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Characterization of Copper(II), Nickel(II), Cobalt(II) and Palladium(II) Complexes of Vicinal Oxime-Imine Ligands; Induced Chelate Isomerism in the Same Molecule of the Nickel(II) Complex†

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Summary. Metal complexes of the title ligands were characterized in order to determine the factors influencing the stability of chelate isomerism in the same molecule. The ligands were prepared by 1:1 condensation of isonitrosoacetylacetone (H*iso*) with either *o*-aminophenol (H_2*isoaph*), *p*-aminophenol (H_2*isopph*), or aniline (H*isoanil*). The following complexes have been synthesized: [(*isoaph*)Cu]$_4$, (H*isoaph*)$_2$Co, (H*isopph*)$_2$$M \cdot nH_2O$ ($M =$ Ni(II), n = 2; $M =$ Pd(II), n = 0; $M =$ Co(II), n = 2), [(*isopph*)Cu·H_2O]$_2$, and (*isoanil*)$_2$$M$ ($M =$ Ni(II), Cu(II), Co(II), or Pd(II)). Both chelate rings in these metal complexes are five-membered. Transimination of one $-C{=}N{-}C_6H_5$ group to $-C{=}NH$ in (*isoanil*)$_2$Ni produced a six-membered chelate ring in (*isoim*)Ni(*isoanil*). The induced chelate isomerism is ascribed to intermolecular hydrogen bonding of the imino-hydrogen and the basic nitrogen of the same six-membered chelate ring of an adjacent square planar molecule. Other types of hydrogen bondings with the oximato oxygen (intra- or intermolecular) favour the formation of five-membered chelate rings. Analytical, spectroscopic, and magnetic moment data are in accordance with the suggested formulations.

Keywords. Induced chelate isomerism; Metal complexes of vicinal oxime-imine ligands; Hydrogen bonding in metal complexes.

Charakterisierung von Kupfer(II)-, Nickel(II)-, Kobalt(II)- und Palladium(II)-Komplexen vicinaler Oxim-Imin-Liganden; induzierte intramolekulare Chelatisomerie des Nickel(II)-Komplexes

Zusammenfassung. Metallkomplexe der im Titel genannten Liganden wurden charakterisiert und die Stabilität der intramolekularen Chelatisomerie beeinflussenden Faktoren bestimmt. Die Liganden wurden durch 1:1 – Kondensation von Isonitrosoacetylaceton (H*iso*) mit *o*-Aminophenol (H_2*isoaph*), *p*-Aminophenol (H_2*isopph*) oder Anilin (H*isoanil*) hergestellt. Folgende Metallkomplexe wurden synthetisiert: [(*isoaph*)Cu]$_4$, (H*isoaph*)$_2$Co, (H*isopph*)$_2$$M \cdot nH_2O$ ($M =$ Ni(II), n = 2; $M =$ Pd(II), n = 0; $M =$ Co(II), n = 2), [(*isopph*)Cu·H_2O]$_2$ und (*isoanil*)$_2$$M$ ($M =$ Ni(II), Cu(II), Co(II) oder Pd(II)). Alle genannten Komplexe bilden 5-gliedrige Chelate.

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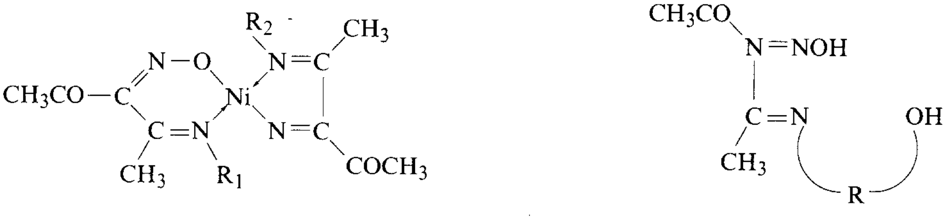
† Part of the Ph.D. thesis of Sana M. Imam

Transiminierung einer $-C=N-C_6H_5$ - Gruppe zu $-CH=NH$ in $(isoanil)_2Ni$ führte zu einer Verbindung (*isoim*)Ni(*isoanil*) mit einem 6-gliedrigen Ring. Die induzierte Chelatisomerie wird auf intermolekulare Wasserstoffbrückenbindung zwischen dem Imino-Wasserstoff und dem basischen Stickstoff des 6-gliedrigen Chelats eines benachbarten quadratisch planaren Moleküls zurückgeführt. Andere Wasserstoffbrückenbindungen mit dem Oximsauerstoff (inter- oder intramolekular) fördern die Bildung 5-gliedriger Chelate. Analytische, spektroskopische und magnetische Daten stimmen mit den vorgeschlagenen Strukturen überein.

