

# Crystallographic determination of three Ni- $\alpha$ -hydroxyoxime-carboxylic acid synergist complexes

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## Abstract

X-ray crystal structures of three dicarboxylato-bis- $\alpha$ -hydroxyoximenickel(II) complexes have been obtained. These contain a short chained ( $C_8$ ) analogue of LIX<sup>®</sup>63 hydroxyoxime, along with either benzoate, isobutyrate or propionate. All three complexes have *pseudo*-octahedral structures in which monodentate carboxylate anions are located *cis* to one another.

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The chelating  $\alpha$ -hydroxyoxime ligands are uncharged with *cis* coordination of the  $\alpha$ -hydroxyl groups and the oxime nitrogen atoms located *trans* to one another. Intra-molecular hydrogen bonding between each anionic acid's carboxylate group and a *cis*-adjacent oxime hydroxyl group is evident. In addition, *inter*-molecular hydrogen bonding between each  $\alpha$ -hydroxyl proton and a neighbouring carboxylate carbonyl group is observed within the lattice resulting in a one dimensional hydrogen bonded polymer structure. Unlike the typical phenolic-based hydroxyoxime-metal complexes, no intra-molecular hydrogen bonding between the hydroxyoxime ligands is apparent. These nickel complex crystal structures, the first ever determined containing aliphatic  $\alpha$ -hydroxyoxime ligands directly comparable to that present in LIX<sup>®</sup> 63, provide the first definitive structural elucidation of the types of nickel complexes which could be formed during synergistic extraction by LIX<sup>®</sup> 63 and carboxylic acids. Spectroscopic investigation to assess whether these solid state structures persist in solution is underway.

## 1. Introduction

The ability of certain mixtures of reagents to impart a synergistic effect on metal extraction is both of scientific interest and of potential value as a commercial solvent extraction (SX) process. A reagent that has been regularly used as a part of laboratory-based synergistic systems is LIX<sup>®</sup> 63, the active component of which is 5,8-diethyl-7-hydroxydodecan-6-oxime. This  $\alpha$ -hydroxyoxime reagent was the first attempt to develop an organic extractant for copper that could be incorporated into a leach / solvent extraction / electrowinning operation.<sup>[1]</sup> Although it was never used commercially for this purpose in its own right, it was used in catalytic quantities alongside LIX<sup>®</sup> 65 benzophenone oxime in the first commercially applied

copper SX reagent, LIX<sup>®</sup>64. In terms of copper extractants, this reagent combination has since been superseded by formulations of phenolic oximes.

The ability of the aliphatic  $\alpha$ -hydroxyoxime to behave synergistically in conjunction with another extractant, di-2-ethylhexyl phosphoric acid, was first noted for copper extraction in 1966.<sup>[2]</sup> The possible stoichiometry or structure of the generated species was not discussed. Since that initial account, research into the role of the  $\alpha$ -hydroxyoxime in synergistic systems for copper, cobalt, and nickel branched into two broad areas that differ in their mechanism of extraction: those using carboxylic or phosphorus-based organic acids, and those using reversed-micelle-forming species (e.g. sulfonic acids). In all systems, structural information on the generated species is sparse.

In the case of the reversed-micelle systems, the ability of the  $\alpha$ -hydroxyoxime to chelate with nickel without deprotonation was said to be a key factor as it permitted extraction to occur at low pH.<sup>[3,4]</sup> It was concluded that the sulfonate micelles were serving to enhance the reaction by solubilising both the hydroxyoxime and nickel ions. The resulting complex was stated to be a nickel-hydroxyoxime complex, and not specifically a mixed ligand complex. Additional work, incorporating equilibrium studies (slope analysis) and the method of continuous variation, concluded that the formation of nickel and cobalt mixed ligand complexes occurred with a metal:hydroxyoxime:sulfonic acid stoichiometric ratio of 1:3:2.<sup>[5,6]</sup> The extracted nickel complex was proposed to be a salt, containing neutral hydroxyoxime in a  $[\text{Ni}(\text{hydroxyoxime})_3]^{2+}$  cation counterbalanced by sulfonate anions. A slightly different stoichiometry (1:2:2) was proposed for microemulsion-derived complexes of Co and Cu when using the sulfosuccinate AOT.<sup>[7]</sup>

Where performed, the determination of the stoichiometry in systems utilising  $\alpha$ -hydroxyoxime and phosphorus-based acidic extractants has also been achieved using

equilibrium studies.<sup>[8,9]</sup> Complexes were proposed to have a nickel:hydroxyoxime:phosphorus-based acid stoichiometry of 1:2:2 as the main or sole species formed. In one case, the hydroxyoxime was concluded to be acting as the anion.<sup>[8]</sup>

The synergistic systems of most interest to the present work have utilised a carboxylic acid. The first published work noted synergistic shifts for both copper and cobalt when  $\alpha$ -hydroxyoxime was used in conjunction with naphthenic acid.<sup>[10]</sup> Based on limited UV-visible data, it was tentatively concluded that the organic acid ‘partially or wholly’ played the role as the organic anion in both the cobalt and copper mixed-ligand complexes.

Subsequent work<sup>[11]</sup> also saw synergistic effects for both nickel and zinc using this reagent combination, and synergistic effects persisted when other carboxylic acids ( $\alpha$ -bromolauric acid and Versatic 9-11) were used. It also saw a shift in opinion to the hydroxyoxime acting as the anion, a conclusion based on the increasing synergistic effect for copper extraction as a function of increasing acidity (decreasing  $pK_a$ ) of the organic acid used. Subsequent work using equilibrium studies indicated a metal:hydroxyoxime:carboxylic acid ratio of 1:2:2 for the nickel:hydroxyoxime:lauric acid complex, with hydroxyoximate again specified as the anion.<sup>[12]</sup> UV-visible analysis was also used to conclude octahedral coordination about the nickel. This stoichiometry was also deemed to be applicable to the major species obtained when using n-dodecanoic acid,<sup>[13]</sup> but differed from the 1:3:2 ratio determined when using Versatic 9-11 as the carboxylic acid.<sup>[14]</sup> The 1:2:2 ratio was also claimed for a number of nickel synergist complexes using different carboxylic acids.<sup>[15]</sup> Importantly, this latter paper also proposed a structure for these types of synergist complexes (Figure 1). It was considered likely that the nitrogen atoms of the two hydroxyoximate ligands were arranged *trans* to one another in a planar configuration to enable hydrogen bonding between the oximic hydroxyl group of one hydroxyoximate ligand and the deprotonated  $\alpha$ -hydroxyl group of the other

