981).
- [29] A. Bold, L. Balusescu. *Rev. Roum. Chim.*, **23**, 1631 (1978).
- [30] I. Kojima, J. Fukūta, M. Tanaka. *J. Inorg. Nucl. Chem.*, **31**, 1815 (1969).
- [31] H. Yamada, M. Tanaka. *J. Inorg. Nucl. Chem.*, **38**, 1501 (1976).
- [32] J.N. van Niekerk, F.R.L. Schoening. *Acta Crystallogr.*, **6**, 227 (1953).
- [33] I.V. Pyatnitskii, A. Omode, V.V. Sukhan. *Zh. Anal. Khim.*, **28**, 2317 (1973).
- [34] A. Aidi, D. Barkat. *J. Coord. Chem.*, **63**, 4136 (2010).
- [35] Y. Marcus, A.S. Kertes. *Ion Exchange and Solvent Extraction of Metal Complexes*, Wiley Interscience, New York (1969).
- [36] R.K. Biswas, M.A. Habib, M.N. Islam. *Ind. Eng. Chem. Res.*, **39**, 155 (2000).
- [37] J.N. van Niekerk, F.R.L. Schoening. *Acta Crystallogr.*, **6**, 227 (1953).
- [38] T. Gündüz, E. Kiliç, E. Canal, F. Köseoglu. *Anal. Chim. Acta*, **282**, 489 (1993).