Introduction

Our earlier investigations of metal complexes LM (H_2L = N,N'-ethylene-*bis*-(isonitrosoacetylacetoneimine); M = divalent Ni(II), Cu(II), or Co(II)) have revealed that chelate isomers could be characterized in separate molecules [1–6]. X-ray analysis [7] has shown that in the case of the Ni(II) complex both chelate isomers can exist in the same molecule when the two chelate rings in the vicinal oxime–imine ligand are not linked together (Scheme 1). The stability of this type of chelate isomerism was ascribed [7–9] to intramolecular hydrogen bonding between the imino-hydrogen of the six-membered chelate ring and the oximato-oxygen of the five-membered one, in addition to other unspecified steric factors [10]. We have shown that the hydrogen bonding is of intermolecular type and is stabilized by a nephelauxetic effect [11]. The present study is aimed at the investigation of the limitations of this conclusion and gives additional evidence by the observation of induced chelate isomerism in the same molecule.



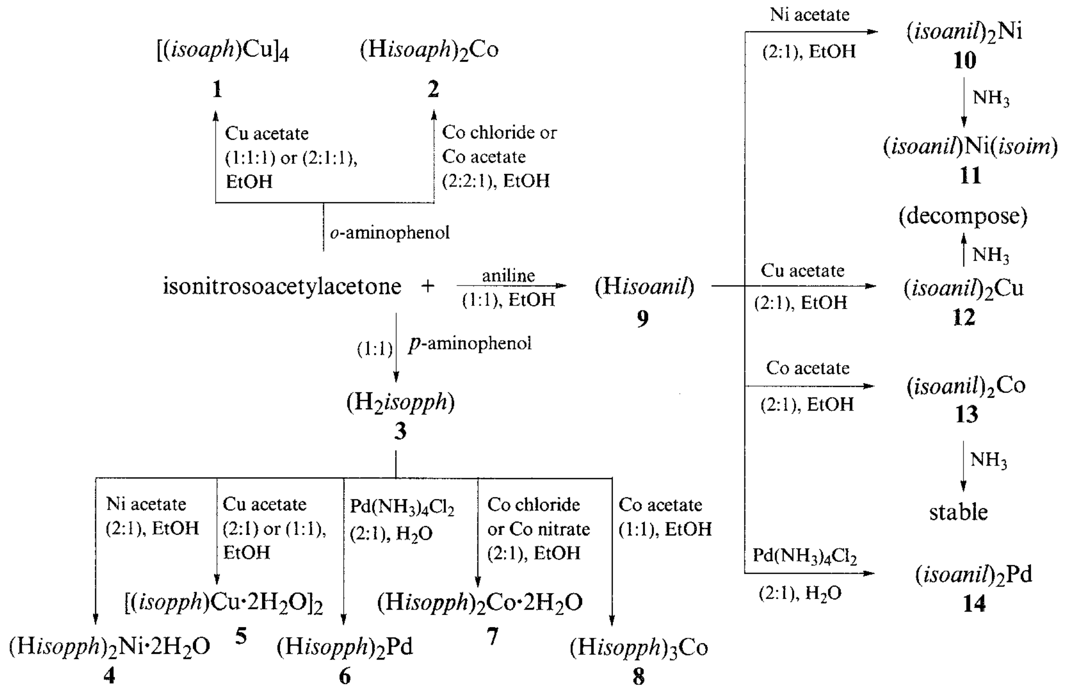
A **B**

ROH = *o*-aminophenol moiety: H_2*isoaph*; ROH = *p*-aminophenol moiety: H_2*isopph*; ROH = aniline moiety: H*isoanil*

Scheme 1. Structural representation for the chelate isomerism in the same molecule (**A**) and general formulation of the vicinal oxime-imine ligands (**B**)

Results and Discussion

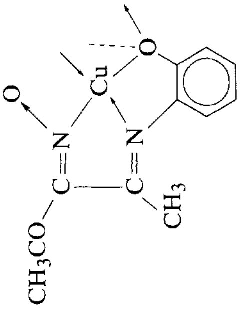
The reactions leading to compounds **1**–**14** are represented schematically in Scheme 2. The suggested formulations of ligands and complexes are shown in Schemes 3 and 4. Analytical data, vibrational featúres and electronic spectra together with magnetic moment data are shown in Tables 1, 2, and 3, respectively. The low molar conductance values ($\Lambda \leq 2.0\,\mathrm{ohm^{-1}\cdot cm^2\cdot mol^{-1}}$) of all metal complexes indicate their non-ionic character. The metal complexes are stable at room temperature but decompose above 200 °C. TGA analysis afforded the number of coordinated water molecules in the metal complexes.