hydroxyoximate ligand. This type of arrangement and the hydrogen bonding arising from it was well known for structurally characterised phenolic-based hydroxyoxime complexes.<sup>[16]</sup> It was proposed that addition of neutral carboxylic acid groups in the two axial positions permitted additional hydrogen bonding between the carboxylic acid proton and a lone pair of electrons in the  $p_z$  orbital on the  $sp_2$ -hybridised hydroxyoxime  $\alpha$ -hydroxyl group (accidentally referred to as the ‘phenolic oxygen atom of the oxime’ previously).<sup>[15]</sup> This hydrogen bonding was considered important in the stabilisation of the synergist complex. This type of geometric orientation or, alternatively, a carboxylate-bridged bimetallic complex, had also been proposed previously, but without specific discussion of hydrogen bonding.<sup>[17]</sup>

Although having been of interest for over forty years, no definitive information on the structure of these  $\alpha$ -hydroxyoxime-containing synergist systems has yet been provided. Given the recent rekindled interest in this system<sup>[18-20]</sup> and the historical focus on nickel-containing complexes over the years, the present work aimed to bridge this gap by the preparation of nickel synergist complexes amenable to X-ray crystallographic analysis by use of a short ( $C_8$ ) chained analogue of the  $\alpha$ -hydroxyoxime present in LIX<sup>®</sup> 63.

## 2. Experimental

### 2.1. Synthesis of 5-hydroxy-4-octanone oxime ( $H_2Ox$ )

5-Hydroxy-4-octanone (9.16 g, 63.5 mmol) was dissolved in ethanol (*ca.* 50 mL), before sodium acetate (5.35 g, 65.2 mmol) was added, followed by hydroxylamine hydrochloride (4.90 g, 70.5 mmol) and the mixture stirred and heated at reflux. After 2 hours, the reaction was removed from the heat, filtered, and the filtrate reduced to a thick yellow oil on the rotary evaporator. The residue was dissolved in dichloromethane (*ca.* 100 mL) and extracted with

water (3 x 50 mL). The organic fraction was dried over MgSO<sub>4</sub>, filtered, and reduced to dryness on the rotary evaporator. The oil was subjected to purification via flash chromatography on silica (ethyl acetate/light petroleum, 25:70) to give a colourless viscous oil of 5-hydroxy-4-octanone oxime (H<sub>2</sub>Ox, 7.44 g, 5.16 mmol, 81%) as a mixture of E and Z oxime isomers.

<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 0.8 – 1.0 (m, 6H, -CH<sub>3</sub>), 1.2 – 1.8 (m, 6H, -CH<sub>2</sub>-), 2.0 – 2.5 (m, 2H, -CH<sub>2</sub>-), 4.20 (dd, 0.8 H, -CH- *anti*), 4.65 (dd, 0.2 H, -CH- *syn*), 6.0 (s, br, 2H, -OH).

## 2.2. Synthesis of Ni(HOx)<sub>2</sub>

A procedure similar to one applied previously<sup>[21]</sup> was used. Ni(NO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub> (1.00 g, 3.45 mmol) was dissolved in water (*ca.* 20 mL) and concentrated NH<sub>3</sub> added dropwise until a deep blue colour appeared in solution. To this was added a solution of H<sub>2</sub>Ox (1.20 g, 8.32 mmol) in ethanol (*ca.* 5 mL), causing the immediate precipitation of a dark red/brown oil, which solidified upon standing. The material was collected and washed with water before being dried under vacuum to give the desired complex (0.91 g) as a dark red/brown solid. This gradually turned dark green and become tacky if exposed to the atmosphere.

## 2.3. Synthesis of *cis*-[Ni(H<sub>2</sub>Ox)<sub>2</sub>(RCO<sub>2</sub>)<sub>2</sub>], R = acetic, propionic, iso-butyric or benzoic

[Ni(HOx)<sub>2</sub>] (0.050 g, 0.13 mmol) was slurried in H<sub>2</sub>O/ethanol (*ca.* 75:25, *ca.* 3 mL) before the relevant carboxylic acid was added (0.26 mmol) and the mixtures stirred overnight. The samples gradually began to redeposit a finely divided light blue solid within hours. The samples were collected and washed with copious quantities of water and ether to give [*cis*-Ni(H<sub>2</sub>Ox)<sub>2</sub>(RCO<sub>2</sub>)<sub>2</sub>] as very fine, light blue solids (0.02-0.04 g).

Crystals of the complexes suitable for the X-ray structure determination were grown by vapour diffusion of light petroleum into a chloroform solution of the complex (acetic acid) or by slow evaporation of a dichloromethane/ethyl acetate solution of the complex (*iso*-butyric and benzoic acids).

#### 2.4. Structure Determinations

The crystal data for the structures are given below and in the Tables and Figures, the latter showing non-hydrogen atom ellipsoids drawn at the 50% probability level. Crystallographic data for the structures were collected at 100(2) K on an Oxford Diffraction Gemini diffractometer fitted with Mo K $\alpha$  radiation (Cu K $\alpha$  radiation for *cis*-[Ni(H<sub>2</sub>Ox)<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub>)<sub>2</sub>]) yielding  $N_{total}$  reflections, these merging to  $N$  unique after multi-scan absorption corrections ( $R_{int}$  cited), with  $N_o$  reflections having  $I > 2\sigma(I)$ . The structures were refined against  $F^2$  with full-matrix least-squares using the program SHELXL-97.<sup>[22]</sup> Hydroxyl hydrogen atoms were refined without restraints, unless specified otherwise. All remaining hydrogen atoms were added at calculated positions and refined by use of a riding model with isotropic displacement parameters based on those of the parent atoms. Anisotropic displacement parameters were employed for the non-hydrogen atoms. Full .cif depositions (excluding structure factor amplitudes) reside with the Cambridge Crystallographic Data Centre, CCDC 772194-772196.

