

**AN INVESTIGATION OF SOME HOMO-
AND HETEROBINUCLEAR COMPLEXES
OF COPPER(II) AND NICKEL(II)
WITH PYRIDINE-2-ALDOXIME***

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The reactions between copper(II) or nickel(II) with the *cis*-pyridine-2-aldoxime complexes of the same metal ions have been investigated by spectrophotometric measurements. The homo and heterobinuclear chelates involved have been isolated as the chlorides and characterized by spectroscopic and thermoanalytical techniques. The first decomposition step is not dependent on the furnace atmosphere (N_2 or O_2) and is accompanied by a large exothermic effect (DSC curves in N_2). TG curves show that binuclear complexes are generally slightly less stable than the respective mononuclear complexes but, in the case of $[Cu(NiL_2)Cl_2(H_2O)_2]$, the complexation of copper(II) gives rise a drastic decrease of its thermal stability.

Liu et al. [1] prepared some homo- and heterobinuclear chelates using *cis* bis(pyridine-2-aldoxime) copper(II), palladium(II) and platinum(II) complexes as chelating agents. The authors have shown that the neutralization of the compounds of palladium and platinum ions results in the inner complex, that is the oxime hydrogens on both of the ligand molecules were lost, while the neutralization of the analogous compound of copper ion yields homopolynuclear chelates.

Following thermoanalytical studies of the complexes of 3d metal ions with pyridinealdoximes [2, 3], the present investigation is concerned with homo- and heterobinuclear chelates obtained by the reaction of the "metal-complex" chelating agents *cis* bis(pyridine-2-aldoxime) copper(II) and nickel(II) with the ions of the same metals.

In this paper the synthesis, spectroscopic characteristics (visible, IR and diffuse reflectance) and thermal properties (as determined by thermogravimetry (TG), differential thermogravimetry (DTG) and differential scanning calorimetry (DSC)) of the compounds are described.

* This work was carried out with financial support by MPI National Project.

Experimental

Apparatus

Thermal measurements were carried out with a Perkin-Elmer TGS-2 thermal analyser and DSC-7 differential scanning calorimeter connected by Model 3600 Data Station equipped with the software package designed to run on the Data Station.

TG and DSC runs were made in a stream of nitrogen or oxygen (flow rate about 50 ml/min); the heating rate was 10 deg/min, with samples of 0.5–2 mg.

The reflectance, IR and visible spectra were recorded using a Beckman DGB spectrophotometer, a Perkin-Elmer 125 grating infrared spectrophotometer and a Perkin-Elmer 320 UV-Vis spectrophotometer.

Magnetic susceptibilities were determined at room temperature using a modified Mettler analytical balance at 8000 G field strength.

The acidity of the solutions was checked with an Amel 333 pH meter equipped with an Ingold type 201 glass electrode and an Ingold type 202 calomel reference electrode.

Reagents

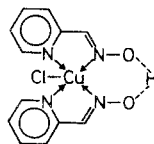
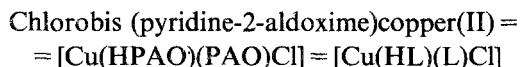
Pyridine-2-aldoxime (HPAO, HL) was a purum grade product of "Aldrich" and was used without further purification.

Copper(II) and nickel(II) salts were in the form of chloride di- and hexahydrate, respectively.

All other chemicals were of analytical-reagent grade.