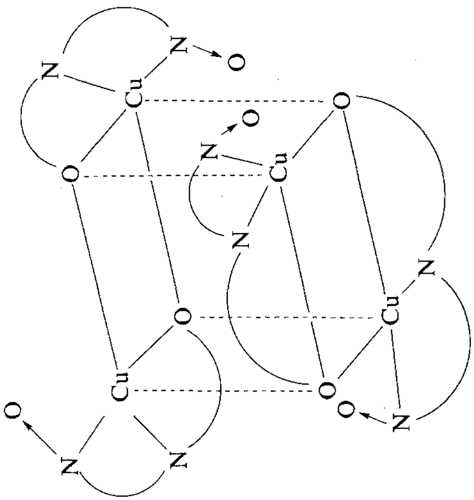
Scheme 2. Schematic illustration for the reactions that lead to the formation of the ligands and their metal complexes

The suggested tetrameric structure of **1** (Scheme 3) is identical with that of acetylacetonemono(*o*-hydroxyanil)copper(II) [12]. N-coordination by the oximato group is evidenced by ν(C=O), ν(C=N), and ν(N–O) which are comparable to those of our earlier findings for the copper(II) complexes of vicinal oxime imine ligands [3]. This assignment is also consistent with the tentative association of ν(C=O) located below 1680 cm^{-1} with N-coordination by the oximato group [9]. The suggested tetrameric structure of the complex is based on several arguments. The electronic spectrum of the complex revealed a d–d transition peak near 620 nm which is characteristic for five-coordinate copper(II) in the tetrameric [Cu(benzoylacetone–ethanolamine]$_4$ complex [13]. Moreover, the phenolic ν(C–O) is shifted to higher frequency than the 1500–1520 cm^{-1} region reported for a similar ligand with side coordination of phenolic oxygen [14–16]. The magnetic moment of this complex was found to be 0.6 B.M. which is lower than the expected 1.9 B.M. value of the d^9 system of copper(II), apparently as a result of spin–spin interactions between the four copper ions in the tetrameric structure [13].

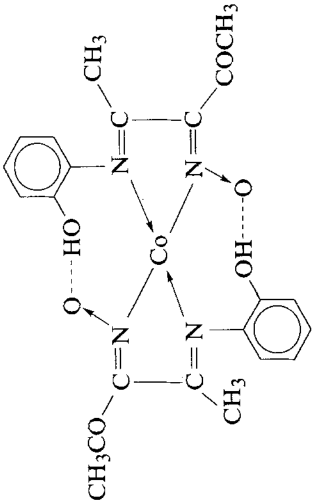
The suggested structure of **2** is square planar with strong intramolecular hydrogen bonding between the phenolic and the oximato oxygen (Scheme 3) in a similar manner to that reported for the corresponding nickel(II) complex [11]. The shift of the broad ν(OH) to lower frequency (3300–2700 cm^{-1}) and the splitting of ν(N–O) to several bands centered at 1168 cm^{-1} are in accordance with the suggested structure of the complex. Vibrational evidence for the N-coordination by the oximato group and ν(C–O) are identical with those of **1**. The shift of the phenolic ν(C–O) to higher frequency than that of a similar ligand is compatible with the



