Ligands containing of a C=O and an –NH–R adjacent to the oxime group and their cobalt(II), nickel(II) and copper(II) complexes

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Ligands having a C=O group and an –NH–R group adjacent to the oxime group have been prepared from ω-chloroisonitrosoacetophenone and aniline or aniline derivatives in the presence of $NaHCO_3$. The Ni(II), Cu(II) and Co(II) complexes of the synthesised ligands have been prepared and characterised. The ligands are proposed to coordinate to the metal ions *via* the oxime oxygen and amide nitrogen atoms. Thermal analyses data reveals that the water in the complexes is non-coordinated to the metal ions. Binuclear and polymeric structures are suggested for all complexes. The complexes showed an antiferromagnetic effect.

Keywords: oxime, carbonyl-oxime, amid-oxime, polymeric complexes, thermal analysis

Organic chelating ligands containing the –C=N–OH group have been named as an oxime compounds.[1] Tscugaeff first introduced dimethylglyoxime as a gravimetric reagent for nickel and since then oxime ligands and their transition metal complexes have been extensively studied.[1-3] Oxime derivatives are very important compounds because of their biological activity, such as insecticidal, miticidal, nematocidal activities, and antidote activities towards organophosphorous poisons. Some oxime complexes have anti carcinogenic activities.[4-6] Also oximes and their derivatives have been used in analytical applications, such as determination and extraction of the metals.[7-12]

Oximes have been named as carbonyl-oximes or amid-oximes relating to position of the groups. While carbonyl-oximes have a carbonyl (C=O) group in the α- position to the oxime group (Fig. 1a), amide-oximes have a –NH–R group in the α- position to the oxime group (Fig. 1b).[1,2,4]

Carbonyl-oximes, amide-oximes and their metal complexes have been studied extensively, but work on amido-carbonyl-oximes (Fig.2), which have –C=O and –NH–R' groups in the same molecule in the α-position to the oxime group are rather few.[13-18]

In this work, four newly synthesised amido-carbonyl-oximes ligands (Scheme 1) and their Ni(II), Cu(II), Co(II) complexes were studied.

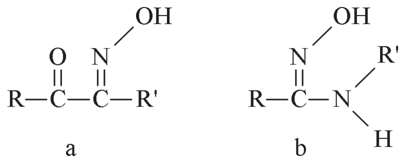


Fig. 1 General structure of carbonyl- oximes (a) and amide-oximes (b).

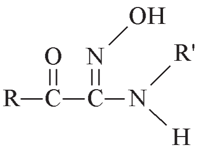


Fig. 2 General structure of amido-carbonyl -oximes.

The alternative nomenclatures of the synthesised ligands are given in Table 1.

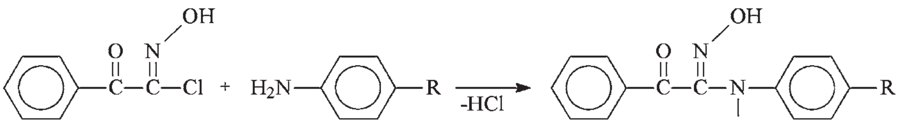
The magnetic measurements, physical properties and elemental analyses of the ligands and complexes are collected in Table 2.

^1H NMR spectra of the ligands

The L^1H_2 and L^3H_2 ligands and their crystal structures were reported previously by us.[16-17] In the ^1H NMR spectra of the

Table 1 The nomenclatures of the ligands

Ligand	R	Name of the ligand
L^1H_2	H	**(a)** N–Hydroxy–2–oxo–2–N'–diphenylacetamidine **(b)** N–Hydroxy–N'–(phenyl)-2-oxo-2-phenylacetamidine **(c)** 1-(Phenylamino)-2-phenyl-1,2-ethandion-1-oxime
L^2H_2	Cl	**(a)** N–Hydroxy–N'–(*p*–chlorophenyl)-2-oxo-2-phenylacetamidine **(b)** 1-(*p*-Chlorophenylamino)-2-phenyl-1,2-ethandion-1-oxime
L^3H_2	CH_3	**(a)** N–Hydroxy–N'–(*p*–Methyphenyl)-2-oxo-2-phenylacetamidine **(b)** N-Hydroxy-2-oxo-2-phenyl-N'-p-tolylacetamidine **(c)** 1-(*p*-Methyphenylamino)-2-phenyl-1,2-ethandion-1-oxime
L^4H_2	OCH_3	**(a)** N-Hydroxy-N'-(4-methoxyhiphenyl)-2-oxo-2-phenyl-acetamidinee **(b)** 1-(*p*-Methoxyphenylamino)-2-phenyl-1,2-ethandion-1-oxime



