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Spectrophotometric Study of the Reaction of Co(II) and Ni(II) With Nitroso-*R*-Salt and α-Nitroso-β-Naphthol

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The complexes of Co(II) and Ni(II) with nitroso-*R*-salt are studied by conductometric titration and spectrophotometric methods in buffer solutions of different *pH*. The study proved the possible formation of (1:1), (1:2) and (1:3) complexes for Co(II) while Ni(II) forms (1:1) and (1:2) complexes (metal: ligand) only. The factors affecting complex formation are established and the formation constants of the complexes are evaluated. The ir spectra of the solid complexes with α-nitroso-β-naphthol revealed that the ligand exhibits the nitrosophenol structure and that the reaction takes place through proton displacement from the OH-group.

(Keywords: Complex formation constants; Conductometric titration; IR)

Spektrophotometrische Studie zur Reaktion von Co(II) *und* Ni(II) *mit Nitroso-R-Salz und α-Nitroso-β-naphthol*

Es wurden die Komplexe von Co(II) und Ni(II) mit Nitroso-*R*-Salz mittels konduktometrischer und spektrophotometrischer Methoden in Puffer-Lösungen mit verschiedenem *pH* untersucht. Für Co(II) wurden (1:1)-, (1:2)- und (1:3)-Komplexe gefunden, während für Ni(II) lediglich (1:1)- und (1:2)-Komplexe (Metall: Ligand) festgestellt werden konnten. Die Faktoren, die die Komplexierung bestimmen, werden diskutiert und die Komplexbildungskonstanten wurden bestimmt. Die IR-Spektren der Komplexe mit α-Nitroso-β-naphthol zeigen, daß der Ligand in der Nitrosophenol-Form vorliegt und daß die Reaktion über eine Protonenverschiebung von der OH-Gruppe verläuft.

Introduction

Nitrosophenols are known to react with transition metal ions forming coloured complexes which can be used for the detection and estimation of traces of some metals[1–6].

The present investigation is concerned with the reaction of 1-nitroso-2-hydroxy-3,6-disulphonate naphthalene which is commonly known as Nitroso-*R*-Salt (*NRS*) with Co(II) and Ni(II) with the view to establish the structure of the resulting complexes and evaluate their stability constants.

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Experimental

A $10^{-2}M$ solution of nitroso-*R*-salt was prepared by dissolving the accurately weighed amount of the A.R. solid (B.D.H.) in conductivity water.

$10^{-2}M$ solutions of Co^{2+} or Ni^{2+} were prepared by dissolving the appropiate amount of the metal chloride (A.R. grade) in acidified conductivity water (5 ml conc. A.R. HCl/l) to prevent hydrolysis. The metal content was checked by recommonded methods of analysis[7]. These were used as stock solutions for the preparation of lower concentrations.

Table 1. *Analysis of the solid complexes*

a) Co^{2}-α-nitroso-β-naphthol

Element	$Co(C_{10}H_6NO_2)\cdot 1/2\,SO_4\cdot 3\,H_2O$		$Co(C_{10}H_6NO_2)_2\cdot 2\,H_2O$		$Co(C_{10}H_6NO_2)_3$	
	Calc.	Found	Calc.	Found	Calc.	Found
Co	15.46	15.46	13.41	13.41	10.24	10.21
S	4.21	4.20	—	—	—	—
C	31.52	31.52	54.68	54.62	62.98	62.92
H	3.17	3.16	3.67	3.56	3.49	3.45
N	7.35	7.34	6.37	6.77	6.89	7.30
H_2O	14.17	14.24	8.22	8.30	—	—

b) Ni^{2+}-α-nitroso-β-naphthol

Element	$NiCl(C_{10}H_6NO_2)\cdot H_2O\cdot C_2H_5OH$		$Ni(C_{10}H_6NO_2)_2\cdot 2H_2O\cdot C_2H_5OH$	
	Calc.	Found	Calc.	Found
Ni	16.85	16.80	12.57	12.56
Cl	10.19	10.32	—	—
C	41.36	41.41	56.40	56.44
H	4.63	4.32	4.26	3.75
N	8.07	7.93	5.97	6.27
H_2O	10.34	10.52	3.86	3.92

The buffer solutions used to control the *pH* and ionic strength are those of the modified universal series of *Britton* and *Robinson*[8].