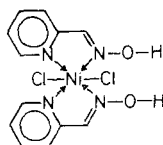
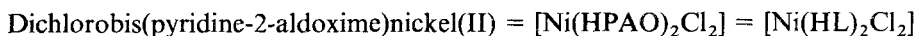
Compounds

"Metal-complex" chelating agents



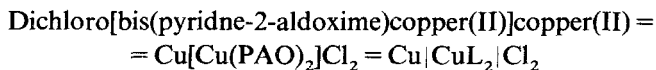
was prepared and analysed as described earlier [2]. A 0.1% aqueous solution of the complex is green and its pH is about 4.3; increasing the pH of this solution the absorption maximum at 596 nm is shifted bathochromically to 628 nm with hyperchromic effect. The IR spectrum exhibits bands at 1545 cm^{-1} $\nu(\text{C}=\text{N})$ and

1130 cm^{-1} $\nu(\text{N—O})$ proving that this complex contains both —C=N—OH and —C=N—O groups [4]. The diffuse reflectance spectrum (bands at 15,380 cm^{-1} and 25,000 cm^{-1}) shows that copper ion is either in an essentially square planar environment, or in an octahedral environment with a very large tetragonal distortion and it is coordinated to the organic ligands *via* the pyridine and the oxime nitrogen atoms.



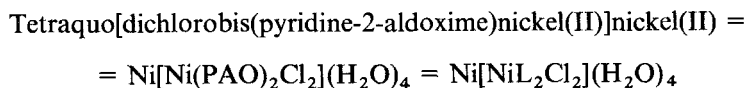
was prepared by adding a solution of the ligand (HPAO) (0.02 mole in about 50 ml of 95% ethanol) to a solution of nickel(II) chloride (0.01 mole in about 50 ml of 95% ethanol). The light-blue-green precipitate, which forms rapidly, was filtered, washed with ethanol first and then with diethyl ether; finally dried in vacuo over silica gel. The results of analysis, performed as described [2], were in agreement with the proposed formula; the nickel content was determined by atomic absorption spectrophotometry. A 0.1% aqueous solution of the complex is pale yellow and its pH is about 3.8; increasing the pH of the solution the colour turns to orange-yellow and its intensity increases to pH = 7.5 and then decreases. The potentiometric titration of the aqueous solution of the complex shows the presence of two moles of acid hydrogen per mole of complex and the successive dissociation constants, calculated *via* spectrophotometric analysis as described below proves the *cis* configuration of the complex [5]. The IR spectrum agrees with that reported by Krause et al. [6]. It shows bands in the region 3200–3000 cm^{-1} , at 1654 cm^{-1} and 1056 cm^{-1} , which can be assigned to —OH , —C=N— and N—O stretching frequencies, respectively, as expected for the complexes containing only non-ionized oxime groups. The magnetic moment of this complex is that generally observed for regular octahedral nickel(II) compounds, being 3.00 BM; this hypothesis is confirmed by the diffuse reflectance spectrum that exhibits absorption bands at 11,000 cm^{-1} [${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$], 17,000 cm^{-1} [${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$] and 27,000 cm^{-1} [${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$].

Homobinuclear chelates

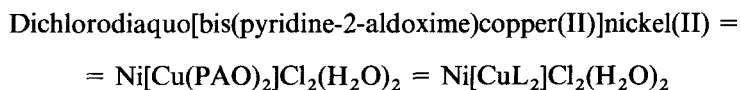


was prepared by adding a solution (0.005 mole in 150 ml of 95% ethanol) of the "metal complex" chelating agent ($[\text{Cu}(\text{HL})(\text{L})\text{Cl}]$), which was neutralized with the

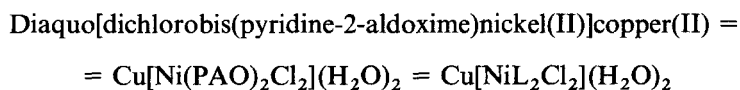
required amount of 0.5 mol/l aqueous NaOH solution, to a solution of copper(II) chloride (0.005 mole in 75 ml of 95% ethanol). The mixture was allowed to stand, with stirring, for two hours at least. A dark green precipitate formed which was filtered, washed with ethanol, then with diethyl ether and finally dried in vacuo over silica gel. The results of analysis of the compound were in agreement with the proposed formula. A 0.1% aqueous solution of the complex is dark green and its pH is 4.8. The visible spectrum of this solution shows a maximum at 630 nm which remains unmodified at increasing pH. On the contrary it is shifted bathochromically ($\lambda = 672$ nm) with increasing copper concentration probably because other polynuclear complexes are formed. The diffuse reflectance spectrum in the visible region is similar to that of the mononuclear complex of copper (bands at $15,380\text{ cm}^{-1}$ and $26,600\text{ cm}^{-1}$), whereas in the IR spectrum the band observed at about 3000 cm^{-1} , $\nu(\text{OH})$ is absent proving that the second copper ion is chelated to both the oximate groups with release of the proton.