R: H for L^1H_2, Cl for L^2H_2, CH_3 for L^3H_2, OCH_3 for L^4H_2

Scheme 1 Synthesis of the ligands ($L^{1\text{-}4}H_2$).

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Table 2 Magnetic measurements, physical properties and elemental analyses of the ligands and complexes

Compound	M_{eff} (B.M.)	Molecular weight/ g/mol	M.p./°c	Colour Yield/%	Calculated (Found)		
					% C	% H	% N
L^1H_2 $C_{14}H_{12}N_2O_2$	–	240.26	147	Yellow 80	70.0 (70.0)	5.0 (5.2)	11.7 (11.8)
$[Co_2(L^1)_2]\cdot 1.5H_2O$ $[Co_2(C_{28}H_{20}N_4O_4)]\cdot 1.5H_2O$	3.11	621.38	129[a]	Green 26	54.1 (53.6)	3.7 (3.2)	9.0 (8.9)
$[NI_2(L^1)_2]\cdot 0.5H_2O$ $[Ni_2(C_{28}H_{20}N_4O_4)]\cdot 0.5H_2O$	2.29	602.88	120[a]	Green 20	55.8 (56.1)	3.5 (3.7)	9.3 (9.4)
$[Cu_2(L^1)_2]\cdot H_2O$ $[Cu_2(C_{28}H_{20}N_4O_4)]\cdot H_2O$	1.46	621.60	129[a]	Green 23	54.1 (53.8)	3.6 (3.0)	9.0 (8.9)
L^2H_2 $C_{14}H_{11}N_2O_2Cl$	–	274.71	154	Yellow 88	61.2 (61.4)	4.0 (4.2)	10.2 (10.5)
$[Co_2(L^2)(L^2H)_2]\cdot 1.5H_2O$ $[Co_2(C_{42}H_{32}N_6O_6Cl_3)]\cdot 1.5H_2O$	3.45	962.98	139[a]	Brown 15	52.3 (51.6)	3.3 (2.9)	8.7 (8.3)
$[Ni_2(L^2)_2]\cdot 0.5H_2O$ $[Ni_2(C_{28}H_{18}N_4O_4Cl_2)]\cdot 0.5H_2O$	2.18	671.77	124[a]	Green 46	50.1 (50.1)	2.8 (3.0)	8.3 (8.3)
$[Cu_2(L^2)_2]\cdot H_2O$ $[Cu_2(C_{28}H_{18}N_4O_4Cl_2)]\cdot H_2O$	1.52	690.49	97[a]	Green 37	48.7 (48.8)	2.9 (2.6)	8.1 (7.9)
L^3H_2 $C_{15}H_{14}N_2O_2$	-	254.29	143	Yellow 65	70.9 (71.1)	5.6 (5.7)	11.0 (11.4)
$[Co_2(L^3)(L^3H)_2]$ $[Co_2(C_{45}H_{38}N_6O_6)]$	3.32	876.70	128[a]	Brown 38	61.7 (61.0)	4.4 (3.9)	9.6 (9.6)
$[Ni_2(L^3)_2]$ $[Ni_2(C_{30}H_{24}N_4O_4)]$	2.23	621.92	176[a]	Green 33	57.9 (57.9)	3.9 (3.9)	9.0 (8.7)
$[Cu_2(L^3)_2]$ $[Cu_2(C_{30}H_{24}N_4O_4)]$	1.68	631.64	144[a]	Green 27	57.1 (57.6)	3.8 (3.5)	8.8 (9.1)
L^4H_2 $C_{15}H_{14}N_2O_3$	–	270.29	138	Yellow 72	66.7 (66.9)	5.2 (5.6)	10.4 (10.6)
$[Co_2(L^4)(L^4H)_2]\cdot 2H_2O$ $[Co_2(C_{45}H_{42}N_6O_9)]\cdot 2H_2O$	3.50	960.73	115[a]	Brown 30	56.3 (56.1)	4.4 (4.1)	8.8 (9.0)
$[Ni_2(L^4)_2]$ $[Ni_2(C_{30}H_{24}N_4O_6)]$	2.15	653.92	161[a]	Green 34	55.1 (55.5)	3.7 (3.9)	8.6 (8.5)
$[Cu_2(L^4)_2]\cdot 1.5H_2O$ $[Cu_2(C_{30}H_{24}N_4O_6)]\cdot 1.5H_2O$	1.61	690.66	144[a]	Green 32	52.2 (52.2)	3.9 (3.5)	8.1 (8.2)