The solid complexes were prepared by mixing a hot ethanolic solution containing α-nitroso-β-naphthol with the appropriate quantity of $NiCl_2$ or $CoSO_4$. The solution was concentrated by evaporation on a water bath and the fine crystals formed on cooling were filtered, washed with alcohol followed by acetone and dried. The analyses of the resulting solids are given in Tab. 1.

The experimental details for working procedure and the apparatus used are the same as given before[9]. The ir spectra were obtained by the aid of a Unicam S.P. 200 G spectrophotometer in the range 750–3,500 cm^{-1} using the KBr disc technique.

Results and Discussion

On mixing a solution containing Co^{2+} or Ni^{2+} ($6 \times 10^{-5} M$) with ($2 \times 10^{-4} M$) nitroso-*R*-salt (*NRS*) a reddish orange colour is developed with Co^{2+} whereas Ni^{2+} yields a yellowish green one. The absorption spectra of the coloured solutions measured against a blank containing $2 \times 10^{-4} M$ nitroso-*R*-salt are shown in Fig. 1*a* and *b*. Time and exposure to light have no apparent effect on the colour developed. The colour of the complexes is stable up to about 95 °C; above this temperature some precipitates are formed probably as a result of the thermal hydrolysis of the complexes.

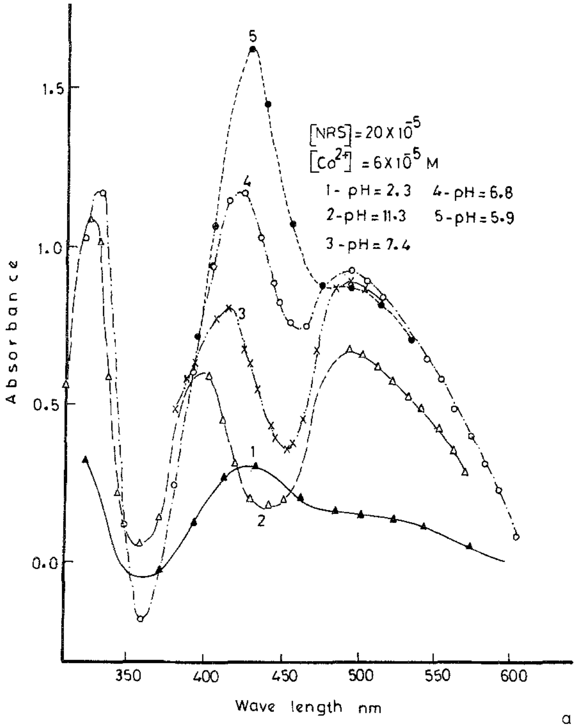


Fig. 1 a. Absorbance curves in buffer solutions

1. *Effect of pH and Buffer Constituents*

The absorption spectra in media of different *pH* and the variation of A_{max} and λ_{max} for the Co^{2+}—*NRS* complexes with *pH* are shown in Fig. 2*a*. It is clear that media suitable for evaluating the *pK* values of Co^{2+}—*NRS* complexes are those having *pH* values between 5 and 6.

The effect of buffer constituents on the Ni^{2+}—*NRS* complexes was also studied. On using the acetate buffer (*pH* = 4.1) or HCl solutions (*pH* = 4.0, 4.8), regular spectra were observed, with the same maxima. On using Na_2HPO_4 (*pH* = 8.4), citrate buffer (citric acid + Na_2HPO_4) *pH* = 7.3 or universal buffer mixture, smooth absorption bands having the same maxima were obtained. This shows that the reaction of Ni^{2+} with *NRS* is not affected by the different anions present, hence, the ligand is the most efficient complexing agent in these media. The maximum colour development occurs in the *pH* range 6–9 (Fig. 2*b*). Thus the experiments on this system are carried out in buffer solutions with *pH* 8.5 or 6.5.