was prepared by adding a solution (0.005 mole in 50 ml of 95% ethanol) of $[\text{Ni}(\text{HL})_2\text{Cl}_2]$ complex, which was neutralized with the required amount of DMB (N,N-dimethylbenzylamine), to a solution of nickel(II) chloride (0.005 mole in 20 ml of 95% ethanol). A yellow-brown compound precipitated on adding diethyl ether to the solution. The compound was washed with 1 : 1 absolute ethanol-diethyl ether mixture, then with diethyl ether and finally dried in vacuo over silica gel. The results of analysis of the compound were in agreement with the proposed formula; the water content was determined by thermal analysis. A 0.1% aqueous solution of the complex is pale yellow and its pH is 6.9; this solution does not show characteristic spectrum in the visible region, but only a shoulder at 440 nm. The IR spectrum exhibits a broad band at about 3400 cm^{-1} due to the four water molecules coordinated; the band in the region $3200\text{--}3000\text{ cm}^{-1}$, $\nu(\text{OH})$ is absent whereas $\nu(\text{C}=\text{N})$ and $\nu(\text{N}=\text{O})$ bands are shifted to 1540 cm^{-1} and 1120 cm^{-1} proving that the second nickel atom is coordinated to the organic ligand *via* the oxime oxygen atoms with release of protons. The lower value of the magnetic moment (2.65 MB) than that found for the $[\text{Ni}(\text{HL})_2\text{Cl}_2]$ complex within the diffuse reflectance spectrum that exhibits a very strong absorption band in the region between $20,000\text{--}30,000\text{ cm}^{-1}$, as expected for square planar derivatives of nickel(II), suggests that the octahedral structure of the mononuclear complex is tetragonally distorted by the bonding of the second nickel ion.

Heterobinuclear chelates

was prepared and analyzed according to the procedure described for homodinuclear complex of copper(II), except that in this case a solution of nickel(II) chloride was used. A 0.1% aqueous solution of the complex was green and its pH was 6.1; this solution absorbs in the visible region with a maximum at 630 nm. The diffuse reflectance and IR spectra are similar to those of the homobinuclear chelate of copper ion; the broad band at about 3400 cm^{-1} is attributed to the coordinated water molecules.



was prepared and analyzed according to the procedure described for the homodinuclear complex of copper(II), except that in this case a solution of $[\text{Ni}(\text{HL})_2\text{Cl}_2]$ complex was used. A 0.1% aqueous solution of the complex was green and its pH was 6.1. The spectroscopic characteristics are like those of the heterobinuclear chelate reported above.

Results and discussion*Equilibria in aqueous solution*

The acid-base equilibria of both the "metal-complex" chelating agents and its complexing reactions with nickel(II) and copper(II) ions have been investigated by visible spectrophotometry.

The stability constants and the molar absorptivities of the complexes at selected wavelengths were calculated by graphical analysis of the absorbance vs. acidity plots, carried out using the usual equations [7].

The results are reported in Table 1.

The large ratio of the first to the second ionization constants of the "metal complex" chelating agents suggests an intramolecular hydrogen bond which is possible only when the compounds are in the *cis* configuration.

The complexing reactions occur *via* release of protons proving that the second metal ion is chelated through both the oximate groups forming a six-membered ring.

