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LIQUID–LIQUID EXTRACTION OF METAL IONS BY CHELATING LIGANDS

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CONTENTS

ABBREVIATIONS

$HL \cap L$	bidentate, monobasic ligand
$\overline{HL \cap L}$	concentration (activity) of $HL \cap L$ in an organic diluent
$K_{D(HL \cap L)}$	distribution coefficient of species $HL \cap L$
$N \cap O^-$	anion of a LIX- or KELEX-reagent
ϵ_0	standard potential
$pH_{1/2(0.01)}$	pH at which the distribution ratio is unity and the equilibrium concentration of extractant in organic phase is 0.01 M
K_E	extraction equilibrium constant
β_2	overall stability constant of a 1,2-complex
DH_2	dimethylglyoxime

A. INTRODUCTION

The initial interest in liquid–liquid extraction resulted from the need for both simple tests and quantitative methods in analytical chemistry. In this connection the cobalt(II) test in which $[Co(NCS)_4]^{2-}$ is extracted with amyl alcohol or the pH-dependent extraction of many heavy metal ions by means of dithizone (Table 1) should be mentioned. This method, combined with photometric evaluation, may be used for the determination of very small quantities [1].

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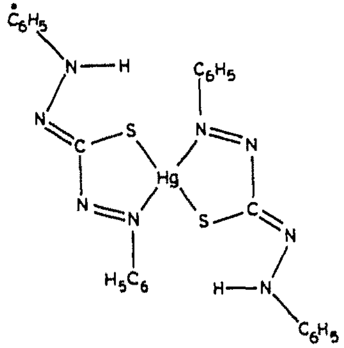
TABLE I

General features of metal extraction

Formation of ion pairs		Formation of metal chelates
$[M(H_2O)_x]^{n+} + nY^- + m\,D$	$[M(H_2O)_x]^{n+} + o\,Y^- + (o-n)\,R^+$	$[M(H_2O)_x]^{n+} + n\,\overline{HL\cap L}$
$\overline{MY_nD_m} + x\,H_2O$	$\overline{R_{o-n}[MY_o]} + x\,H_2O$	$\overline{M(L\cap L)_n} + n\,H^+ + x\,H_2O$
Example: $UO_2(NO_3)_2(TBP)_2$	$(NH_4)_2[Co(NCS)_4]$	

Practical application commenced with nuclear technology. The problem was the recovery of uranium from a solution obtained by the dissolution of nuclear fuel wastes (the present position has been reviewed by Chesné [2]). Another important event was the introduction of LIX-reagents into hydrometallurgy. At first copper production was the favoured process, but today other non-ferrous metals (cobalt, nickel, zinc [3]) are recovered as well.

Extraction processes take a leading part in the design of flow sheets for the working-up of sea nodules [3,4] or scrap metals and wastewaters [5]. In the latter case the disposal of materials causing environmental pollution is combined with the recovery of valuable metal compounds.

Up to the 1970s, metal extraction took place on an empirical basis. Basic research, which was preceded by and initiated as a result of technical experience, resulted first in partly contradictory ideas. The main reason was the direct use of the industrial extractants which were mixtures of compounds and hence of variable composition and chemical behaviour [6]. Thus, it was reported that an early lot of KELEX 100 was capable of loading nickel(II) from acidic solution, whereas later material was not [7]. Therefore, the present practice is to use pure extractants and then to study systematically the influence of diluents, accelerators, retardants, anions, etc. [8–10].

In Table 1 the three most important types of metal extraction are given. Metals may be extracted as part both of the cation and of the anion of an ion pair. The extraction of metal chelates, which is always connected with the formation of protons, is represented by the dithizonate method. In this case control of the extraction by the pH value is possible. We shall deal only with metal extraction by chelating ligands which is interesting from a coordination chemistry point of view.

Of great importance for the course of the extraction reactions given in Table 1 is the lability of the hydrated metal ions, which may be estimated by the rate constant for solvent exchange (eqn. (1), Table 2). On this basis the

$$M(H_2O)_x^{n+} + H_2O^* \xrightarrow{k_{23}} M(H_2O)_{x-1}(H_2O^*)^{n+} + H_2O \qquad (1)$$

metal ions may be divided into four classes [11]. High extraction rates are to be expected for class I and II ions, but very low rates for class IV ions. There are some problems with class III ion extraction. Of special interest is the utilization of differences in extraction rates for separation of class II and class III ions. Thus the practical experience with the commercial extractant LIX 64 N reads as follows: "You need two minutes to get your copper out—if you leave it for five you get iron as well" [12].