[a] Decomposition point.

ligands, a singlet peak for the OH proton of oxime group are observed at 11.28–11.01 ppm. The N–H protons adjacent to the oxime groups in the ligands resonate at 9.08–8.47 ppm. The aromatic C–H protons resonate at 8.15–6.74 ppm while aliphatic C–H protons at 2.16–3.64 ppm. The O–H and N–H peaks of the ligands disappeared with the addition of deuterium oxide to the solutions. These results are in good agreement with those of known oximes.[4,14,19] The ^1H NMR spectral data are given in the Table 3.

Thermal analyses of the complexes

The thermal analyses results (Table 4) indicated that the water in the complexes in non-coordinated to the metals. Both the elemental and thermal analyses data of the complexes coincide with each other and metal-ligand ratios were found to be 1:1 for Ni(II) and Cu(II) complexes of all ligands, 2:3 for Co(II) complexes of $L^{2\text{-}4}H_2$ ligands, but 1:1 for Co(II) complex of L^1H_2. Based on elemental and thermal analyses data, general structures for Ni(II) and Cu(II) complexes of $L^{1\text{-}4}H_2$ and Co(II) complex of L^1H_2 are suggested as $[M_2(L^{1\text{-}4})_2]\cdot XH_2O$,but $[M_2(L^{2\text{-}4})(L^{2\text{-}4}H)_2]\cdot XH_2O$ for the remaining Co(II) complexes.

For all the complexes which have water, it is removed at 102–121 °C and DTA_{max} is approximately 100 °C. This indicates that the waters in the complexes is hydrated water.[20] The water removes as endothermically. After dehydration, the ligands in all complexes decomposed in three stages exothermically by forming metal oxides. The thermal analyses data are given in Table 4.

Table 3 ^1H NMR spectra of the ligands in DMSO-d_6

Ligand	R	O–H	N–H	H_{arom}	CH_3	OCH_3
L^1H_2	H	11.28	8.69	7.99-6.76	–	–
L^2H_2	Cl	11.44	9.08	8.15-6.76	–	–
L^3H_2	CH_3	11.14	8.79	7.98-6.66	2.16	–
L^4H_2	OCH_3	11.01	8.47	7.97-6.74	–	3.64