The $[\text{Cu}(\text{NiL}_2)]$ complex is much more stable than $[\text{Cu}(\text{CuL}_2)]$ and $[\text{Ni}(\text{CuL}_2)]$ which can be understood considering the higher basicity of the oximate groups of

Table 1 Molar absorptivities and equilibrium constants in 0.05 M NaCl aqueous solution; $T = 25.0 \pm 0.2$ °C*

Equilibria**	Log constants	Species**	ϵ , l Mol ⁻¹ cm ⁻¹ (λ , nm)
$[\text{Cu}(\text{HL})_2] = [\text{Cu}(\text{HL})\text{L}] + \text{H}$	-2.77 (ref. 4)	$[\text{Cu}(\text{HL})\text{L}]$	100 ± 3 (628)
$[\text{Cu}(\text{HL})\text{L}] = [\text{CuL}_2] + \text{H}$	-6.70 (ref. 4)	$[\text{CuL}_2]$	243 ± 5 (628)
	-6.84 \pm 0.05		
$[\text{Ni}(\text{HL})_2] = [\text{Ni}(\text{HL})\text{L}] + \text{H}$	-5.86 \pm 0.05	$[\text{Ni}(\text{HL})_2]$	17 ± 2 (440)
$[\text{Ni}(\text{HL})\text{L}] = [\text{NiL}_2] + \text{H}$	-8.96 \pm 0.05	$[\text{Ni}(\text{HL})\text{L}]$	194 ± 3 (440)
		$[\text{NiL}_2]$	97 ± 3 (440)
$\text{Cu} + [\text{Cu}(\text{HL})\text{L}] = [\text{Cu}(\text{CuL}_2)] + \text{H}$	-0.27 \pm 0.06		
$\text{Cu} + [\text{CuL}_2] = [\text{Cu}(\text{CuL}_2)]$	6.57 \pm 0.11	$[\text{Cu}(\text{CuL}_2)]$	280 ± 5 (630)
$\text{Ni} + [\text{Cu}(\text{HL})\text{L}] = [\text{Ni}(\text{CuL}_2)] + \text{H}$	-0.65 \pm 0.09		
$\text{Ni} + [\text{CuL}_2] = [\text{Ni}(\text{CuL}_2)]$	6.19 \pm 0.14	$[\text{Ni}(\text{CuL}_2)]$	188 ± 3 (630)
$\text{Cu} + [\text{Ni}(\text{HL})_2] = [\text{Cu}(\text{NiL}_2)] + 2\text{H}$	-5.43 \pm 0.07		
$\text{Cu} + [\text{NiL}_2] = [\text{Cu}(\text{NiL}_2)]$	9.39 \pm 0.17	$[\text{Cu}(\text{NiL}_2)]$	148 ± 2 (630)

* The reported values are the average of at least four measurements; the error is expressed by the mean deviation.

** Charges and coordinated inorganic ligands are omitted.

the $[\text{NiL}_2]$ "metal-complex" chelating agent than those of $[\text{CuL}_2]$. The $[\text{Cu}(\text{CuL}_2)]$ complex is slightly more stable than $[\text{Ni}(\text{CuL}_2)]$ according to the stability order found by Irving and Williams [9] for the complexes in solution. Unfortunately it has been impossible to determine the stability constant of $[\text{Ni}(\text{NiL}_2)]$ complex because it does not absorb in the visible region.

Thermal studies

The results of thermal analysis (TG, DTG and DSC) are summarized in Table 2; TG and DSC curves of the binuclear complexes are reported in Figs 1 and 2.

The complexes which have coordinated water molecules show a continuous slow mass loss which begins at about room temperature and is complete just before the decomposition of the complexes. The dehydration reaction is quite reversible so that, stopping the heating at an appropriate temperature and cooling the sample in air, the water molecules are entirely recovered.