The time-scale of minutes shows that the extraction of metals, independent of the individual influence of the central atom, proceeds much more

TABLE 2

Classification of hydrated metal ions according to their first-order substitution rate constants k_{23} [11]

	k_{23} (s^{-1})
Class I: group Ia, group IIa (except Be^{2+}), group IIb	$\geqslant 10^8$
Class II: first transition series (M^{2+}), lanthanides	10^4-10^8
Class III: Be^{2+}, Ga^{3+}, V^{3+}, Mn^{3+}, Fe^{3+}	$1-10^4$
Class IV: Cr^{3+}, Co^{3+}, Pt^{2+}, Pt^{4+}	<1

slowly than complex formation in homogeneous solution. This is, first of all, a result of the required transition of the metal ions from one liquid phase to another and enforces the following consideration:

The solubility of metal ions in non-polar diluents for the extractants, and also the solubility of the extractant in water are very low. Therefore complex formation may not proceed in the bulk of the aqueous solution or of the diluent, but in the interface between the two liquid phases. In such a case the interfacial pressure should be of importance for the course of reaction [13] and this will be demonstrated for copper(II) extraction by *o*-hydroxyoximes (Section B). Section C is concerned with the influence of the redox properties of cobalt(II), and Section D with that of different coordination numbers of nickel(II) on the extraction.

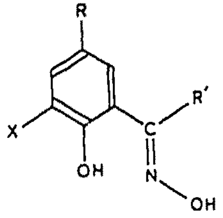
B. KINETICS OF COPPER(II) EXTRACTION BY *O*-HYDROXYOXIMES

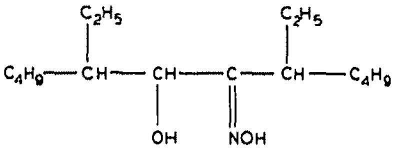
The bidentate copper extracting ligands are phenols containing an sp^2-hybridized nitrogen as a further ligator (Table 3). They are derivatives either of salicylaldoxime or of 8-hydroxyquinoline; the alkyl substituents improve the solubility of the extractant and its metal chelates in non-polar solvents.

Bis(salicylaldoximato)copper has a distorted octahedral structure [15]; the copper atoms of planar species with the donor set N_2O_2 (Fig. 1) interact with the oxygen atoms of oxime groups of two adjacent species (Cu–O distance 2.66 Å). Bis(5-chlorosalicylaldoximato)copper has a similar structure [16], but there is one important difference: the oxygen atoms not of oxime groups but those of two adjacent phenolic groups participate in the axial interaction, and the Cu–O distance is elongated to 3.01 Å. Axial interactions of both types are of great importance for the solubility and also for the extraction behaviour of copper(II) chelates; elongation of the Cu–O distance should improve the solubility in non-polar solvents. Lingafelter's results [15,16] demonstrate that substituents in a position far away from the donor

TABLE 3

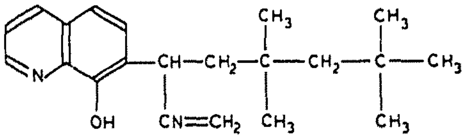
Copper(II) extractants





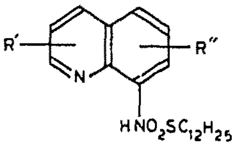
LIX 63

	R	R′	X
LIX 65N	C_9H_{19}	C_6H_5	H
LIX 70	C_9H_{19}	C_6H_5	Cl
SME 529	C_9H_{19}	CH_3	H
P 17	C_9H_{19}	$CH_2C_6H_5$	H
P 50	C_9H_{19}	H	H
I	C_7H_{15}	CH_3	H



KELEX100

LIX 64 N:
LIX 65 N+LIX 63 (as an accelerator)



LIX 34 [14]

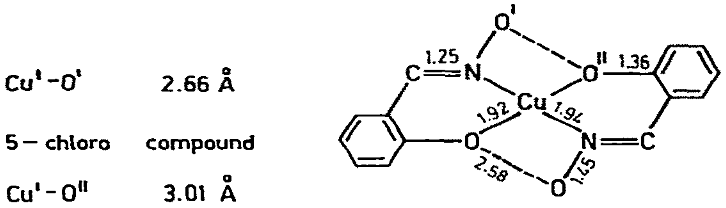


Fig. 1. Structure of bis(salicylaldoximato)copper(II) and bis(5-chlorosalcylaldoximato)copper(II) (Cl omitted). (Distances in Å.)

atoms can influence the structure of *o*-hydroxyoxime complexes of copper(II) and in this way also, the extraction behaviour.