##### 2.4.1 Crystal / refinement data

*cis*-[Ni(H<sub>2</sub>Ox)<sub>2</sub>(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>]. C<sub>20</sub>H<sub>40</sub>N<sub>2</sub>NiO<sub>8</sub>,  $M_r = 495.25$ . Triclinic, space group  $P\bar{1}$ ,  $a = 9.5575(8)$ ,  $b = 10.0866(5)$ ,  $c = 13.6347(11)$  Å,  $\alpha = 96.427(5)$ ,  $\beta = 99.661(7)$ ,  $\gamma = 100.640(6)^\circ$ ,  $V = 129.57(16)$  Å<sup>3</sup>.  $D_c$  ( $Z = 2$ ) = 1.306 g cm<sup>-3</sup>.  $\mu_{Mo} = 0.814$  mm<sup>-1</sup>; specimen: = 0.21 x 0.12 x

0.08 mm; absorption  $T_{\min/\max} = 0.95$ .  $2\theta_{\max} = 62^\circ$ ;  $N_{\text{total}} = 12180$ ,  $N = 6883$  ( $R_{\text{int}} = 0.0496$ ),  $N_o = 3964$ ;  $RI(I > 2\sigma(I)) = 0.0460$ ,  $wR2$  (all data) = 0.0724.

***cis*-[Ni(H<sub>2</sub>Ox)<sub>2</sub>((CH<sub>3</sub>)<sub>2</sub>CHCO<sub>2</sub>)<sub>2</sub>]**. C<sub>24</sub>H<sub>48</sub>N<sub>2</sub>NiO<sub>8</sub>,  $M_r = 551.35$ . Triclinic, space group  $P\bar{1}$ ,  $a = 10.7007(6)$ ,  $b = 10.7140(6)$ ,  $c = 13.1495(9)$  Å,  $\alpha = 94.843(5)$ ,  $\beta = 96.983(5)$ ,  $\gamma = 97.938(5)^\circ$ ,  $V = 1474.16(15)$  Å<sup>3</sup>.  $D_c$  ( $Z = 2$ ) = 1.242 g cm<sup>-3</sup>.  $\mu_{\text{Mo}} = 0.702$  mm<sup>-1</sup>; specimen: = 0.48 x 0.04 x 0.03 mm; absorption  $T_{\min/\max} = 0.95$ .  $2\theta_{\max} = 52^\circ$ ;  $N_{\text{total}} = 11245$ ,  $N = 5777$  ( $R_{\text{int}} = 0.0601$ ),  $N_o = 3329$ ;  $RI(I > 2\sigma(I)) = 0.0441$ ,  $wR2$  (all data) = 0.0559.

***cis*-[Ni(H<sub>2</sub>Ox)<sub>2</sub>((C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub>)<sub>2</sub>)]**. C<sub>30</sub>H<sub>44</sub>N<sub>2</sub>NiO<sub>8</sub>,  $M_r = 619.28$ . Triclinic, space group  $P\bar{1}$ ,  $a = 10.577(2)$ ,  $b = 12.6062(16)$ ,  $c = 12.8089(17)$  Å,  $\alpha = 96.659(11)$ ,  $\beta = 98.597(14)$ ,  $\gamma = 108.221(15)^\circ$ ,  $V = 1579.8(4)$  Å<sup>3</sup>.  $D_c$  ( $Z = 2$ ) = 1.302 g cm<sup>-3</sup>.  $\mu_{\text{Cu}} = 1.299$  mm<sup>-1</sup>; specimen: = 0.17 x 0.06 x 0.02 mm; absorption  $T_{\min/\max} = 0.74$ .  $2\theta_{\max} = 67^\circ$ ;  $N_{\text{total}} = 11686$ ,  $N = 5497$  ( $R_{\text{int}} = 0.0738$ ),  $N_o = 2997$ ;  $RI(I > 2\sigma(I)) = 0.0717$ ,  $wR2 = 0.1851$ . Hydroxyl hydrogen atoms were refined with geometrical restraints.

## 2.5. UV-Visible analyses

Solution-state UV-visible spectra were acquired on a GBC UV/Vis 916 spectrophotometer. The solid-state reflectance UV-visible spectrum was obtained on a Jasco V-670 spectrophotometer, with ~20 mg of the solid sample spread evenly over the quartz window, and then pressed into a thin film by the black backing plate before acquisition commenced.

## 3. Results and Discussion



### 3.1 Synthetic approach

The aim of this work was to prepare and structurally characterise model complexes of known synergistic extractant systems, based on 5-hydroxy-4-octanone oxime (as an analogue of the hydroxyoxime extractant in LIX<sup>®</sup>63), and carboxylic acids (as analogues of Versatic 10). Initial attempts were made to directly prepare Ni(II) complexes with a mixture of the hydroxyoxime and carboxylic acid ligands with a Ni:hydroxyoxime:carboxylic acid stoichiometry of 1:2:2, based on previous work.<sup>[12]</sup> Solutions containing this molar ratio were made using various organic solvents including ethanol, methanol, and acetonitrile. Although isolation of the complexes as crystalline solids was attempted (in both the presence and absence of added base), these proved unsuccessful, instead yielding only oils or mixtures of solids.

Given the failure to isolate well defined crystalline materials *via* the concurrent addition of ligands, an alternative method using sequential addition of the ligands (see Experimental section) was utilised for the preparation and isolation of the mixed ligand complexes.<sup>[23]</sup> The generated solids were redissolved and successfully recrystallised in a form suitable for single crystal X-ray structure determinations.