The first decomposition step of all the studied complexes is not dependent on the furnace atmosphere and is accompanied by a large exothermic effect (DSC curves), probably because of a structural rearrangement that produces a thermally stable intermediate. The ΔH values, calculated in nitrogen atmosphere, show that the mononuclear complex of nickel(II) and its binuclear derivatives have the highest energetic gain during this decomposition step. The chemical and spectroscopic

Table 2 TG and DSC analytical data of mono- and binuclear complexes of pyridine-2-aldoxime with copper(II) and nickel(II)

Compounds	TG						DSC		
	Gas	H ₂ O loss %		1 st decomp. step		Residual oxide %		1 st decomp. step T, °C	ΔH, kJ/mol
		T, °C	calcd.	found	T, °C	mass loss %	T, °C		
[Cu(HL)(L)Cl]	N ₂	205			41		173-208		-137
		175-215							
Cu[CuL ₂]Cl ₂	O ₂	205			42	390	23.2	23.0	
		175-210							
Cu[CuL ₂]Cl ₂	N ₂	195			21		162-230		-179
		165-220							
Cu[CuL ₂]Cl ₂	O ₂	195			17	400	36.1	35.6	
		165-240							
Ni[CuL ₂]Cl ₂ (H ₂ O) ₂	N ₂	70	7.6	7.0	26		190-273		-142
		30-140							
Ni[CuL ₂]Cl ₂ (H ₂ O) ₂	O ₂	70	7.6	7.5	14	600	32.7	33.0	
		30-140							
[Ni(HL) ₂ Cl ₂]	N ₂	270			22		256-294		-248
		250-290							
[Ni(HL) ₂ Cl ₂]	O ₂	280			18	575	20.0	19.0	
		260-290							
Ni[NiL ₂ Cl ₂](H ₂ O) ₄	N ₂	65	14.3	14.0	15		255-348		-227
		30-245							
Ni[NiL ₂ Cl ₂](H ₂ O) ₄	O ₂	65	14.3	14.0	12	575	29.7	29.0	
		30-245							
Cu[NiL ₂ Cl ₂](H ₂ O) ₂	N ₂	60	7.6	7.0	23		170-283		-306
		30-125							
Cu[NiL ₂ Cl ₂](H ₂ O) ₂	O ₂	65	7.6	7.0	13	475	32.7	33.0	
		30-125							

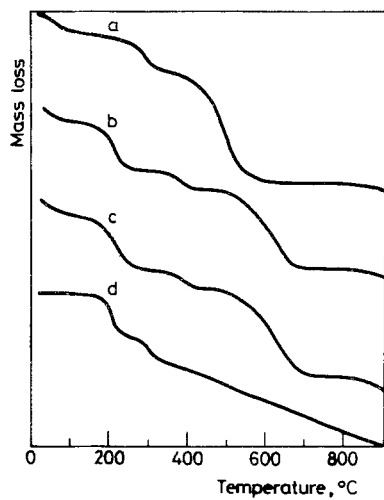


Fig. 1 TG curves in nitrogen atmosphere for: a) $\text{Ni}[\text{NiL}_2\text{Cl}_2](\text{H}_2\text{O})_4$; b) $\text{Ni}[\text{CuL}_2]\text{Cl}_2(\text{H}_2\text{O})_2$; c) $\text{Cu}[\text{NiL}_2\text{Cl}_2](\text{H}_2\text{O})_2$; d) $\text{Cu}[\text{CuL}_2]\text{Cl}_2$

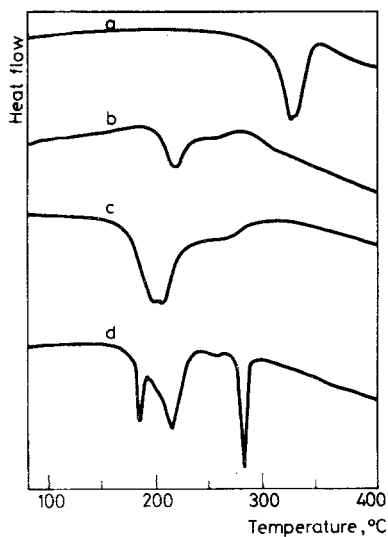


Fig. 2 DSC curves in nitrogen atmosphere for: a) $\text{Ni}[\text{NiL}_2\text{Cl}_2](\text{H}_2\text{O})_4$; b) $\text{Ni}[\text{CuL}_2]\text{Cl}_2(\text{H}_2\text{O})_2$; c) $\text{Cu}[\text{NiL}_2\text{Cl}_2](\text{H}_2\text{O})_2$; d) $\text{Cu}[\text{CuL}_2]\text{Cl}_2$