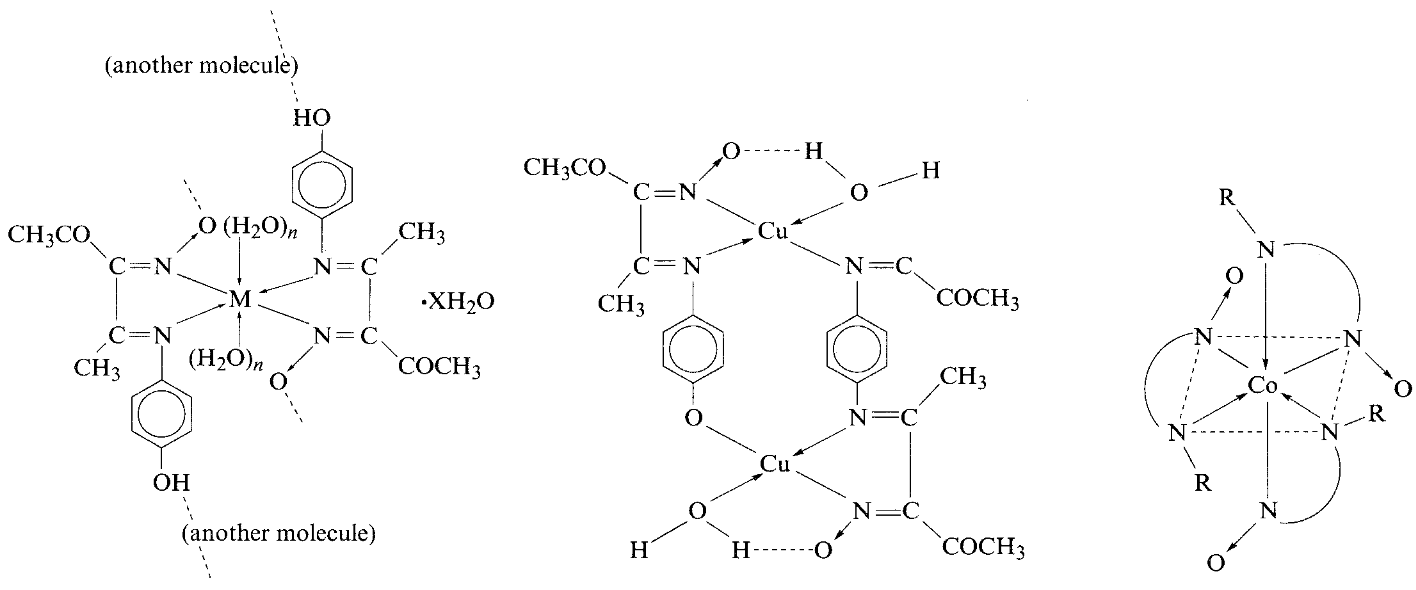
monomeric 1



tetrameric 1



2

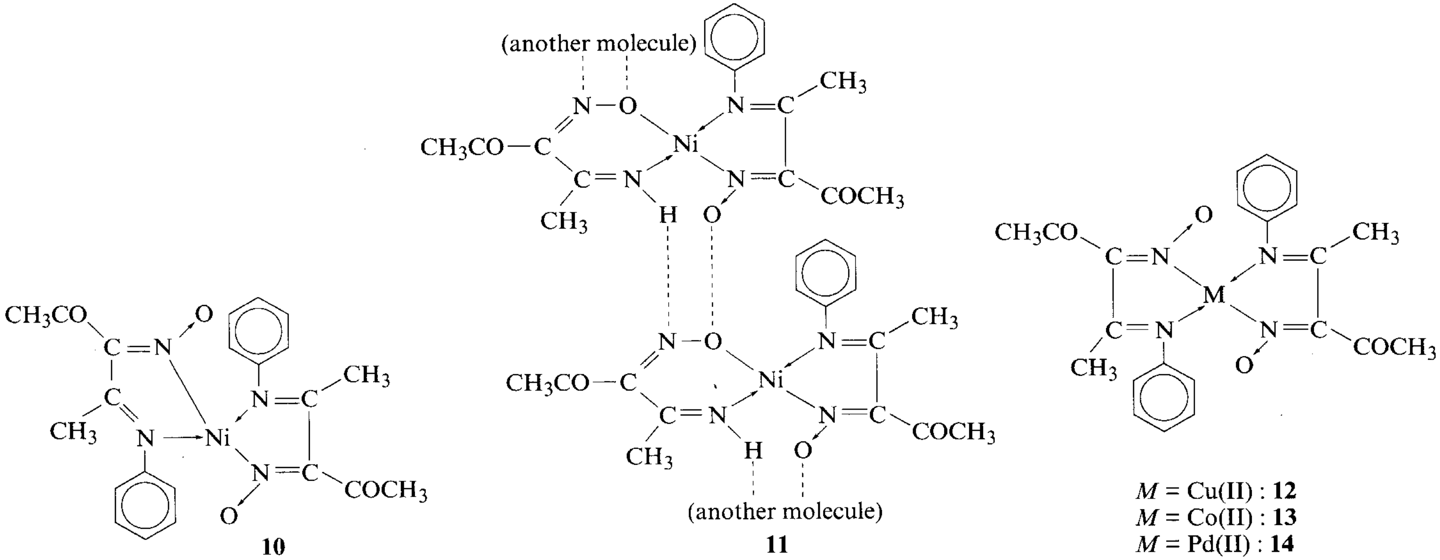


5

8

M = Ni, n = 1, X = 0 Complex **4**
M = Pd, n = 0, X = 0 Complex **6**
M = Co, n = 0, X = 2 Complex **7**

Scheme 3. Suggested structures of **1**, **2**, **4**–**8**; for **3**, see Scheme 1



10

11

M = Cu(II) : **12**
M = Co(II) : **13**
M = Pd(II) : **14**

Scheme 4. Suggested structures of **10–14**; for **9**, see Scheme 1

Table 1. Suggested formulations, analytical data, and colour of ligands and metal complexes