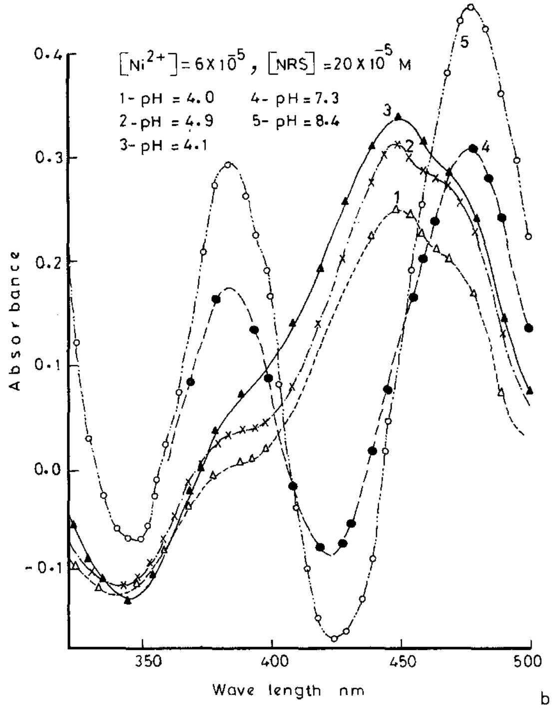


Fig. 1b. Absorbance curves in buffer solutions

The increased tendency for complex formation with increasing *pH* can be explained on the basis that the reaction between the ligand and metal ion leads to the liberation of hydrogen ion[10]. The decrease of absorbance beyond the maximum is due to hydrolysis of the complexes to hydroxy-derivatives as the OH^- ion concentration increases. It is

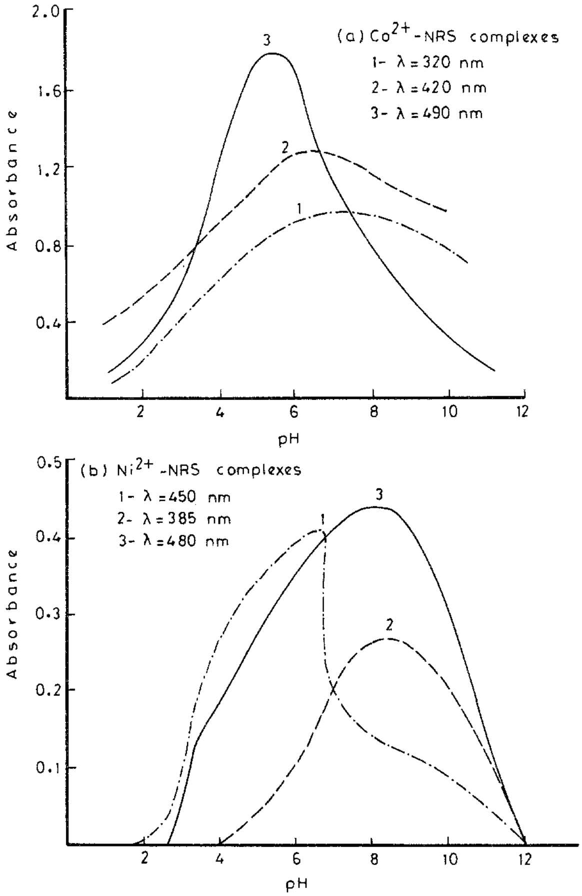


Fig. 2. *pH* absorbance curves

worthy to mention that this behaviour is common among ligands which react through H^+ ion displacement from the ligand[9, 10].

2. *Effect of Ligand Concentration*

On keeping the metal ion concentration constant at $5 \times 10^{-5} M$ while that of the ligand is varied from 1×10^{-5} to $25 \times 10^{-5} M$, the absorbance increases rapidly at low concentrations of the ligand but tends to attain a limiting value at higher ones. The change of ligand concentration does not cause apparent changes in the position of λ_{max} denoting that either one complex dominates under such conditions or that the different complexes liable to exist would have more or less the same absorption maxima.