Hitherto the best investigated extraction process is that of copper(II) by LIX 65 N which is the main component of the proprietary extractant LIX 64 N. By experimental precautions (single drop technique [17], extraction kinetics apparatus [18]) mass transfer control of copper extraction was eliminated and the kinetics of the real chemical reaction were followed.

Several authors [17,18] discovered the following rate law which is valid within certain limits

$$-\frac{d[Cu^{2+}]}{dt}=k\frac{[Cu^{2+}]\overline{[HL\cap L]}^{2}}{[H^{+}]}$$

This is consistent with a two-step mechanism according to eqs. (2) and (3)

$$Cu^{2+}+HL\cap L\overset{fast}{\rightleftharpoons}Cu(L\cap L)^{+}+H^{+} \tag{2}$$

$$Cu(L\cap L)^{+}+HL\cap L\overset{slow}{\rightleftharpoons}Cu(L\cap L)_2+H^{+} \tag{3}$$

((3) is rate limiting). But there are different ideas as to the site of reactions (2) and (3).

Preston and Luklinska [17] emphasize the high interfacial pressure of extractants of the *o*-hydroxyoxime type. Their interface concentration $[HL\cap L]_{int}$ is proportional to the interfacial pressure which can be measured by means of the drop-volume method. For the *o*-hydroxyoxime, I, a linear relation between the logarithms of the extraction rate and the interfacial pressure and a slope of 2.2 were stated. Therefore, we must assume that $[HL\cap L]_{int}$ and not $\overline{[HL\cap L]}$ is decisive for the extraction rate and that the sites of reactions (2) and (3) are the interface [20,21] (It is an unresolved question how far the interface runs across the aqueous and the organic phase [19]). Interface phenomena may be also used for an explanation of the influence of accelerators and retardants [22].

However, Carter and Freizer [18] assume reactions (2) and (3) to proceed in the aqueous bulk phase. They split the rate constant k according to

$$k = \frac{k_{\mathrm{I}} K_{\mathrm{I}} K_{(\mathrm{HL} \cap \mathrm{L})}}{K_{\mathrm{D}(\mathrm{HL} \cap \mathrm{L})}}$$

where

$$K_{\mathrm{D}(\mathrm{HL} \cap \mathrm{L})} = \frac{\overline{[\mathrm{HL} \cap \mathrm{L}]}}{[\mathrm{HL} \cap \mathrm{L}]}, \quad K_{(\mathrm{HL} \cap \mathrm{L})} = \frac{[\mathrm{H}^+][\mathrm{L} \cap \mathrm{L}^-]}{[\mathrm{HL} \cap \mathrm{L}]}$$

and

$$K_{\mathrm{I}} = \frac{[\mathrm{Cu}(\mathrm{L} \cap \mathrm{L})^+]}{[\mathrm{Cu}^{2+}][\mathrm{L} \cap \mathrm{L}^-]}$$

Starting with the experimental value of $K_{\mathrm{D}(\mathrm{HL} \cap \mathrm{L})}$ and an estimated value of $K_{\mathrm{I}} \cdot K_{(\mathrm{HL} \cap \mathrm{L})}$, k_{I} (the rate constant of reaction (3) in a homogeneous aqueous solution) was calculated. The value of $2.2 \cdot 10^7\ \mathrm{M}^{-1}\mathrm{s}^{-1}$ is in agreement with generally observed rate constants for copper substitution reactions in aqueous media.

A comparison of the calculated k-values is very interesting. The value of Carter and Freizer [18] is $1.37\ \mathrm{M}^{-1}\mathrm{s}^{-1}$. No k-value is given by Preston and Luklinska [17], but an estimate starting with the reported data of compound **I** shows $k \sim 100\ \mathrm{M}^{-1}\mathrm{s}^{-1}$. Firstly we must ask whether this big difference in values originates in the differences of R and R′ for LIX 65 N [18] and compound **I** [17]. But considering the extensive studies of Preston and Luklinska [17] this cannot be so. Therefore, the main reason for the difference in k seems to be the diluent [23]: Carter and Freizer used chloroform for LIX 65 N [18], whereas Preston and Luklinska used toluene for compound **I** [17].