### 3.2 Structural determination of the three nickel synergist complexes

All three structurally characterised synergist complexes exhibited a *cis*-[Ni(H<sub>2</sub>Ox)<sub>2</sub>(RCO<sub>2</sub>)<sub>2</sub>] configuration and can be considered *pseudo*-isomorphous. The X-ray crystal structure of the isobutyrate-containing complex is shown in Figure 2, with coordination geometrical parameters and hydrogen bonding parameters of the three structures listed in Table 1 and Table 2, respectively. The nickel – donor atom bond distances range from 2.01 to 2.10 Å, and are typical for a six-coordinate nickel complex. Inspection of the structural data

shows the carboxylic acid groups are coordinated as deprotonated monodentate carboxylates, and the hydroxyoxime ligands are in a neutral form, coordinated in a bidentate fashion through the oxime nitrogen atom, and the oxygen atom of the  $\alpha$ -hydroxyl group. The uncoordinated carbonyl oxygen atom of each carboxylate forms a hydrogen bond with the *cis*-adjacent oxime hydroxyl group. The locations of these H(34O) and H(44O) protons are the key determinant of which ligand is assigned as the anion, and for two of the three structures, the position of these H atoms was able to be fully refined, indicating that the H atom positions have been correctly designated. The present assignment of ligand protonation state is based on the two oxime hydroxyl O-H interatomic distances of 0.89 and 0.93 Å in the isobutyrate complex being considerably less than the 1.74 and 1.64 Å seen for the carboxylate O $\cdots$ H interatomic distances (Table 2).

*Inter*-molecular hydrogen bonding between the synergist complex molecules is also observed in the crystal lattice. In particular, bonding between the  $\alpha$ -hydroxyl protons of the hydroxyoxime ligands and the uncoordinated carboxylic acid oxygen atoms of the centrosymmetrically-related molecules at 1-x,1-y,1-z and 1-x,1-y,-z is evident. This forms a one dimensional hydrogen bonded polymer along the crystallographic *c* axis (Figure 3). As per above, inspection of Table 2 shows the two hydroxyl O-H interatomic distances of 0.89 and 0.89 Å in the isobutyrate complex are considerably less than the 1.69 and 1.74 Å seen for the carboxylate O $\cdots$ H interatomic (and inter-molecular) distances (Table 2). This inter-molecular hydrogen bonding was also observed in the other two crystal structures.

### 3.3 Structural comparison with phenolic oxime complexes

No crystal structure of a mononuclear aliphatic  $\alpha$ -hydroxyoxime metal complex has been reported previously. The vast majority of the crystal structure information currently available

for hydroxyoxime complexes involves phenolic-based systems, where the archetypal example is the square planar complex formed with two such ligands stabilised by  $\text{NOH}\cdots\text{O}$  hydrogen bonds.<sup>[16]</sup> An obvious way to add two monodentate ligands to the nickel atom is via axial coordination to the square planar complex, as in the previously proposed structure of the aliphatic hydroxyoxime-based synergist complex.<sup>[15]</sup> This expansion of the nickel coordination sphere to six donor atoms will lengthen the Ni–(O, N) bonds from  $\sim 1.8$  Å to  $\sim 2.0$  Å. This might be expected to have some impact on the hydroxyoxime ligand hydrogen bonds, but it has been shown that this hydrogen bonding persists upon the addition of axial pyridine derivatives.<sup>[24,25]</sup> If the coordination sphere is instead expanded by the addition of a bidentate, *cis*-chelating ligand, a more significant structural rearrangement is required. Such structures have been observed upon addition of an aliphatic<sup>[26]</sup> or aromatic<sup>[27]</sup> diamine, with the two salicylaldoxime ligands arranged in a ‘folded’ *cis* conformation. Despite this structural rearrangement, intra-molecular hydroxyoxime-hydroxyoxime hydrogen bonding persists. It is of interest to note that in those complexes, the oxime N atoms are arranged *cis*, and the phenolic O atoms *trans*, in contrast to the examples reported here.

Unlike all of these aforementioned phenolic oxime-based complexes, the ligand hydrogen bonding in the examples reported here is carboxylate-hydroxyoxime and not hydroxyoxime-hydroxyoxime based. To our knowledge, the only previously reported phenolic oxime-based complex structure comparable to these involves relatively exotic salicylaldoxime ligands with a protonated secondary amine side arm, along with two benzoate co-ligands.<sup>[28]</sup> In that case, the ligand geometric arrangement and inter-ligand hydrogen bonding is comparable to the present structures. Key differences are that all the coordinated O atoms are deprotonated (with the oxime ligands having a zwitterionic structure with protonated amine moieties), and the hydrogen bond structure includes supporting interactions with the amine side chains<sup>[28]</sup> as

opposed to the inter-molecular interactions seen in the present structures. Although the crystal structures show it does not occur here, it should also be noted that the “pseudo-macrocycle” that would be formed by hydrogen bonding between the two  $\alpha$ -hydroxyoxime ligands used here and akin to that seen in the phenolic oxime complexes would result in a 12-membered ring. This should intrinsically favour the folded *cis* conformation as it is known to be a poor fit for a square planar nickel(II) complex, unlike the phenolic oximes which form a 14-membered ring which favours the square planar configuration.<sup>[29]</sup>

It is important to note that the marked synergistic effect observed for the aliphatic  $\alpha$ -hydroxyoxime / carboxylic acid systems has not historically been reproduced when a phenolic-based  $\beta$ -hydroxyoxime / carboxylic acid system is used.<sup>[30]</sup> From these observations we can conclude that the difference in the synergist effect between the aliphatic  $\alpha$ -hydroxyoxime / carboxylic acid and phenolic-based  $\beta$ -hydroxyoxime / carboxylic acid systems is not due to an inherent difference in the structural chemistry capability of the various ligand classes, but must result from subtle interplay between various factors, including the protonation state of the ligands and the hydrogen bonding interactions which in turn are related to ligand geometry. An understanding of the ability of the aforementioned zwitterionic complex to behave synergistically could be instructive in clarifying the relative importance of these factors, although it should always be noted that extrapolation of the solid-state structural results to the solution phase should be treated with caution.

#### 3.4 Preliminary spectroscopic analysis of the three nickel synergist complexes

The single ligand nickel complexes and the synergist nickel complex prepared *in situ* via mixing of the commercial reagents in Shellsol D70 solvent with an aqueous nickel sulphate solution are readily distinguishable by their UV-visible spectra (Figure 4). Attempts were

therefore made to compare the visible absorption spectra of these newly synthesised products with those generated using the commercial reagents. It was found that dissolution of the model complexes in solvents such as chloroform and dichloromethane gave greenish solutions, and not the light blue colours of the solid materials. This change in colour became more prominent after allowing the solutions to stand for some hours. It is thought that this is due to partial dissociation of the complexes in solution. Despite this, a representative visible spectrum for a freshly prepared solution (Figure 5) revealed absorbance maxima at about 380 and 620 nm, which best compares to the nickel synergist complex spectrum obtained using the commercial reagents (Figure 4).