3. *Effect of Metal Concentration*

On keeping the ligand concentration constant at $2.5 \times 10^{-4} M$ while that of the metal ions is varied, the absorbance increases steadily. *Beer*'s law is obeyed in the concentration range $0.2\text{-}6.0 \times 10^{-5} M$ for Co^{2+} and $0.16\text{-}7.8 \times 10^{-5} M$ for Ni^{2+}. At lower or higher concentrations negative deviations are observed. These limits together with the high λ_{max} values denote that *NRS* can be readily utilised for the microdetermination of Co^{2+} and Ni^{2+}.

The deviation from linearity can be explained by the possible dissociation of the complexes at low metal ion concentration and the presence of insufficient quantity of the ligand at high metal concentrations.

4. *Stoichiometry of the Complexes in Solutions*

i) Conductometric Titration

The measurements of the specific conductivity values were made in buffer solutions because little changes in conductivity were observed in water. On titrarting 100 ml of $10^{-4} M$ Co^{2+} or Ni with $10^{-3} M$ *NRS* in buffer solution of $pH = 5.9$ or the titration of $10^{-4} M$ *NRS* with $10^{-3} M$ Co^{2+} or Ni^{2+} at *pH*'s 5.9 and 9.2, inflections in the curves were obtained. The curves for the Co^{2+}—*NRS* system exhibit three apparent inflections at molar rations 1:1, 1:2 and 1:1 while those of the Ni^{2+}—*NRS* system display two apparent inflections at molar ratios 1:1 and 1:2. Therefore Co^{2+} can form three complexes while Ni^{2+} forms only two.

ii) Spectrophotometric Measurements

Spectrophotometric investigation of the Co^{2+}—*NRS* reactions were carried out at *pH* 4.1, 5.9 and 8.25 for Co^{2+} and at *pH* 5.9, 7.4 and 9.2 for Ni^{2+} applying the frequently used methods namely, the molar ratio[11], the straight line[12], the continuous variation[13], slope ratio[14] and limiting logarithmic[15] method. Comulative data are summarized in Tab. 2. The results reveal the formation of 1:1, 1:2 and 1:3 complexes for Co^{2+} and 1:1 and 1:2 for Ni^{2+} complexes confirming the results of conductometric titration. Representative results are given in Figs. 3 *a*, *b* and 4.

5. *The Apparent Formation Constants*

The apparent formation constants of the complexes formed in solution are determined from the results of spectrophotometric measurements, for the equilibrium reaction.

Table 2. *Stoichiometry of the complexes traced for NRS chelates with* Co^{2+} *and* Ni^{2+}

Method	Complexes traced					
	Co^{2+} complexes			Ni^{2+} complexes		
Molar ratio		(Co^{2+} 2 *NRS*)	(Co^{2+} 3 *NRS*)	(Ni^{2+} *NRS*)	(Ni^{2+} 2 *NRS*)	—
Continuous variation	(Co^{2+} *NRS*)	(Co^{2+} 2 *NRS*)	(Co^{2+} 3*NRS*)	(Ni^{2+} *NRS*)	(Ni^{2+} 2*NRS*)	—
Straight line	(Co^{2+} *NRS*)	—	—	(Ni^{2+} *NRS*)	—	—
Slope ratio	(Co^{2+} *NRS*)	(Co^{2+} 2 *NRS*)	—	—	(Ni^{2+} 2 *NRS*)	—
Limiting logarithmic	(Co^{2+} *NRS*)	—		(Ni^{2+} *NRS*)	—	—