	Suggested formula	Elemental analysis (%)				Colour
		Found (calc.)				
		C	H	N	M	
1	$[(\mathit{isoaph})\mathrm{Cu}]_4$	46.6	3.6	9.6	22.3	Deep brown
	$C_{44}H_{40}N_8O_{12}Cu_4$	(46.9)	(3.6)	(9.9)	(22.6)	
2	$(\mathrm{H}\mathit{isoaph})_2\mathrm{Co}$	52.9	4.6	11.9	12.2	Orange
	$C_{22}H_{22}N_4O_6Co$	(53.1)	(4.5)	(11.3)	(11.9)	
3	$\mathrm{H}_2\mathit{isopph}$	60.5	5.3	13.0	–	Faint yellow
	$C_{11}H_{12}N_2O_3$	(60.0)	(5.5)	(12.7)		
4	$(\mathrm{H}\mathit{isopph})_2\mathrm{Ni}\cdot 2H_2O$	50.1	5.2	10.2	11.3	Brown
	$C_{22}H_{26}N_4O_8Ni$	(49.6)	(4.9)	(10.5)	(11.0)	
5	$[(\mathit{isopph})\mathrm{Cu}\cdot H_2O]$	44.3	4.2	9.5	21.0	Green
	$C_{22}H_{24}N_4O_8Cu$	(44.1)	(4.0)	(9.4)	(21.2)	
6	$(\mathrm{H}\mathit{isopph})_2\mathrm{Pd}$	48.1	4.2	10.0	19.9	Brown
	$C_{22}H_{22}N_4O_6Pd$	(48.5)	(4.1)	(10.3)	(19.5)	
7	$(\mathrm{H}\mathit{isopph})_2\mathrm{Co}\cdot 2H_2O$	49.3	4.9	10.9	11.3	Reddish-brown
	$C_{22}H_{26}N_4O_8Co$	(49.5)	(4.9)	(10.5)	(11.1)	
8	$(\mathrm{H}\mathit{isopph})_3\mathrm{Co}$	55.4	5.2	11.8	8.5	Orange
	$C_{33}H_{36}N_6O_9Co$	(55.1)	(5.0)	(11.7)	(8.2)	
9	$\mathrm{H}\mathit{isoanil}$	65.5	5.5	13.6	–	Pale yellow
	$C_{11}H_{11}N_2O_2$	(65.0)	(5.5)	(13.8)		
10	$(\mathit{isoanil})_2\mathrm{Ni}$	57.2	5.0	12.3	12.5	Yellowish-brown
	$C_{22}H_{22}N_4O_4Ni$	(56.8)	(4.8)	(12.1)	(12.6)	
11	$(\mathit{isoim})\mathrm{Ni}(\mathit{isoanil})$	49.5	4.9	14.8	15.3	Orange-red
	$C_{16}H_{18}N_4O_4Ni$	(49.4)	(4.7)	(14.4)	(15.1)	
12	$(\mathit{isoanil})_2\mathrm{Cu}$	56.3	4.8	11.5	13.2	Green
	$C_{22}H_{22}N_4O_4Cu$	(56.2)	(4.7)	(11.9)	(13.5)	
13	$(\mathit{isoanil})_2\mathrm{Co}$	57.3	5.0	12.3	12.4	Red-orange
	$C_{22}H_{22}N_4O_4Co$	(56.8)	(4.8)	(12.0)	(12.7)	
14	$(\mathit{isoanil})_2\mathrm{Pd}$	51.2	4.5	11.3	20.5	Yellowish-red
	$C_{22}H_{22}N_4O_4Pd$	(51.5)	(4.3)	(10.9)	(20.8)	

suggested intramolecular hydrogen bonding between the phenolic and the oximato oxygen [11]. The magnetic moment of 1.8 B.M. is indicative of d^7 low-spin configuration of the Co(II) ion. The electronic spectrum of the complex shows a broad peak centered at 500 nm which is in accordance with the suggested square planar structure of the complex [5, 17].

Vibrational evidence for N-coordination by the oximato group (five membered chelate ring) in **4** is identical with that of **2**. The observed shift of ν(C–O) to higher frequency compared with the ligand suggests intermolecular hydrogen bonding between the phenolic and the oximato oxygen of an adjacent molecule. The magnetic moment of the complex is 3.1 B.M., indicating high-spin nickel(II). An octahedral structure is suggested for this complex at least in the solid state since its electronic spectrum in nujol reveals a broad peak at 600 nm [18]. However, this peak shifts

Table 2. Infrared data (cm^{-1}) of ligands and metal complexes

	ν(OH) water (w) oxime (o)	ν(OH) phenolic	ν(C=O)	ν(C=N) imine	ν(C=N) oxime	ν(C–O)	ν(N–O)	ν(metal-oximino nitrogen)
1	–	–	1677(s) 1668(s)	1588(m)	1570(s)	1550(s)	1143(s)	665(m)
2	–	3300–2700 (br)	1680(s) 1670(s)	1600(m)	1580(m) 1565(m)	1530(m)	1168(s)	688(m)
3	3120–2200 (br) (o)	3420(m)	1660(s)	1600(m)	1630(m)	1498(m)	998(s)	–
4	3600–2800 (br) (w)	mixed with ν(OH)H_2O	1680(s) 1700(s)	1580(m)	1550(m)	1530(m)	1140(m)	660(m)
5	3500–2800 (br) (w)	–	1678(s)	1580(m)	1550(m)	1530(m)	1133(m)	650(m)
6	–	3550–2800 (br)	1650(s)	1580(m)	1550(m)	1530(m)	1180(m)	650(m)
7	3550–2800 (br) (w)	mixed with ν(OH)H_2O	1680(s) 1660(s)	1590(m)	1575(m)	1530(m)	1160(m)	650(m)
8	–	3550–3000 (br)	1680(s) 1660(s)	1590(m)	1570(m)	1525(m)	1180(m) 1160(m)	682(m)
9	3300–2300 (br) (o)	–	1665(s)	1600(m)	1635(m)	–	995(s)	–
10	–	–	1660(s) 1670(s)	1590(m)	1580(s) 1570(s)	–	1150(s) 1140(s)	650(m)
11	–	–	1688(s) 1658(s)	1590(m)	1610(m) 1550(m)	–	1193(m) 1170(m)	630(m)
12	–	–	1765(s) 1668(s)	1590(m)	1580(s)	–	1140(m)	680(m)
13	–	–	1652(s) 1645(s)	1590(m)	1550(m)	–	1180(m)	695(m)
14	–	–	1645(s)	1580(m)	1550(m)	–	1175(m)	670(m)