The distribution coefficients of LIX 65 N for chloroform/water and toluene/water differ only slightly ($K_{\mathrm{D}(\mathrm{HL} \cap \mathrm{L})} = 10^{4.6}$ [18] or $10^{4.9}$ [17]). But in contrast to toluene, chloroform interacts with *o*-hydroxyoximes by hydrogen bonding. In this way an enrichment of the extractant in the chloroform/water interface and direct contact of polar OH– and NOH– groups with the aqueous solution is hindered. Evidently, the consequence is a retardation of the interface reaction to such a degree that there may be competition with the reaction in the aqueous bulk phase. The apparent change of the extraction mechanism (interface reaction for toluene, reaction in the aqueous bulk for chloroform) which is caused only by a change of the diluent should be considered in further studies.

C. REDOX PROPERTIES OF COBALT(II) CHELATES AND LIQUID–LIQUID EXTRACTION

Cobalt(II) may be extracted from an ammoniacal solution by LIX- or KELEX-reagents [6]. But a complete reextraction by acids is only possible if it is performed immediately after the extraction [7]. Otherwise the chelates $Co^{II}(N \cap O)_2$ in the organic phase are oxidized to stable cobalt(III) complexes (eqn. 4) [24].

$$2\,Co^{II}(N \cap O)_2 + 2\,N \cap OH + 1/2\,O_2 \rightarrow 2\,Co^{III}(N \cap O)_3 + H_2O \qquad (4)$$

The interference may be overcome by a “reductive” extraction, i.e. an extraction in the presence of copper or cobalt powder [25]. Another possibility is the application of a synergist, such as VERSATIC 911 (a tertiary aliphatic carbonic acid). A mixture of KELEX 100 and VERSATIC 911 extracts a mixed ligand complex of probable composition **II** (eqn. 5) [6,24].

$$[Co(N \cap O)_2(N \cap OH)]_2 + 2\,RCOOH \rightleftharpoons \underset{\textbf{II}}{[Co(N \cap O)(N \cap OH)(RCOO)]_2} + 2\,N \cap OH \qquad (5)$$

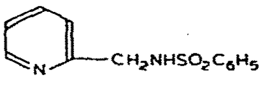
Evidently **II** has an octahedral structure with the donor set N_2O_4. The predominance of the O-ligators lifts the redox potential (cf. eqns. (6) and

$$[Co(NH_3)_6]^{2+} \rightleftharpoons [Co(NH_3)_6]^{3+} + e \quad \epsilon_0 = 0.1\,V \qquad (6)$$

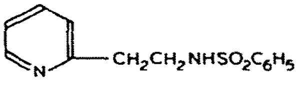
$$[Co(H_2O)_6]^{2+} \rightleftharpoons [Co(H_2O)_6]^{3+} + e \quad \epsilon_0 = 1.84\,V \qquad (7)$$

(7)) and prevents the oxidation of extracted cobalt(II) by oxygen. Therefore, a reextraction is possible independent of the age of the solution.

The difficulties of reextraction disappear whenever NH-acidic compounds are applied which form air-stable cobalt(II) chelates [26,27]. By the reaction of cobalt(II) salts with pyridyl substituted sulfonamides such as NC_2NHR and NC_3NHR, $Co(NC_2NR)_2$ and $Co(NC_3NR)_2$ with coordination polymeric structures were obtained [28]. Polarographic studies demonstrated that up to a potential of +1.3 V these complexes are not oxidized. On the contrary, the irreversible $Co(II) + e \rightleftharpoons Co(I)$ wave is discovered (ca. −1.8 V).



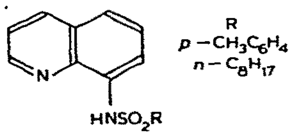
NC_2NHR



NC_3NHR

The ligands NC_nNHR, because of the low solubility of their metal chelates in hydrocarbons, are poor metal extractants. But they may be considered as models for other recently described sulfonamide based extractants [29]. These compounds also extract other divalent transition metal ions (copper(II), zinc(II), cadmium(II))

$$\mathrm{M}^{2+}_{\mathrm{aq}} + 2\,\overline{\mathrm{N} \cap \mathrm{NHR}} \rightleftharpoons \overline{\mathrm{M}(\mathrm{N} \cap \mathrm{NR})_2} + 2\,\mathrm{H}^{+}_{\mathrm{aq}} \tag{8}$$

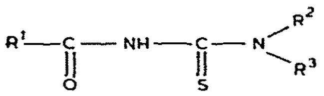


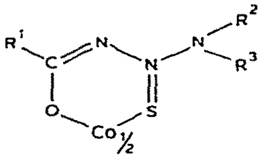
N∩NHR

Hence the separation of copper(II) and cobalt(II), and also of cobalt(II) and zinc(II) is possible ($\mathrm{pH}_{1/2}$ (water/kerosene): Cu(II) 1.75; Zn(II) 5.10: Co(II) 6.2).