Table 4 Thermal analyses data of the complexes in static air atmosphere

Complex	Stage	Temperature range /°C	DTA$_{maks.}$ /°C	Loss of mass	Removal group	Total loss of mass	Residual
				Found (calculated)		Found (calculated)	
$[Ni_2(L^1)_2]\cdot0.5H_2O$	1	33–120	105	1.7 (1.5)	H_2O	77.0 (75.2)	NiO
	2-3 4	120–282 282–399	196–258 368	25.7 49.6	$C_{28}H_{20}N_4O$		
$[Cu_2(L^1)_2]\cdot H_2O$	1	20–121	103	2.2 (2.9)	H_2O	76.1 (74.4)	CuO
	2 3 4	121–185 185–315 315–481	184 – 447	22.1 15.2 36.7	$C_{28}H_{20}N_4O$		
$[Co_2(L^1)_2]\cdot1.5H_2O$	1	20–121	106	4.19 (4.35)	H_2O	75.4 (75.9)	CoO
	2 3 4	121–192 192–252 252–428	189 221 381	13.52 13.94 45.70	$C_{28}H_{20}N_4O_2$		
$[Ni_2(L^2)_2]\cdot0.5H_2O$	1	20–120	101	1.7 (1.3)	H_2O	80.7 (77.8)	NiO
	2 3 4	120–301 301–391 391–475	259 374 433	37.0 32.5 9.6	$C_{28}H_{18}Cl_2N_4O_3$		
$[Cu_2(L^2)_2]\cdot H_2O$	1	31–102	100	2.9 (2.6)	H_2O	84.1 (77.0)	CuO
	2 3 4	102–201 201–554 554–678	198 289–495 630	28.1 35.5 17.6	$C_{28}H_{18}Cl_2N_4O_4$		
$[Co_2(L^2)(L^2H)_2]\cdot1.5H_2O$	1	20–119	102	3.0 (2.8)	H_2O	87.7 (84.6)	CoO
	2 3 4	119–243 243–334 334–610	185–212 311 397–413	23.1 16.0 45.6	$C_{42}H_{29}Cl_3N_6O_6$		
$[Ni_2(L^3)_2]$	1 2 3	176–225 225–278 278–423	– 252 385	8.1 12.6 55.4	$C_{30}H_{24}N_4O_2$	76.1 (76.0)	NiO
$[Cu_2(L^3)_2]$	1 2 3	144–201 201–317 317–502	172 263 344	26.3 9.6 44.3	$C_{30}H_{24}N_4O_2$	80.2 (74.8)	CuO
$[Co_2(L^3)(L^3H)_2]$	1 2 3 4	128–300 300–371 371–407 407–439	176–212 – 406 –	27.0 6.1 23.3 23.8	$C_{45}H_{38}N_6O_4$	80.2 (82.9)	CoO
$[Ni_2(L^4)_2]$	1 2 3	161–218 218–347 347–463	199 337 401	5.5 17.3 53.7	$C_{30}H_{24}N_4O_4$	76.5 77.2	NiO
$[Cu_2(L^4)_2]\cdot1.5H_2O$	1	20–114	106	3.8 (3.9)	H_2O 1.5 mol	72.2 (76.9)	CuO
	2 3 4	114–183 183–379 379–520	176 – 434–462	17.2 18.1 33.1	$C_{30}H_{24}N_4O_4$		
$[Co_2(L^4)(L^4H)_2]\cdot2H_2O$	1	25–115	100	3.4 (3.8)	H_2O 2 mol	80.0 (84.4)	CoO
	2 3 4	115–181 181–253 253–450	172 205 312	3.5 8.9 64.2	$C_{30}H_{24}N_4O_4$		

IR spectra of the ligands and complexes

In the IR spectra of the ligands, bands at 3344–3309, 3325–3115, 1668–1648, 1633–1616, 1310–1306 and 984–924 cm^{-1} belong to N–H, O–H, C=O, C=N, –C–N– and N–O vibrations, respectively. These values are in accord with those of previously reported substituted oximes.[5,7,14,19] IR spectra of ligands and complexes were summarised in Table 5. All complexes should not show any peak for N–H and O–H belongs to the ligands since complexes form upon deprotonation of N–H and O–H hydrogens.[14,21] Carbonyl groups (C=O) and the oxime nitrogen of the ligands remained non-coordinated to the metals as C=O and C=N stretching vibrations shifted to higher frequencies.[5,7,14] However, C–N– shifted to higher frequencies and N–O stretching vibrations shifted to lower frequencies (Table 5) and these results indicate that the ligands coordinate to the metal ions through the oxygen atoms of oxime groups and nitrogen atoms of amide groups.[5,7,14,19]

For the sake of convenience the discussion of IR is divided into two parts.