analyses of the intermediate at 230° of the mononuclear complex of copper(II) have shown the rearrangement of the organic ligand into acid amide [2]; on the contrary, none of the other intermediates shows this behaviour probably because of higher decomposition temperatures and/or of the second metal ion chelated on the oxygen atoms.

The successive thermal decomposition process involves unresolved steps and, in oxygen atmosphere, occurs more rapidly than in nitrogen atmosphere, the sample reaching a constant weight which corresponds to the stoichiometric formation of the oxide of the metal ions. In nitrogen atmosphere the residue continues to lose mass at a slow rate up to about 800°; the difference between the calculated (for metallic copper and/or nickel) and found weight is due to the sublimation of metal-containing volatile compounds formed during the thermal treatment.

Analysis of the evolved gas provides evidence of chloride ions only in the last decomposition step, except for the mononuclear complex of nickel(II) which loses one mole of chloride per mole of complex between 290–330°.

Conclusion

Studies on the equilibria in aqueous solution prove that the *cis* pyridine-2-aldoxime complex of copper(II) or nickel(II) can act as chelating agents forming homo- and heterobinuclear complexes. The second metal ion is chelated through both the oximate groups forming a six-membered ring. $[\text{Cu}(\text{NiL}_2)]$ is the most stable among the investigated complexes.

A comparison of the initial decomposition temperature of mononuclear complexes shows that the nickel(II) compound is more stable than the copper(II) compound proving, as it has been found in previous studies [8], the thermal unstabilizing effect of copper(II) ion. The homo- and heterobinuclear complexes are slightly less stable than the respective "metal-complex" chelating agents, but, in the case of $\text{Cu}[\text{NiL}_2\text{Cl}_2](\text{H}_2\text{O})_2$ the complexation of copper(II) ion gives rise to a drastic decrease of the thermal stability.

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Zusammenfassung — Die Reaktionen zwischen Kupfer(II) und Nickel(II) mit den cis-Pyridin-2-aldoxim-Komplexen der gleichen Metallionen wurden spektrophotometrisch untersucht. Die homo- und heterobinuklearen Chelate wurden als Chloride isoliert und durch spektroskopische und thermoanalytische Methoden charakterisiert. Der erste Zersetzungsschritt ist unabhängig von der Ofenatmosphäre (N_2 oder O_2) und ist stark exotherm (s. DSC-Kurven in Abb. 1). Die TG-Kurven lassen erkennen, dass zweikernige Komplexe im allgemeinen etwas weniger stabil als die entsprechenden einkernigen Komplexe sind, im Falle von $[Cu(NiL_2)Cl_2(H_2O)_2]$, aber die Anlagerung von Liganden an das Kupfer zu einer drastischen Verminderung der Stabilität führt.

Резюме — Спектрофотометрически исследованы реакции двухвалентных меди или никеля с комплексами цис-пиридин-2-альдоксима с теми же ионами металлов. В виде хлоридов выделены гомо- и гетеродвухядерные хелаты, охарактеризованные спектроскопическими и термоаналитическими методами. Первая стадия разложения скорее не зависит от атмосферы печи (азот или кислород) и сопровождается значительным экзотермическим эффектом, как показали ДСК-кривые, измеренные в атмосфере азота. Кривые ТГ показали, что двухядерные комплексы, в общем, слегка менее стабильные соответствующих моноядерных, за исключением $[Cu(NiL_2)Cl_2(H_2O)_2]$, для которого наблюдается резкое уменьшение термостойчивости.