It is remarkable that iron(III) is not extracted. Again an explanation is given by the behaviour of the model ligands $\mathrm{NC}_n\mathrm{NHR}$ [28]. No uncharged complexes are formed, but instead the low-spin salts $[\mathrm{Fe}(\mathrm{NC}_n\mathrm{NHR})_3](\mathrm{NO}_3)_3$. Naturally, these are insoluble in non-polar solvents.

As another type of copper(II) extractants *N*-acyl thioureas are recommended [30]. The chelates, **III**, can be extracted from acid solutions. They are stable to oxidation, if an alkaline reaction is avoided.





III

D. NICKEL(II) EXTRACTION

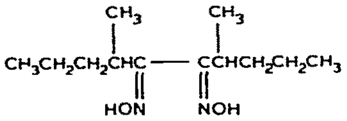
In 1975 Burkin and Preston [31] reported the synthesis of 1,2-dioximes with bulky side chains. $\mathrm{BuMe^4DH_2}$ is easily soluble in hydrocarbons and extracts both copper(II) ($\mathrm{pH}_{1/2\,(0.001)} = 1.6$) and nickel(II) ($\mathrm{pH}_{1/2\,(0.001)} = 0.9$) from acid solution. Two observations are of interest: (i) the $\mathrm{pH}_{1/2\,(0.001)}$ for nickel(II) is lower than that for copper(II), and the reverse is valid for log K_{E}; (ii) minutes are required to establish equilibrium (9) for copper(II), but days in the case of nickel(II).

$$\mathrm{M}^{2+}_{\mathrm{aq}} + 2\,\overline{\mathrm{RDH}_2} \rightleftharpoons \overline{\mathrm{M}(\mathrm{RDH})_2} + 2\,\mathrm{H}^{+}_{\mathrm{aq}} \tag{9}$$

$$K_{\mathrm{E}} = \frac{[\overline{\mathrm{M}(\mathrm{RDH})_2}][\mathrm{H}^+]^2}{[\mathrm{M}^{2+}][\overline{\mathrm{RDH}_2}]^2} \qquad \beta_2 = \frac{[\mathrm{M}(\mathrm{RDH})_2]^2}{[\mathrm{M}^{2+}][\mathrm{RDH}^-]^2}$$

$$\log K_{\mathrm{E}} = 2\log\underbrace{\frac{K_{(\mathrm{RDH}_2)}}{K_{\mathrm{D}(\mathrm{RDH}_2)}}}_{\mathbf{IV}} + \underbrace{\log\left(\beta_2 \cdot K_{\mathrm{D}[\mathrm{M}(\mathrm{RDH})_2]}\right)}_{\mathbf{V}} \tag{10}$$

(i) The extraction equilibrium constant K_E may be split according to eqn. (10). Item **IV** is independent of the metal. Therefore, it is concluded from the



$BuMe^4DH_2$

experimental extraction data that item **V** for nickel(II) must be higher than for copper(II). β_2 and $K_{D[M(RDH)_2]}$ are unknown for $Cu(BuMe^4DH)_2$ and $Ni(BuMe^4DH)_2$, and more simple complexes must be used for a comparison. For the system chloroform/water log $K_{D[Cu(DH)_2]}$is -0.93, log $K_{D[Ni(DH)_2]}$ is 2.51. The reason for such a big difference is seen in the formation of an aquo complex $[Cu(DH)_2(H_2O)]$ in the case of copper(II), but not in the case of nickel(II). The hydrophilic aquo complex remains preferentially in the aqueous phase [32].