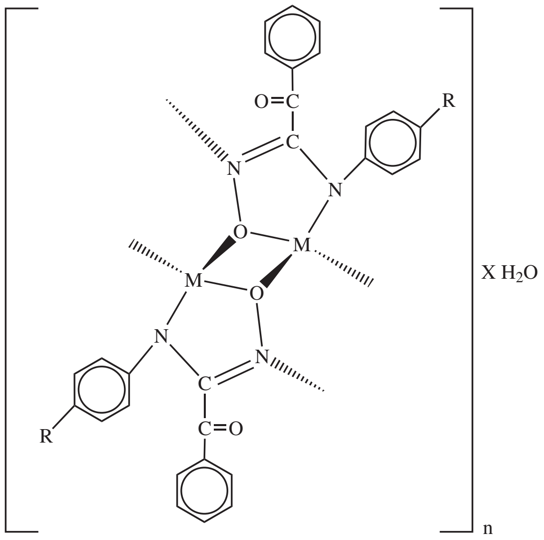
Ni(II) and Cu(II) complexes (1): The ligands $L^{1\text{-}4}H_2$ have four potential donor sites: a) the oxygen of the C=O groups, b) the nitrogen of the oxime group (C=N), c) the oxygen of oxime group (C=N–O–), and d) the deprotonated nitrogen of the amide group (–C–N–). Coordination through the deprotonated nitrogen of the amide groups is unexpected, but some amide oxime ligands show this coordination mode.[5]

Complexes having water, that is the Co(II), Ni(II) and Cu(II) complexes of L^1H_2, Ni(II) and Cu(II) complexes of L^2H_2 and Cu(II) complexes of L^4H_2, show a broad band at 3700–3200 cm^{-1} region, because of hydrated water[19,21] (Table 4).

Ni(II) and Cu(II) complexes of L^3H_2 and Ni(II) complex of L^4H_2 have no bands in the 3700–3200 cm^{-1} region in their IR spectra, indicating the N–H proton of the amide group and the O–H proton of the oxime group were released upon complex formation.[5,14] This is inferred by the increase of ν(C–N) from the free ligand L^3H_2. The –C–N– vibration for L^3H_2 at 1310 cm^{-1} is shifted to 1334 cm^{-1} for Ni(II) and 1352 cm^{-1} for Cu(II) complexes, supporting bonding to the metal through the nitrogen of the amide group. C=O vibrations of L^3H_2 (at 1651 cm^{-1}) shifted to 1672 and 1687 cm^{-1} for Ni(II) and Cu(II) complexes, respectively.[5,14,21] C=N vibrations (at 1616 cm^{-1} for the free L^3H_2 ligand) shifted to 1614 and 1625 cm^{-1} for Ni(II) and Cu(II) complexes, respectively. This results indicated the oxygen of the C=O and nitrogen of the oxime group remained as a non-coordinated to the metals.[5,14] The N-O absorption for free L^3H_2 at 925 shifted to lover frequency in the Ni(II) (905 cm^{-1}) and Cu(II) (914 cm^{-1}) complexes indicating that the oxime oxygen coordinated to the metals.[5,14,19] Similar shifting for all groups was seen for the Ni(II) and Cu(II) complexes of the other ligands (Table 5). Thus the overall IR results conclude that the ligands behave as an anionic ligand coordinating through their deprotonated oxime oxygen and deprotonated amide nitrogen.

The suggested structures of the complexes were given in Fig. 3. In the structure (Fig. 3), four-membered chelate rings are formed by two ligands, bridging together with oxime oxygens. The low magnetic moments (Table 2) are expected for such complexes.[14,22,23] In the UV-Vis. spectra, the high ε for d→d transitions of all complexes indicates that the metals have tetrahedral geometry in the complexes (Table 6).

*Co(II) complexes (**2**):* The Co(II) complex of L^1H_2 has same structure as the Ni(II) and Cu(II) complexes based on elemental analyses, thermal analyses, magnetic susceptibility



L^1H_2	L^2H_2	L^3H_2	L^4H_2
R= H	R= Cl	R= CH_3	R=OCH_3
M=Co(II), X=1.5	M=Ni(II), X=0.5	M=Ni(II), X=0	M=Ni(II), X=0
M=Ni(II), X=0.5	M=Cu(II), X=1	M=Cu(II), X=0	M=Cu(II), X=1.5
M=Cu(II), X=1			

Fig. 3 The suggested structures of Ni(II) and Cu(II) complexes of $L^{1\text{-}4}H_2$ ligands and Co(II) complex of L^1H_2.