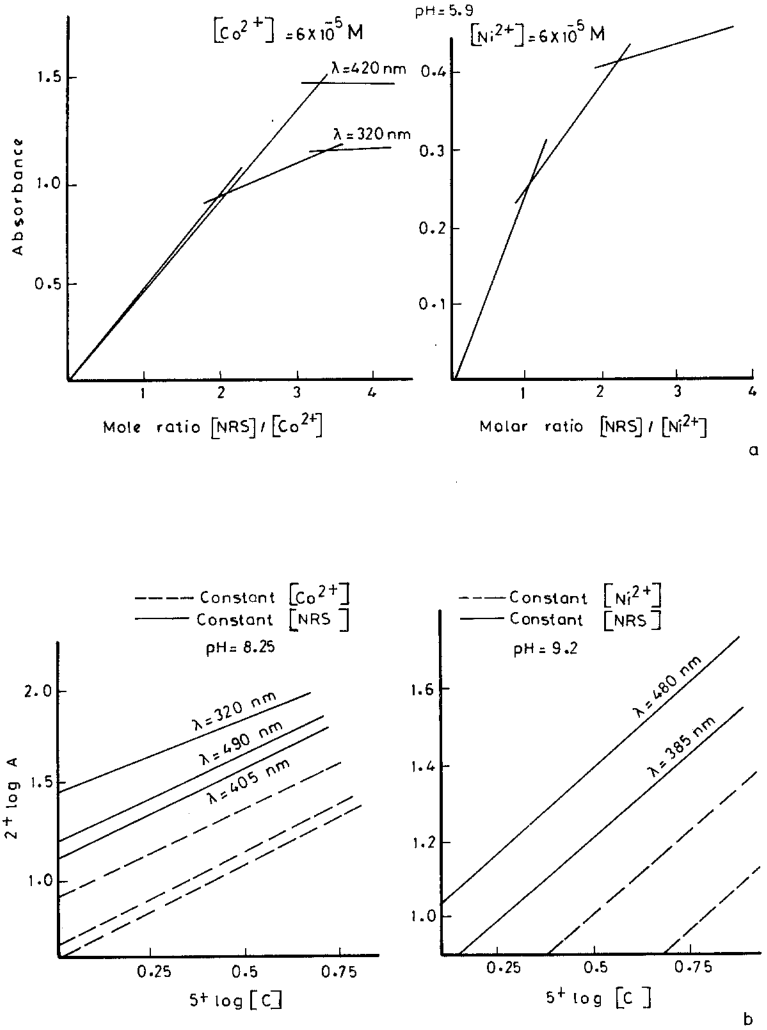


Fig. 3. *a* Molar ratio method, *b* limiting logarithmic method

$$M^{2+} + n\,NRS \rightleftharpoons [M(NRS)_n]^{(2-n)+} + n\,\mathrm{H}^+$$

where $M^{2+} = \mathrm{Co}^{2+}$ or Ni^{2+}.

In the molar ratio[11] and the continuous variation[13] methods, the following relation is applied

$$\beta_n = \frac{(A/A_m)}{(1-(A/A_m)^{n+1}\, n^2\,(C_{NRS})^n}$$

in which

A_m = limiting absorbance
A = absorbance at given NRS concentration (C_{NRS})
n = the stoichiometric ratio.

Similar expressions based on the limiting logarithmic[15] and the straight line[12] methods can be used for determination of B.

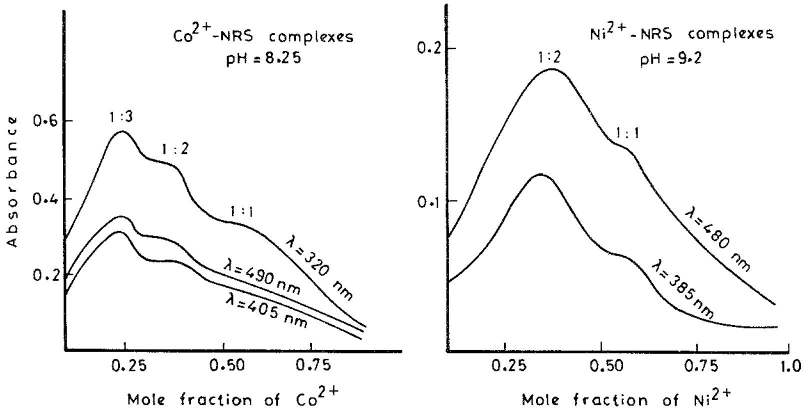


Fig. 4. Continuous variation method

When the formation of metal complexes involves an acid—base equilibrium, the variation of absorbance with pH can be used for calculating the formation constant of the complex[10]. The reaction, $n\,HL + M^{a+} \rightleftharpoons [M\,(L)_n]^{(a-n)+} + n\,\mathrm{H}^+$ can be considered to take place in two steps:

a) The ionization of the ligand

$$n\,L\mathrm{H} \overset{K_i^n}{\rightleftharpoons} n\,L^- + n\,\mathrm{H}^+$$

for which

$$K_i^n = \frac{(C_L—)^n \cdot (C_{\mathrm{H}}+)^n}{(C_{L\mathrm{H}})^n\ a+)} \tag{1}$$

b) The reaction of the ionised ligand with the metal ion:

$$n\,L^- + M^{a+} \rightleftharpoons (M \cdot n\,L)^{(a-n)+}$$

$$\beta_n = \frac{C_{(M \cdot n\,L)}{}^{(a-n)+}}{(C_L—)^n \cdot (C_M} \tag{2}$$

from (1) and (2)

$$\beta_n K_i^n = \frac{C_{(M\cdot nL)}{}^{(a-n)+} \cdot (C_{\mathrm{H}}+)^n}{(C_M a+)\cdot (C_{L\mathrm{H}})^n} \tag{3}$$

since

$$(C_M a+) = (C_{0\,M} a+) - C_{(M\cdot nL)}{}^{(a-n)+} \tag{4}$$

and

$$C_{(M\cdot nL)}{}^{(a-n)+} = A/\varepsilon \tag{5}$$

From (3) and (5) we obtain

$$\beta_n K_i^n = \frac{A/\varepsilon \cdot C_{(\mathrm{H}^+)}{}^n}{(C_{0\,M} a+ - A/\varepsilon)\,(C_{L\mathrm{H}})^n} \tag{6}$$

taking

$$C_{0M}\, a+ = A_m/\varepsilon \tag{7}$$

Then

$$\frac{1}{(C_{\mathrm{H}}+)^n} = \frac{A}{\beta_n K_i^n (A_m - A)\,(C_{L\mathrm{H}})^n} \tag{8}$$

Taking the logarithmic form

$$n\,pH = \log\left(\frac{A}{A_m - A}\right) - n \log C_{L\mathrm{H}} + n\,p K_i^n - \log \beta_n \tag{9}$$

$$n\,pH + n \log C_{L\mathrm{H}} = \log\left(\frac{A}{A_m - A}\right) + n\,p K_i^n - \log \beta_n$$

Thus β_n can be determined by plotting log $(A/(A_m - A))$ vs. pH of the medium.

The results obtained for the formation constants of the 1:1, 1:2 and 1:3 complexes are given in Table 3. It is clear that the stability of Co^{2+} and Ni^{2+} complexes increases with the increase of the ligand: metal ratio.

6. *Infra-Red Spectra of Solid Complexes*

The structure of metal chelates with *o*-nitrosophenols has been the subject of many discussions and some contraversial assumptions are met with[6, 7]. However, with *NRS*, it is difficult to isolate the solid complex in a pure from and accordingly the Co^{2+} or Ni^{2+} chelates with α-nitroso-β-naphthol are used.

Table 3. *The formation constant* (K^f) *of* Co^{2+} *and* Ni^{2+} *complexes with NRS* Co^{2+}—*NRS*

pH	mu	1:1 Straight line	Limiting logarithmic	1:2 Molar ratio	1:3 Molar ratio
4.1	320	—	—	3.1×10^{10}	1.3×10^{12}
5.9	420	3.2×10^{4}	1.99×10^{4}	—	—
	320	—	—	—	1.2×10^{12}
	420	5.0×10^{4}	2.51×10^{4}	—	1.3×10^{12}
	320	4.5×10^{4}	3.20×10^{4}	1.0×10^{10}	1.4×10^{12}
8.25	405	—	1.58×10^{4}	2.5×10^{10}	1.2×10^{12}
	490	3.2×10^{4}	1.99×10^{4}	—	1.3×10^{12}
Analytical method	420	3.25×10^{4}		2.58×10^{10}	1.27×10^{12}
	325	3.5×10^{4}		2.82×10^{10}	1.3×10^{12}