The stability constants β_2 of soluble 1,2-dioximato complexes of copper(II) are higher than those of nickel(II) [33] (log $\beta_2 = 17.1_5$ for $Cu(AcDH)_2$ and 14.9_0 for $Ni(AcDH)_2$). But the difference of log β_2 is smaller than that of log$K_{D[M(DH)_2]}$. Therefore, the conclusion as to the relative values of item **V** for copper(II) and nickel(II) is confirmed by these model considerations.

The distribution coefficient $K_{D[Cu(BuMe^4DH)_2]}$, because of the bulky hydrophobic substituents of the ligand, is probably higher than $K_{D[Cu(DH)_2]}$ and approaches $K_{D[Ni(BuMe^4DH)_2]}$. But we must also expect a destabilization of the above-mentioned aquo complex by the bulky substituent and as a consequence a lowering of log β_2 for $Cu(BuMe^4DH)_2$.

The importance of aquation for the stability of copper(II) 1,2-dioximato complexes is reflected in the dependence of the formation constants $\beta_{2(F)}$ on the dioxane content of the solvent (Table 4). For copper(II), because of the more difficult aquation, log β_2 decreases with increasing dioxane content of the solution, but no apparent change is observed in case of nickel(II).

(ii) The differences in the extraction rate of copper and nickel can hardly be attributed to interface effects. More probably they must be ascribed to differences in the mechanism of the chemical reaction. The solvent exchange (eqn. 1) for nickel(II) is orders of magnitude slower than for copper(II) [11]. The main reason is a certain kinetic stability of octahedral $[Ni(H_2O)_6]^{2+}$ ($3d^8$-configuration) and a labilization of the aquo ligands of $[Cu(H_2O)_n^{2+}$ as a result of the Jahn–Teller effect ($3d^9$-configuration). A further retarding effect, especially for nickel(II) extraction by 1,2-dioximes (eqn. 9), results in the change of the spin-state (triplet → singlet).

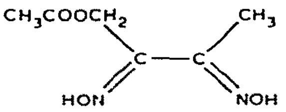
Good kinetics of nickel(II) extraction are to be expected, whenever the substitution of water takes place within an octahedral complex (aqueous solution, interface) which is directly followed by the elimination of the

TABLE 4

Formation constants $\beta_{2(F)}$[a] of copper(II) and nickel(II) complexes in dioxane/water mixtures (25°C; 0.1 *m* KNO_3)

log $\beta_{2(F)}$	Dioxane content % by vol.			
	0	25	50	75
Cu^{2+}	-2.4_0	-2.8_0	-3.3_5	-4.0_0
Ni^{2+}	-4.6_5	-4.5_0	-4.5_5	-4.6_5

[a] $\beta_{2(F)} = \dfrac{[M(AcDH)_2][H^+]^2}{[M^{2+}][AcDH_2]^2}$



AcDH$_2$

surplus monodentate ligands (H_2O, L″; eqns. 11,12). Therefore, possible

$$\underset{\text{paramagnetic}}{[Ni(H_2O)_6]^{2+}} + 2\,HL\cap L' \xrightleftharpoons[-4\,H_2O]{} \underset{\text{paramagnetic}}{\underset{\textbf{VI}}{[Ni(H_2O)_2(L\cap L')_2]}} \xrightleftharpoons[-2\,H_2O]{} \underset{\text{(square-planar)}}{\underset{\text{diamagnetic}}{[Ni(L\cap L')_2]}} \qquad (11)$$

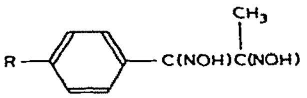
$$[Ni(H_2O)_6]^{2+} + 2\,HL\cap L' \xrightleftharpoons[-6\,H_2O]{+2\,L''} \underset{\textbf{VII}}{[NiL_2''(L\cap L')_2]} \xrightleftharpoons[-2\,L'']{} \underset{\textbf{VIII}}{[Ni(L\cap L')_2]} \qquad (12)$$

extractants should form hydrophobic uncharged chelates **VIII**, but these chelates must be capable of sequestering bases such as water or ammonia to form octahedral complexes (**VI**, **VII**). This condition is fulfilled by *o*-hydroxyoximato or pyridylsulfonamido complexes of nickel(II) [28,34]. Therefore, it is quite understandable that both LIX 65 N and LIX 34 have been recommended for loading of nickel(II) from ammoniacal solution [6,15]. In case of LIX 34 the coextraction of ammonia as part of ammine complexes was proved [35].