Table 5 Characteristic I.R. bands of the ligands and their complexes as KBr pellets (cm^{-1})

Compound	N–H	O–H	C=O	C=N	C–N–	N–O	M–O	M–N
L^1H_2	3344	3290–3115	1668	1633	1310	945	–	–
$[Co_2(L^1)_2]\cdot1,5H_2O$	–	3680–3200	1672	1672	1342	900	613–576	363
$[Ni_2(L^1)_2]\cdot0,5H_2O$	–	3650–3250	1672	1656	1352	900	617–570	370
$[Cu_2(L^1)_2]\cdot H_2O$	–	3670–3240	1674	1656	1378	918	613–568	354
L^2H_2	3309	3275	1648	1624	1305	984	–	–
$[Co_2(L^2)(L^2H)_2]\cdot1,5H_2O$	3500–3310		1672	1624	1334	900	588–544	366
$[Ni_2(L^2)_2]\cdot0,5H_2O$	3690–3230		1672	1625	1348	900	584–557	343
$[Cu_2(L^2)_2]\cdot H_2O$	3620–3250		1676	1623	1374	912	590–575	376
L^3H_2	3313		1651	1616	1310	925	–	–
$[Co_2(L^3)(L^3H)_2]$	3294	–	1672	1614	1346–1326	916	642–593	347
$[Ni_2(L^3)_2]$	–	–	1672	1614	1334	905	590–505	352
$[Cu_2(L^3)_2]$	–	–	1687	1625	1352	914	584–505	324
L^4H_2	3325		1649	1622	1306	924	–	–
$[(CoL^4)(L^4H)_2]\cdot2H_2O$	3510–3352		1672	1672	1334	900	630–688	310
$[Ni_2(L^4)_2]$	–	–	1672	1672	1329	912	582–526	312
$[Cu_2(L^4)_2]\cdot1,5H_2O$	3520–3218		1674	1674	1376	910	588–557	308

Table 6 UV–Vis spectral data for complexes in $CHCl_3$ solution

Compound	Charge transfer (nm) (ε) ($M^{-1}cm^{-1}$)	d→d (nm) (ε) ($M^{-1}cm^{-1}$)	
$[Co_2(L^1)_2]\cdot1.5H_2O$	475 (5269)	–	–
$[Ni_2(L^1)_2]\cdot0.5H_2O$	425 (4028)	598 (2047) 678 (2218)	$^3T_1(F)\rightarrow{}^3A_2$ $^3T_1(F)\rightarrow{}^3T_1(P)$
$[Cu_2(L^1)_2]\cdot H_2O$	427 (6266)	–	–
$[Co_2(L^2)_2(L^2H_2)]\cdot1.5H_2O$	468 (9752)	–	–
$[Ni_2(L^2)_2]\cdot0.5H_2O$	428 (6756)	667 (3714)	$^3T_1(F)\rightarrow{}^3T_1(P)$
$[Cu_2(L^2)_2]\cdot H_2O$	407 (6088)	668 (2293)	$^2T_2\rightarrow{}^2E$
$[Co_2(L^3)_2(L^3H_2)]$	499 (7077)	–	–
$[Ni_2(L^3)_2]$	451 (5958)	701 (3723)	$^3T_1(F)\rightarrow{}^3T_1(P)$
$[Cu_2(L^3)_2]$	402 (5943)	–	–
$[Co_2(L^4)_2(L^4H_2)]\cdot2H_2O$	496 (7894)	–	–
$[Ni_2(L^4)_2]$	460 (5412)	699 (4279)	$^3T_1(F)\rightarrow{}^3T_1(P)$
$[Cu_2(L^4)_2]\cdot1.5H_2O$	400 (7975)	668 (2559)	$^2T_2\rightarrow{}^2E$

and IR spectral data. The structure of the Co(II) complex of L^1H_2 was seen in Fig. 3c.

The Co(II) complexes with $L^{2-4}H_2$ differ from Ni(II) and Cu(II) complexes in two aspects. First, based on elemental and thermal analyses data, the general structures were found to be as $[Co_2(L^{2-4})(L^{2-4}H)_2]\cdot XH_2O$ for Co(II) complexes of $L^{2-4}H_2$. Second, the complexes have different IR spectra then the Ni(II) and Cu(II) complexes (Table 5). The complexes can not be crystallised. So, the Co(II) complexes of the $L^{2-4}H_2$ are reported as materials of uncertain composition.