In order to try to obtain a UV-visible spectrum uncompromised by possible dissociation, a solid-state visible absorption spectrum of the complex *cis*-[Ni(H<sub>2</sub>Ox)<sub>2</sub>((CH<sub>3</sub>)<sub>2</sub>CHCO<sub>2</sub>)<sub>2</sub>] was obtained (Figure 5). This shows a more prominent absorption at ~620 nm relative to the solution spectrum. These results are consistent with the hypothesis that the light blue solids obtained are potentially representative of the synergistic complexes formed when using the corresponding commercial solvent extraction reagents.

#### 4 Conclusions

Three crystal structures have been obtained for nickel: $\alpha$ -hydroxyoxime:carboxylic acid synergist complexes. These are pseudo-isomorphous, with the *cis* coordinated carboxylate ligands present in the anionic form (extractant), and the hydroxyoximes acting as neutral bidentate ligands (synergist). The nitrogen atoms of the hydroxyoxime ligands are located *trans* to one another. Intra- and inter-molecular hydrogen bonding between the different ligands is observed in the crystal lattice.

These nickel complex crystal structures, the first ever determined containing aliphatic  $\alpha$ -hydroxyoxime ligands directly comparable to that present in LIX<sup>®</sup>63, are the strongest structural information obtained to date on these interesting mixed-ligand synergistic systems and therefore represent a material advance in the understanding of the coordination chemistry possible in these types of synergistic systems. However, it needs to be stressed that at this stage these results are only illustrative of the solid state nickel synergist complex and are not necessarily representative of what exists in solution. Procurement and reconciliation of additional spectroscopic data of the isolated solids (both as solids and in solution) and the 'real' system is still required. Such work is currently in progress, using the crystal structures as a structurally defined reference point. Extension of this model work to other metals is also in progress and will be reported in due course, along with results from density functional theory (DFT) analysis of these and related complexes.

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### **References**

1. Kordosky, G.A. Copper recovery using leach / solvent extraction / electrowinning technology: forty years of innovation, 2.2 million tonnes of copper annually. In *Proc.*

- ISEC 2002*; Sole, K.C., Cole, P.M., Preston, J.S., Robinson, D.J., Eds.; Chris van Rensburg Publications (Pty) Ltd: South Africa, 2002; 853-862.
2. Joe, E.G.; Ritcey, G.M.; Ashbrook, A.W. Uranium & copper extraction by liquid ion exchange. *J. Metals*, **1966**, *18* (1), 18-21.
  3. Osseo-Asare, K.; Keeney, M.E. Aspects of the interfacial chemistry of nickel extraction with Lix63-HDNNS mixtures. *Metall. Trans. B-Process Metallurgy*, **1980**, *11* (1), 63-67.
  4. Osseo-Asare, K.; Keeney, M.E. Sulfonic-acids - catalysts for the liquid-liquid-extraction of metals. *Sep. Sci. Technol.*, **1980**, *15* (4), 999-1011.
  5. Osseo-Asare, K.; Renninger, D.R. Synergic extraction of nickel and cobalt by Lix63-dinonylnaphthalene sulfonic-acid mixtures. *Hydrometallurgy*, **1984**, *13* (1), 45-62.
  6. Zheng, Y.; Osseo-Asare, K. The selectivity of nickel over iron in the LIX 63-HDNNS solvent extraction system. *Solvent Extr. Ion Exch.*, **1985**, *3* (6), 825-837.
  7. Miyake, Y.; Nakata, Y.; Suzuki, T.; Teramoto, M. Synergistic extraction of metal ion with LIX63 in microemulsion system. In: *Solvent extraction 1990: Proc. ISEC '90*; Sekine, T. Ed.; Elsevier, Japan, 1992; 823-828.
  8. Elizalde, M.P.; Cox, M.; Aguilar, M. Synergistic extraction of Ni(II) by mixtures of Lix 63 and bis-(2-ethylhexyl)phosphoric or di-n-octylphosphinic acids in toluene. *Solvent Extr. Ion Exch.*, **1996**, *14* (5), 833-48.
  9. Yamashita, K.; Kakoi, T.; Kosaka, H.; Goto, M.; Nakashio, F. Synergistic extraction of nickel by liquid surfactant membranes. *Sep. Sci. Technol.*, **1998**, *33* (3), 369-85.
  10. Flett, D.S.; Titmuss, S. Synergistic effect of LIX63 on the extraction of copper and cobalt by naphthenic acid. *J. Inorg. Nucl. Chem.*, **1969**, *31* (8), 2612-3.

11. Flett, D.S.; West, D.W. Extraction of metal ions by LIX63/carboxylic acid mixtures. In *Proc. Int. Solv. Extr. Conf.*; Gregory, J.G., Evans, B., Weston, P.C. Eds.; Soc. Chem. Ind., London, 1971; Vol. 1, 214-223.
12. Flett, D.S., Cox, M., Heels, J.D. Extraction of nickel by  $\alpha$ -hydroxy oxime/lauric acid mixtures. In *Proc. ISEC '74*; Jeffreys, G.V. Ed.; Soc. Chem. Ind., London, 1974; Vol 3, 2560-2575.
13. Elizalde, M.P.; Castresana, J.M.; Aguilar, M.; Cox, M. Synergic extraction of Ni(II) by mixtures of 5,8-diethyl-7-hydroxydodecan-6-oxime and n-dodecanoic acid in toluene. *Solvent Extr. Ion Exch.*, **1986**, 4 (6), 1095-1107.
14. Tammi, T. Extraction of nickel and cobalt with hydroxyoxime-containing extraction agents. *Tutkimus Tek*, **1976**, 4, 44-5.
15. Castresana, J.M.; Elizalde, M.P.; Aguilar, M.; Cox, M. Synergistic extraction of nickel by mixtures of alpha-hydroxyoximes and carboxylic-acids. *Solvent Extr. Ion Exch.*, **1988**, 6 (2), 265-274.
16. Smith, A.G.; Tasker, P.A.; White, D.J. The structures of phenolic oximes and their complexes. *Coord. Chem. Rev.*, **2003**, 241 (1-2), 61-85.
17. Keeney, M.E.; Osseo-Asare, K.; Woode, K.A. Transition-metal hydroxyoxime complexes. *Coord. Chem. Rev.*, **1984**, 59, 141-201.
18. Barnard, K.R. LIX<sup>®</sup>63 stability in the presence of Versatic 10 under proposed commercial extract and strip conditions, part I: Operation at high temperature. *Hydrometallurgy*, **2008**, 91, 1-10.
19. Barnard, K.R.; Turner, N.L. LIX<sup>®</sup>63 stability in the presence of Versatic 10 under proposed commercial extract and strip conditions, part II: Oxime isomer inter-