s = strong, m = medium, w = weak, br = broad

to 560 nm in ethanol. This could be ascribed to site occupancy changes in ethanolic solution of the complex [19, 20]. This observation is consistent with the suggested intermolecular hydrogen bonding (broad ν(OH)) between the phenolic group and the oxygen atom of the N-coordinated oximato group of separate molecules. The dissociation of these molecules in ethanolic solution is expected to have a direct effect on the charge transfer peaks which are probably mixed with those of the d–d transition type. It is believed that steric considerations are in favour of the oximato oxygen site for the intermolecular hydrogen bonding (which explains the formation of the five-membered chelate ring) rather than the basic nitrogen of the oximato group or the oxygen atom of the acetyl group which stabilizes the six-member chelate ring [11].

The suggested structure of **5** (Scheme 3) indicates that the phenolate ion is directly coordinated to the metal ion like in the copper(II) complex **1**, owing to the higher affinity of the metal ion to this coordination site. This is shown by the shift of ν(C–O) of the ligand from 1498 cm^{-1} to 1550 cm^{-1}. Vibrational evidence for N-coordination

Table 3. Electronic spectra and magnetic moments of ligands and metal complexes

	Solvent	λ_{max} (nm)[a]	μ_{eff} (B.M.)
1	Nujol	665 (br), 570 (br)	0.6
	$CHCl_3$	650(250), 550(940), 510(2340), 450(2600), 345(18230), 250(26650)	
2	Nujol	500 (br)	3.8
	$CHCl_3$	500(450), 380(9260), 345(14250), 270(27260)	
3	EtOH	340(1310), 290(14260)	diamagnetic
4	Nujol	600 (br)	3.1
	EtOH	560(300), 400(3180), 335(10250) 280(18210)	
5	Nujol	720 (br), 450 (br)	1.3
	EtOH	720(180), 650(253), 580(1900), 380(3820)	
6	Nujol	485 (br)	diamagnetic
	EtOH	460(2600), 340(7260), 270(21880)	
7	Nujol	500 (br), 420 (br)	1.9
	EtOH	500(280), 425(1100), 340(7400), 265(16700)	
8	Nujol	620 (br), 440 (br)	diamagnetic
	EtOH	615 (br), 425(1400), 345(9880), 270(17780)	
9	EtOH	340(1100)	diamagnetic
10	Nujol	590 (br)	2.8
	$CHCl_3$	590(110), 390(3000), 345(8200), 280(14500)	
11	Nujol	480 (br)	
	$CHCl_3$	475(2750), 380(4800), 350(10580) 275(21780)	diamagnetic
12	Nujol	710 (br)	1.8
	EtOH	705(140), 560(180), 340(5720), 308(8010), 260(14200)	
13	Nujol	470 (br)	1.9
	$CHCl_3$	450(990), 385(1290), 340(1520) 270(5160)	
14	Nujol	490 (br)	diamagnetic
	$CHCl_3$	470(2650), 340(7800), 270(20800)	

[a] Values in parentheses: molar absorptivities ($dm^3 \cdot mole^{-1} \cdot cm^{-1}$)

by the oximato group is similar to that mentioned above for **1**. The water molecule is coordinated to the metal ion (Table 2) and is lost above 160 °C. The electronic spectrum of the complex shows peaks near 700 nm which are ascribed to the square planar structure of the complex [21, 22]. The spin–spin interactions between the two copper(II) ions in the planar structure of the complex are evidenced by its magnetic moment of 1.3 B.M. which is significantly lower than the normal magnetic moment of *ca.* 1.8 B.M.

The suggested structure for **6** (Scheme 3) is square planar, based on vibrational evidence for the N-coordination of the oximato group (Table 2) and the similarity of its electronic spectrum (Table 3) with that of known square planar complexes of Pd [5]. Evidence for intermolecular hydrogen bonding in the complex is identical with that for **4** (Table 2).