The magnetic susceptibility measurements (Table 2) indicated that all the complexes are paramagnetic and show an antiferromagnetic effect.

The UV-Vis spectra and magnetic susceptibility of the complexes

The molar absorption coefficients (ε) of the complexes were calculated from the UV-Vis spectra of three solutions different in concentration. The high ε for d→d transitions of all complexes indicates that the metals have tetrahedral geometry in the complexes (Fig. 3).

In the UV-Vis spectra of the Co(II) complexes, d→d transitions were not observed because the peaks were under the charge transfer bands. In the UV-Vis. Spectra of the Ni(II) complexes with L^1H_2 show two bands that belong to d→d transitions and the third band was not seen as it shifted to the IR region. Ni(II) complexes with $L^{2-4}H_2$ had one band the for d→d transitions and the other bands were under the charge transfer bands or shifted to the IR region. One band was observed for the Cu(II) complex with L^2H_2 and L^4H_2. But the expected single bands for the Cu(II) complexes with L^1H_2 and L^3H_2 were not observed because of the charge transfer bands. The UV-Vis spectral data are given Table 6.

Experimental

All starting materials were commercially available and were reagent grade. The ^1H NMR spectra were recorded on a Bruker AC-200 FT-NMR spectrometer, utilising deuterated dimethylsulphoxide as a solvent and TMS was used as an internal standard. IR spectra (4000–400 cm^{-1}) were recorded on a Jasco-430 FT-IR spectrophotometer with sample prepared as KBr pellets. The magnetic moments of the complexes were measured using a Sherwood scientific MX1 model Gouy magnetic susceptibility balance at room temperature. UV.Vis. spectra were recorded with a Unicam UV2 UV-Vis spectrometer in chloroform solution. TG and DTA curves were recorded simultaneously in a static air atmosphere with a Rigaku TG8110 thermal analyser. The heating rate was 10 °C min^{-1} and the temperature ranges were between 20 and 1000 °C

Synthesis of the ligands ($L^{1-4}H_2$)

The ligands were prepared from the reaction of ω-chloroisonitrosoacetophenone[28] with the corresponding amines (Scheme 1).

Ligands ($L^{1-4}H_2$) can be synthesised in two different methods.[15-18]

(a) A solution of 0.03 mol aniline derivatives (2.78 g for aniline, 3.82 g for *p*-chloroaniline, 3.22 g for *p*-methylaniline, 3.70 g for *p*-methoxyaniline) in EtOH (20 ml) was added dropwise to a solution of ω-chloroisonitrosoacetophenone (0.03 mol, 5.5 g) in ETOH, and then solid $NaHCO_3$ (0.03 mol, 2.52 g) was added to the mixture. After 1 h, H_2O (20 ml) was added dropwise to the mixture. The precipitated product was filtered, washed with water and then recrystallised from EtOH.

(b) A solution of ω-chloroisonitrosoacetophenone (0.015 mol, 2.75 g) in dichloromethane (20 ml) was added slowly to a solution of 0.03 mol aniline derivatives (2.78 g for aniline, 3.82 g for *p*-chloroaniline, 3.22 g for *p*-methylaniline, 3.70 g for *p*-methoxyaniline) in dichloromethane (20 ml). After 1 h, aniline hydrochloride derivatives were precipitated. The precipitates were filtered off. The solutions were kept over night and then the crystalline products were collected by filtration and dried in air. Different nomenclatures of the ligands are given in Table 1, molecular weights, melting points, colors, yields and elemental analyses results are given in Table 2.

Ni(II), Cu(II), Co(II) complexes

The solutions of metal salts (3 mmol) $[Ni(CH_3COO)_2\cdot4H_2O$, $Cu(CH_3COO)_2\cdot H_2O$ and $Co(CH_3COO)_2\cdot4H_2O]$ in H_2O (8 ml) were added to a solution of the ligands (3 mmol) dissolved in EtOH (15 ml). The colours of the ligand solutions were changed immediately from yellow to green for complex formation. In order to isolate complexes by precipitation, concentrated aqueous NH_3 (0.1 ml) was added. The precipitates were filtered, washed with 70% cold EtOH and dried in air. The colours, melting points, molecular weights, magnetic measurements and elemental analysis data are given in Table 2.

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