- conversion and the effect of oxime degradation products on selected physical properties. *Hydrometallurgy*, **2008**, *91*, 11-19.
20. Cheng, C.Y. Solvent extraction of nickel and cobalt with synergistic systems consisting of carboxylic acid and aliphatic hydroxyoxime. *Hydrometallurgy*, **2006**, *84*, 109-117.
  21. Keeney, M.E.; Osseo-Asare, K. Synthesis and characterization of copper and nickel-complexes of Lix63 oxime. *Polyhedron*, **1984**, *3* (6), 641-649.
  22. Sheldrick, G.M. A short history of SHELX. *Acta Cryst.*, **2008**, *A64*, 112-122.
  23. Cox, M. Private communication, **2007**.
  24. Ma, Y.; Zhang, W.; Xu, G.F.; Yoshimura, K.; Liao, D.Z.; Jiang, Z.H.; Yan, S.P. Synthesis, structure and magnetic properties of a novel nickel(II) radical heterospin complex with salicylaldoxime. *Z. Anorg. Allg. Chem.*, **2007**, *633*, 657-660.
  25. Ma, Y.; Zhang, W.; Ou-Yang, Y.; Yoshimura, K.; Liao, D.Z.; Jiang, Z.H.; Yan, S.P. A three-spin complex [Ni(Salox)(2)(Im4py)(2)] containing salicylaldoxime and nitronyl nitroxide: structure and magnetic properties. *J. Mol. Struct.* **2007**, *833*, 98-101.
  26. Hultgren, V.M.; Atkinson, I.M.; Beddoes, R.L.; Collison, D.; Garner, C.D.; Helliwell, M.; Lindoy, L.F.; Tasker, P.A. Formation of folded complexes retaining intramolecular H-bonding in the extraction of nickel(II) by phenolic oxime and aliphatic diamine ligands. *Chem. Commun.*, **2001**, 573-574.
  27. Lalia-Kantouri, M.; Hatzidimitriou, A.; Uddin, M. Synthesis and characterization of new addition compounds of bis(2-hydroxyaryloximato) nickel(II) with alpha-diimines. Crystal and molecular structure of [Ni(saox)<sub>2</sub>phen].H<sub>2</sub>O. *Polyhedron*, **1999**, *18*, 3441-3450.

28. Henderson, D.K.; Davidson, J.E.; Tasker, P.A.; Parson, S.; White, F. Private communication to the Cambridge Structural Database, deposition number CCDC 660851, **2007**.
29. Bianchi, A.; Micheloni, M.; Paoletti, P. Thermodynamic aspects of the polyazacycloalkane complexes with cations and anions. *Coord. Chem. Rev.*, **1991**, *110*, 17-113.
30. Szymanowski, J.; Borowiakresterna, A. Chemistry and analytical characterization of the effect of hydroxyoxime structure upon metal-complexing and extraction properties. *Crit. Rev. Anal. Chem.*, **1991**, *22*, 519-566.

Table 1 Selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ]

	$[\text{Ni}(\text{H}_2\text{Ox})_2(\text{CH}_3\text{CO}_2)_2]$	$[\text{Ni}(\text{H}_2\text{Ox})_2((\text{CH}_3)_2\text{CHCO}_2)_2]$	$[\text{Ni}(\text{H}_2\text{Ox})_2((\text{C}_6\text{H}_5\text{CO}_2)_2)]$
Ni(1)-O(21)	2.0257(13)	2.0089(18)	2.032(4)
Ni(1)-O(11)	2.0322(17)	2.0338(17)	2.022(4)
Ni(1)-N(34)	2.0571(18)	2.063(2)	2.033(5)
Ni(1)-N(44)	2.0610(19)	2.056(2)	2.042(4)
Ni(1)-O(45)	2.0762(17)	2.1020(18)	2.073(4)
Ni(1)-O(35)	2.0826(14)	2.0676(19)	2.099(4)
C(11)-O(11)	1.248(3)	1.249(3)	1.241(6)
C(11)-O(12)	1.273(3)	1.274(3)	1.269(6)
C(21)-O(21)	1.250(2)	1.257(3)	1.261(6)
C(21)-(O22)	1.273(2)	1.267(3)	1.265(6)
O(21)-Ni(1)-O(11)	91.29(6)	88.96(7)	91.40(16)
O(21)-Ni(1)-N(34)	103.93(6)	103.28(8)	103.82(16)
O(11)-Ni(1)-N(34)	84.47(7)	85.31(8)	84.92(16)
O(21)-Ni(1)-N(44)	90.47(6)	87.62(8)	83.70(16)
O(11)-Ni(1)-N(44)	104.64(7)	103.17(8)	103.41(15)
N(34)-Ni(1)-N(44)	162.91(7)	166.44(8)	168.79(18)
O(21)-Ni(1)-O(45)	87.05(6)	88.34(7)	91.52(15)
O(11)-Ni(1)-O(45)	177.71(6)	177.24(8)	176.97(16)
N(34)-Ni(1)-O(45)	94.39(7)	94.77(8)	95.17(16)
N(44)-Ni(1)-O(45)	76.96(7)	77.28(8)	76.12(15)
O(21)-Ni(1)-O(35)	177.15(8)	177.48(8)	178.55(16)
O(11)-Ni(1)-O(35)	91.47(6)	93.25(7)	90.05(16)
N(34)-Ni(1)-O(35)	77.03(6)	78.14(8)	76.28(16)
N(44)-Ni(1)-O(35)	88.16(6)	78.14(8)	96.00(16)
O(45)-Ni(1)-O(35)	90.21(6)	89.46(7)	87.03(16)

Table 2 Hydrogen bonding parameters [ $\text{\AA}$  and  $^\circ$ ].