7 is formulated as a square planar structure with two water molecules which are not coordinated since thay are lost above 100 °C without decomposition of the complex. Moreover, its electronic spectrum shows a strong and broad peak near 500 nm [5, 7]. The magnetic moment of the complex was found to be 1.9 B.M. Evidence for the N-coordination by the oximato group and intermolecular hydrogen bonding are identical with those discussed above **4**. Complex **8** is diamagnetic and its electronic spectrum shows a broad peak near 600 nm, indicating low spin state and octahedral structure [23]. Other vibrational evidences and their significances are identical with those discussed above for **4** (Table 2).

The monoanionic ligand **9** is deprived from the phenolic group of the dianionic H_2*isoaph* and H_2*isopph* where intramolecular and intermolecular hydrogen bondings were observed in their metal complexes. Vibrational evidence for the ν(OH), ν(C=O), and ν(N–O) of **9** are identical with those of **3** (Table 2). For **10** (Scheme 4), evidence for N-coordination by the oximato group is identical with that of **4**. Whereas the splitting of the ν(C=O) vibration (and, to a lesser extent, ν(C=N)) is a characteristic feature of N-coordinated oximato groups [9], this is not the case with ν(N–O). ν(C=N) and ν(N–O) are split in complex **10** into two bands indicating the non-equivalence of the two N-coordinated oximato groups. The electronic spectrum of the complex shows a broad peak near 600 nm [17]. The magnetic moment of **10** was found to be 2.8 B.M. (high spin nickel(II)). This evidence is compatible with the suggested tetrahedral structure of **10**.

A comparison between the structure of **10** and that of the square planar *bis*-(4-iminopentane-2,3-dione-3-oximato)Ni(II) [7–10, 24], abbreviated (*isoim*)$_2$Ni, revealed that the structural differences are related to chelate isomerism in the same molecule of the latter complex and a more pronounced manifestation for the crystal field stabilization energy in the square planar complex (low spin). These differences are directly associated with the replacement of the $=N-C_6H_5$ group by the =NH in **10**. In order to confirm this observation, the transimination of **10** was carried out by the action of ammonia. The analytical data of the resulting complex **11** show that only one $-C=N-C_6H_5$ group in **10** was transiminated to form –C=NH. The suggested square planar structure for **11** with induced chelate isomerism in the same molecule is based on spectral and magnetic moment evidence. The ν(NH) vibrations were observed at the expected regions of 3270 and 3150 cm^{-1}. Two well resolved and separated ν(C=O) bands, identical with those reported for (*isoim*)$_2$Ni [24], were detected. The higher frequency band (1688 cm^{-1}) is located in the 1690–1670 cm^{-1} region which is ascribed to ν(C=O) of the carbonyl group attached to the six-membered chelate ring (O-coordination by the oximato group) [2–5, 9]. The lower frequency band (1658 cm^{-1}) is located in the 1670–1630 cm^{-1} region associated with ν(C=O) of the carbonyl group attached to the five-membered chelate ring of the N-coordinated oximato group [2–5, 9, 24]. Two vibrations were observed at 1610 and 1550 cm^{-1} which are assigned to ν(C=N) of the O-coordinated and N-coordinated oximato groups, respectively.

Similarly, two ν(N–O) vibrations were detected at 1193 and 1170 cm^{-1}. The higher frequency band is assigned to the N-coordinated oximato group (N–O bond with higher double bond character), whereas the lower frequency band is associated with the O-coordinated oximato group (N–O bond with lower double bond character) [2–5, 24]. These bands replace the coupled ν(N–O) vibration of (*isoim*)$_2$Ni at 1202 cm^{-1} [24]. The absence of the latter band in **11** is a convincing evidence for the mono-transimination reaction since di-transimination will produce (*isoim*)$_2$Ni. The 630 and 520 cm^{-1} bands have no counterparts in the IR spectrum of **10** but are similarly observed with (*isoim*)$_2$Ni and are, therefore, assigned to ν(Ni–N) (oximino-nitrogen) and ν(Ni–O) (oximato-oxygen), respectively. Furthermore, **11** is diamagnetic and its electronic spectrum shows a broad peak near 480 nm [17]. We suppose that the transimination of one $-C=N-C_6H_5$ group to $-C=NH$ in **11** is followed by (*a*) rearrangement of N-coordination of the oximato group to the O-coordination mode by the basic reaction conditions as reported earlier [2], (*b*) electronic shift from the chelate ring to the carbonyl group, and (*c*) stabilization of the chelate isomerism in the same molecule by intermolecular hydrogen bonding between the imino-hydrogen of this chelate ring and the basic nitrogen of the O-coordinated oximato group of an adjacent molecule (Scheme 4). The latter step allows a more suitable orientation for the manifestation of the *nephelauxetic effect* of the oximato-oxygen of the five-membered chelate ring on the (N–O) bond of the six-membered of the adjacent molecule (Scheme 4). This accounts for the observed conversion of the tetrahedral structure of **10** to the more favourable square planar structure of **11**. The extent of the latter effect is limited by the steric requirement of the phenyl group of the five-membered ring as shown by the lowering of the ν(N–O) vibrations of **11** (Table 3) compared with the coupled ν(N–O) at 1202 cm^{-1} of (*isoim*)$_2$Ni. Transimination of the second $-C=N-C_6H_5$ group was not required for the achieved chelate isomerism in **11**. It is worth noting that the Ni(II) complex on which X-ray analysis was carried out had the substituent $-C=N-CH_3$ in the five-membered chelate ring [7] instead of $-C=N-C_6H_5$. A similar reaction to that described for the preparation of **10** using either copper(II), cobalt(II), or palladium(II) ions (Scheme 2) afforded complexes **12**, **13**, and **14**, respectively. The suggested square planar structure of these complexes is based on identical evidence with those discussed above for **1**, **2**, and **6**, respectively. It could be concluded, therefore, that chelate isomerism in the same molecule took place only after the molecule had acquired the square planar structure in order to allow for intermolecular hydrogen bonding between the imino-hydrogen and the basic nitrogen of the oximato group of an adjacent molecule (Scheme 4). This will prevent the latter group from rearranging to the energetically more favourable N-coordination mode and leads to an electronic shift from the chelate ring to the carbonyl group by the action of the nephelauxetic effect of the oximato group of the five-membered chelate ring.