Ni^{2+}—*NRS* Complexes

pH	mn	1:1 Straight line	Limiting logarithmic	1:2 Molar ratio
5.9	450	1.20×10^{4}	2.09×10^{4}	0.64×10^{9}
7.4	385	—	—	0.68×10^{9}
	450	2.40×10^{4}	2.90×10^{4}	0.43×10^{9}
9.2	385	0.60×10^{4}	2.50×10^{4}	0.16×10^{9}
	480	2.3×10^{4}	1.41×10^{4}	0.76×10^{9}
Analytical method	480	2.53×10^{4}	2.45×10^{4}	0.59×10^{9}
	385	2.35×10^{4}	2.6×10^{4}	0.63×10^{9}

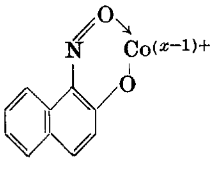
Table 4. *Assignment of some IR-bands* (cm^{-1}) *of α-nitroso-β-naphthol and its* Co^{2+} *and* Ni^{2+} *chelates*

Ligand	Co^{2+} chelate 1:1	1:2	1:3	Ni^{2+} chelate 1:1	1:2	Assignment
—	3390	3420	—	3295	3295	νOH
1610		disappear		1600	1600	C=O
1605		disappear		1590	1590	C=N
1595		disappear		1585	1585	C=C
—	1540	1540	1540	—	—	N=O
1400	1400	1400	1400	1400	1400	δOH
960		disappear		disappear		δN—OH (oxime)

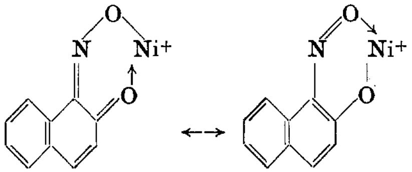
Useful information about the structure of the ligand in the bonded state and the groups involved in complex formation can be obtained by comparing the ir spectra of the solid complexes with those of the organic ligands. This is shown in Table 4. It reveals the following:

i) The bands corresponding to the C=O, N—OH and C=C have completely disappeared with the appearance of a new band at 1,540 cm^{-1} due to the N=O stretching vibration. The spectra also show a broad absorption band in the 3,400 cm^{-1} region due to the water molecules present in the chelates; the intensity of this band decreases with increasing ligand groups in the chelate compound till it almost vanishes in the spectrum of 1:3 complexes.

Accordingly, it can be concluded that the Co^{2+} ion is bonded to the ligand groups through a proton displacement forming amore or less covalent bond and a coordinate bond with the N=O group; in the mean time, a change of the molecular structure of α-nitroso-β-naphthol from the ketooxime form, in which it is known to exist, to the nitrosophenol structure takes place. The formation of neutral 1:3 complex[17] also denotes that cobalt exists in the trivalent state. Considering the spectral changes observed on chelation together with the results of analysis, the bonding of Co^{2+} or Co^{3+} ions in the different complexes can be represented as follows:



$x = 2$ or 3



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ii) The bands corresponding to the C=O, C=N and C=C show a red shift on chelation with Ni^{2+} ion. At the same time the intense bands of the vibrations related to the OH-group, essentially the N—OH band, are no more apparent in the spectra of the complexes. The spectra also show a broad absorption band in the region of 3,295 cm^{-1} due to water and alcohol molecules present in the chelates.

It can therefore be concluded that the chelation of Ni^{2+} ion to the α-nitroso-β-naphthol takes place through the hydrogen displacement and a coordination bond with the C=O group (structure I). The apparent red shift of the C=O, C=N and C=C band can be explained by the increased participation of tautomeric form (structure II). Accordingly the complex tends to exhibit the nitrosophenol form more than the ligand itself.

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