D-H...A	d(D-H)	d(H...A)	d(D...A)	$\angle(\text{DHA})$
[Ni(H <sub>2</sub> Ox) <sub>2</sub> (CH <sub>3</sub> CO <sub>2</sub> ) <sub>2</sub> ]				
O(34)-H(34O)...O(22)	0.83(2)	1.77(3)	2.599(2)	175(3)
O(35)-H(35O)...O(12) <sup>1</sup>	0.80(2)	1.79(2)	2.584(2)	171(2)
O(44)-H(44O)...O(12)	0.89(3)	1.70(3)	2.595(3)	174(3)
O(45)-H(45O)...O(22) <sup>2</sup>	0.84(2)	1.78(3)	2.623(2)	174(3)
Symmetry transformations used to generate equivalent atoms: <sup>1</sup> 1-x,1-y,1-z ; <sup>2</sup> 1-x,1-y,-z				
[Ni(H <sub>2</sub> Ox) <sub>2</sub> ((CH <sub>3</sub> ) <sub>2</sub> CHCO <sub>2</sub> ) <sub>2</sub> ]				
O(34)-H(34O)...O(22)	0.89(3)	1.74(3)	2.621(3)	166(3)
O(35)-H(35O)...O(12) <sup>1</sup>	0.89(3)	1.69(3)	2.576(2)	171(3)
O(44)-H(44O)...O(12)	0.93(3)	1.64(3)	2.565(2)	174(3)
O(45)-H(45O)...O(22) <sup>2</sup>	0.89(3)	1.74(3)	2.613(3)	166(3)
Symmetry transformations used to generate equivalent atoms: <sup>1</sup> 1-x,1-y,1-z ; <sup>2</sup> 1-x,1-y,-z				
[Ni(H <sub>2</sub> Ox) <sub>2</sub> (C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> ) <sub>2</sub> ]				
O(34)-H(34O)...O(22)	0.89(4)	1.71(4)	2.595(6)	172(6)
O(35)-H(35O)...O(12) <sup>1</sup>	0.80(4)	1.85(4)	2.638(5)	168(7)
O(44)-H(44O)...O(12)	0.81(4)	1.79(4)	2.597(5)	171(6)
O(45)-H(45O)...O(22) <sup>2</sup>	0.83(4)	1.82(5)	2.605(5)	157(7)
Symmetry transformations used to generate equivalent atoms: <sup>1</sup> 1-x,1-y,1-z ; <sup>2</sup> 1-x,-y,1-z				

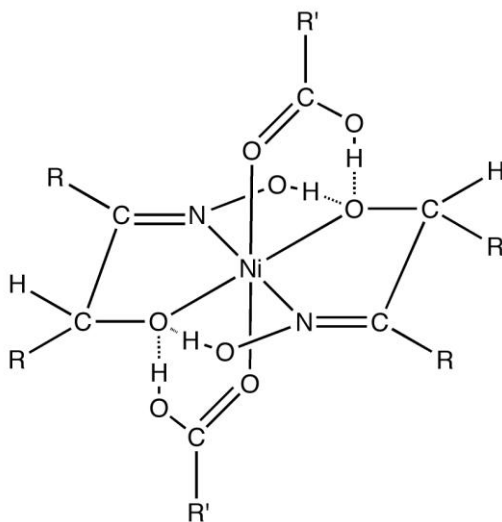


Figure 1 Previously proposed structure of the  $\text{Ni}(\alpha\text{-hydroxyoximato})_2(\text{carboxylic acid})_2$  assembly formed on extraction by synergist mixtures (Adapted from Castresana et al., 1988).

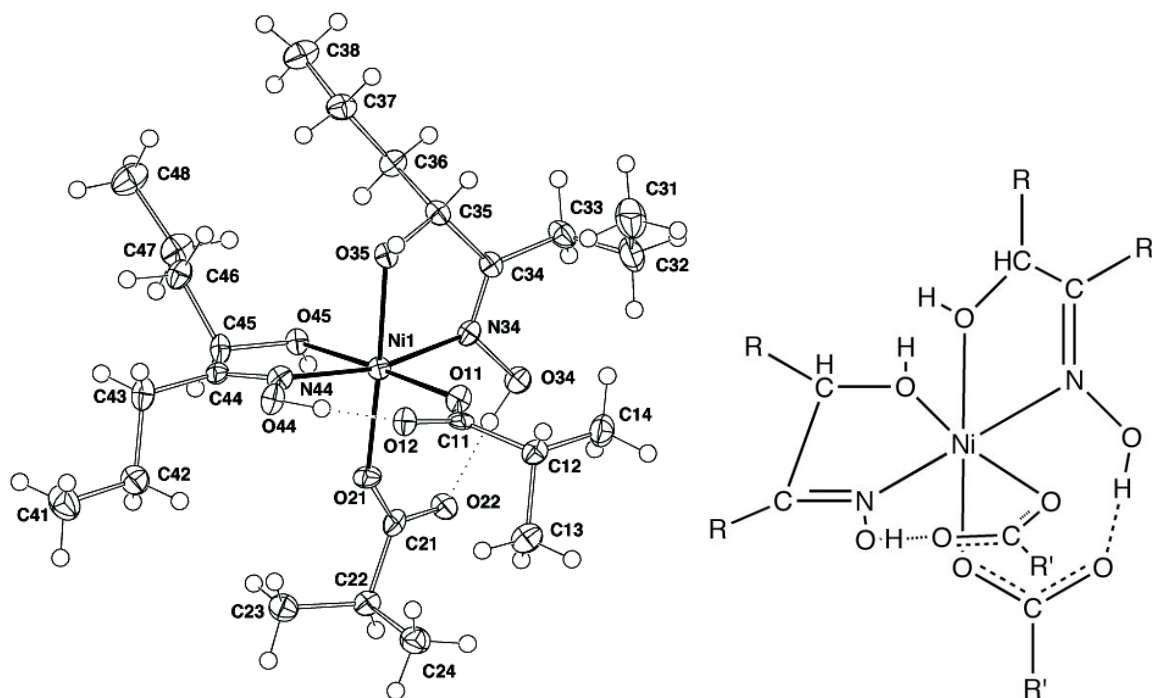


Figure 2 Structure and schematic representation of  $cis-[Ni(H_2Ox)_2((CH_3)_2CHCO_2)_2]$ .