Experimental

Reagent grade chemicals were used. Isonitrosoacetylacetone was prepared as described before [1]. The spectoscopic and magnetic moment measurements were carried out as reported earlier [11]. C, H and N analyses were determined at the Analytical Department of Cairo University. Standard methods were used for the determination of the metal ions. All compounds were dried *in vacuo* over P_4O_{10}.

Preparation of ligands and their metal complexes

1, **2**: Isonitrosoacetylacetone (H*iso*, 0.0385 mol) was mixed with an equimolar amount of *o*-aminophenol and fused together just above the melting point of the mixture. After cooling and extract with ethanol (70 cm^3), the ethanolic extract was refluxed for 2 h and filtered. An ethanolic solution (100 cm^3) of $(MeCO_2)_2Ni \cdot 4H_2O$ for **1** and $(MeCO_2)_2Co \cdot 4H_2O$ or $CoCl_2 \cdot 6H_2O$ for **2** (0.019 mol) was added while stirring; the reaction mixture was refluxed for 2 h and left to cool. The precipitated complex was filtered off, washed with ethanol, and dried. It was crystallized from chloroform in the case of **1** which could also be obtained from an 1:1:1 molar ratio reaction. Several attempts to prepare H_2*isoaph* from either the ethanolic solution of the fused reactants as described above or from the 1:1 molar ratio reaction of H*iso* with *o*-aminophenol in ethanol were unsuccessful.

3: This compound was prepared from the fused 1:1 molar ratio mixture of H*iso* with *p*-aminophenol (0.0385 mol). The reaction product was heated with chloroform (20 cm^3), to dissolve the unreacted material, filtered, and crystallized from diethylether (m.p. 141 °C).

4–**8**: Complexes **4**–**7** were prepared as described for **1** and **2** from the 2:1 molar ratio of the ligand (H_2*isoph*, 0.0136 mol) with $(MeCO_2)_2M \cdot nH_2O$ ($M = Ni$, n = 4 for **4**; $M = Cu$, n = 1 for **5**), $Pd(NH_3)_4Cl_2$ for **6**, and $CoX_2 \cdot 6H_2O$ (X = chloride or nitrate) for **7** in ethanol except **6** which was prepared in water. Complex **8** was prepared from a 1:1 molar ratio reaction (2 days reaction time).

9: The ethanolic solution (30 cm^3) of aniline (0.0385 mol) was added to the equimolar amount of H*iso* in the same solvent (40 cm^3). The resulting reaction mixture was warmed while stirring for 1 h to precipitate the ligand which was filtered off, washed with ethanol, and dried (m.p. 154 °C).

10–**14**: Complex **10** was prepared from the 2:1 molar ratio of H*isoanil* with nickel(II) acetate tetrahydrate as described for **4**. The transimination of **10** (0.0026 mol) to **11** was carried out by treating its ethanolic solution (80 cm^3) with aqueous ammonia (0.026 mol) solution (10 cm^3) in a stoppered flask. The reaction solution was stirred for 24 h, filtered, and washed several times with ethanol. Complexes **12**–**14** were prepared as described for **10** using the corresponding metal salts used for **4**–**8**. The attempted application of the transimination reaction on the Cu(II) complex **12** led to its decomposition, whereas the Co(II) complex **13** was recovered unchanged.

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