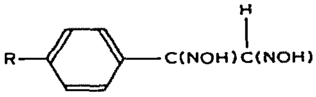
$$\underset{\text{paramagnetic}}{[Ni(H_2O)_6]^{2+}} + 2\,NC_3NHR \xrightarrow[+NEt_3]{\text{methanol}} \underset{\text{paramagnetic}}{[Ni(H_2O)_2(NC_3NR)_2]}$$

$$\xrightarrow[\text{benzene}]{\text{warming}} \underset{\text{diamagnetic}}{[Ni(NC_3NR)_2]}$$

No octahedral complexes of type **VI** or **VII** are formed by bisdioximato complexes of nickel(II), and this may be the explanation for the slow extraction of nickel(II) by $BuMe^4DH_2$. But we must not forget the results of van der Zeeuw and Kok [21]: when using asymmetrically substituted 1,2-dioximes (**IX**, **X**), the equilibrium (9) is established not within days but within hours, and a temperature of 50°C increases the rates further to a level where they start to be attractive. The dioxime group is argued to be more "exposed" than that of $BuMe^4DH_2$ and this is thought to be the reason for the better kinetics. But in this connection the following insight cannot be neglected. Every synthesis of 1,2-dioximes affords a mixture of geometrical isomers



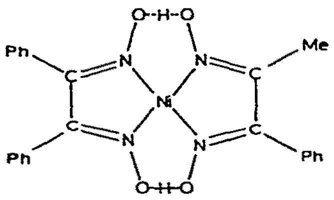
IX



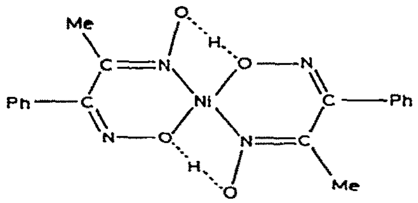
X

(*syn*, *anti*, *amphi*). Nickel(II) complexes are formed only by the *anti*- and *amphi*-isomers. Considering the aliphatic and the aryl-aliphatic dioximes the nickel(II) chelates of the *anti*-isomers are thermodynamically most stable and can be obtained by a catalytic isomerization of the complexes of the *amphi*-isomers [35]. Deviations of this rule are known for certain cycloaliphatic 1,2-dioximes such as camphorquinone dioxime [36,37].

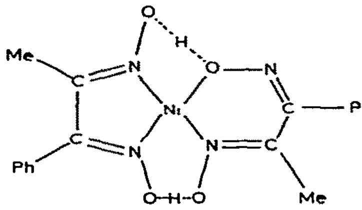
IX is an alkylated phenyl methylglyoxime. It is this compound where both the *trans-anti* and the *trans-amphi* chelates (**XI**, **XII**) are known [36]. By proton catalysis in chloroform, possibly via **XIII**, **XII** is rearranged to **XI**. It is remarkable that **XII** has the same donor atom set (N_2O_2) and the same



XI



XII



XIII

hydrogen bond system as nickel(II) complexes of *o*-hydroxyoximes (Fig. 1). This knowledge enforces the idea of a similar tendency of nickel(II) complex formation for both types of ligands and promotes the discussion of the following model of nickel(II) extraction by 1,2-dioximes. During the extraction of nickel(II) by compound **IX**, in a first step a chelate of the *amphi*-isomer is formed (**XII** or **XIII**, but substituted by R). In a second step and in any case in the organic phase, by a catalytic rearrangement or by a ligand exchange with the *anti*-isomer, compound **XII** (or **XIII**) is converted into the stable chelate **XI**. In a patent [38] the extraction of nickel(II) is claimed by means of a mixture of compound **IX** isomers, the content of *anti*-isomer being not higher than 60%. Further studies are needed; the detection of the different isomeric nickel(II) complexes (see **XI**, **XII** and **XIII**) should be possible by NMR spectroscopy [36].

E. CONCLUSIONS

We can expect that the technical importance of liquid–liquid extraction will increase. The main fields of application will be the hydrometallurgy of low-grade ores and the reprocessing of metal containing wastes and wastewaters.

A thorough investigation of equilibria, kinetics and mechanisms of extraction processes is wanted, and the experience of coordination chemists in the field of solution chemistry (influence of ligands, central atoms and solvent on complex formation) is demanded. But some additional parameters must be considered which were hitherto hardly the subject of coordination chemistry (interface properties of chelating ligands, distribution of ligands and chelates between two immiscible liquid phases). This means both an enrichment of research in coordination chemistry and an extension of practical application.

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