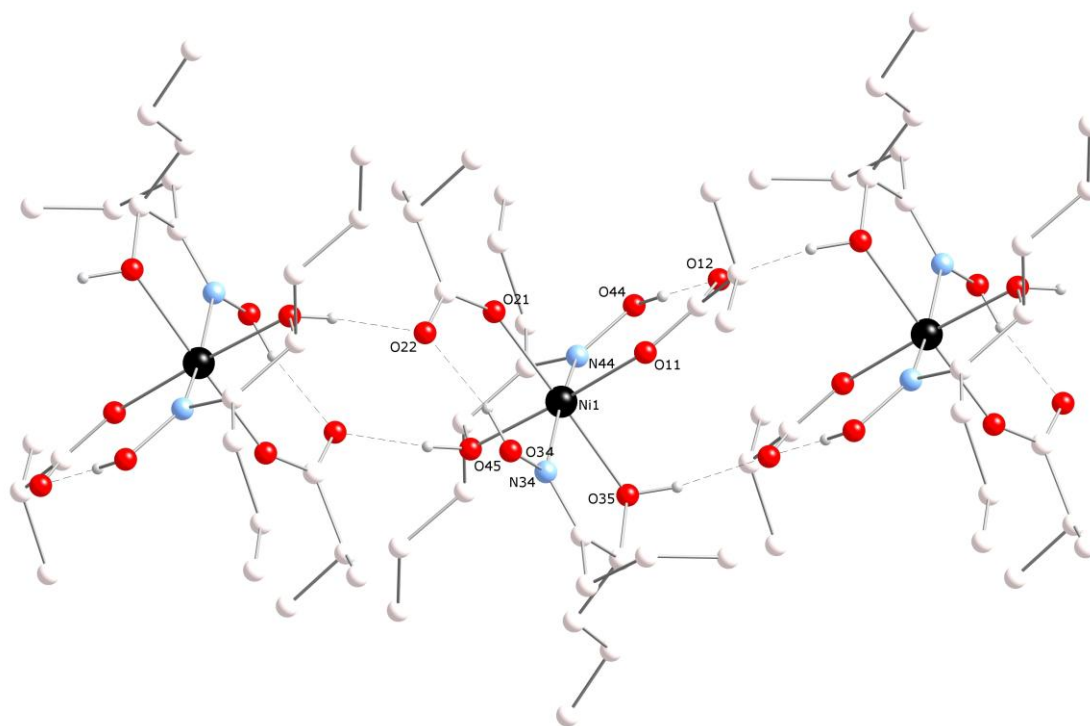


Figure 3 A simplified view of the one-dimensional hydrogen bond polymer formed in *cis*- $[\text{Ni}(\text{H}_2\text{O})_2((\text{CH}_3)_2\text{CHCO}_2)_2]$  along the *c*-axis.

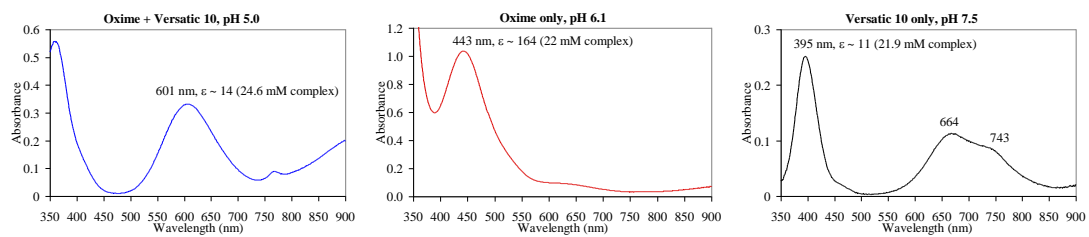


Figure 4 UV-visible spectra of nickel complexes formed *in situ* using the commercially available reagents.



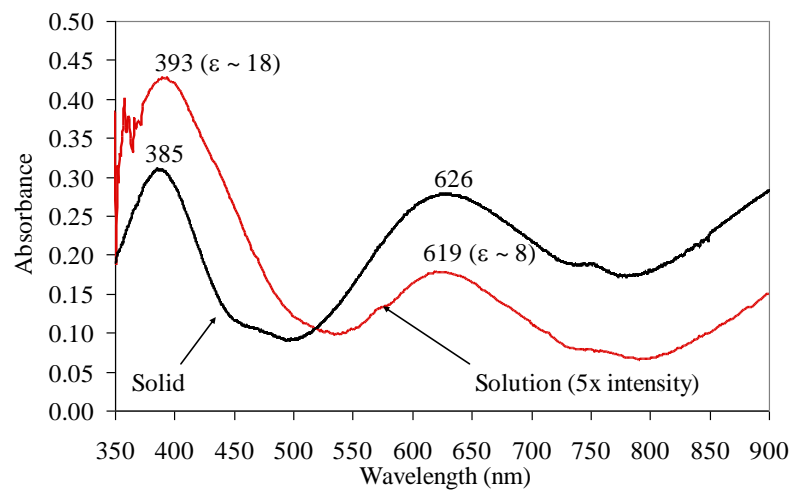


Figure 5 Solution and solid state visible spectra for *cis*-[Ni(H<sub>2</sub>Ox)<sub>2</sub>((CH<sub>3</sub>)<sub>2</sub>CHCO<sub>2</sub>)<sub>2</sub>]. The solution spectrum was obtained in chloroform (molar absorptivity values approximate, conc. ~ 2 mg/mL).