NOVEL SCHIFF BASES WITH OXIME GROUPS AND THEIR HOMO- AND HETERONUCLEAR COPPER(II) COMPLEXES

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Two novel tetradentate Schiff bases containing oxime groups and their homodinuclear, homotrinuclear Cu(II) and heterodinuclear Cu(II)–Mn(II) and Cu(II)–Co(II) complexes were synthesized. The Schiff base ligands (H_2L^1 and H_2L^2) were prepared by condensing of diethylenetriamine with 2-(biphenyl-4-yl)-*N*-(4-chlorophenyl)-*N′*-hydroxy-2-oxoacetimidamide (HL^1) and 2-(biphenyl-4-yl)-*N′*-hydroxy-*N*-(4-methylphenyl)-2-oxoacetimidamide (HL^2). Structure assignments are supported by a combination of FT-IR, elemental analyses, inductively coupled plasma optical emission spectroscopy (ICP-OES), magnetic susceptibility, molar conductivity and thermal analyses studies. The free ligands were also characterized by ^1H and ^{13}C NMR spectra. Elemental analyses, stoichiometric and spectroscopic data indicated that the metal:ligand ratio is 2:1 for the dinuclear copper(II) complexes and 3:2 for the trinuclear copper(II) complexes. The copper(II) ions are coordinated to the oxime and imine nitrogen atoms. Pyrolytic decomposition occurred in melting the metal complexes and metal oxides were the ultimate products.

Keywords: Schiff base; Oxime; Polynuclear; Thermochemistry; Copper complexes.

Due to the increasing use of coordination compounds in analytical and medicinal chemistry, in biochemistry and paint and coatings industry, plentiful investigators have dealt with these topics, in particular the important role of azomethine[1] and oxime[2–4] complexes. A large number of Schiff bases, oximes and their complexes have been studied for their interesting and important properties, such as their ability to reversibly bind oxygen[5], catalytic activity in hydrogenation of olefins[6], photochromic[7] and optical properties[8,9]. Syntheses of new Schiff bases and oximes, and their metal complexes continue to be the aim of many recent investigations[10–14].

The design and syntheses of new bridging ligands used in polynuclear complexes, as well as their photochemical, photophysical and electrochemical properties have been intensively studied in recent years, with a focus on photoinduced energy- and electron-transfer processes in supramolecular systems[15–17]. The presence of copper(II) ion in these complexes is mainly

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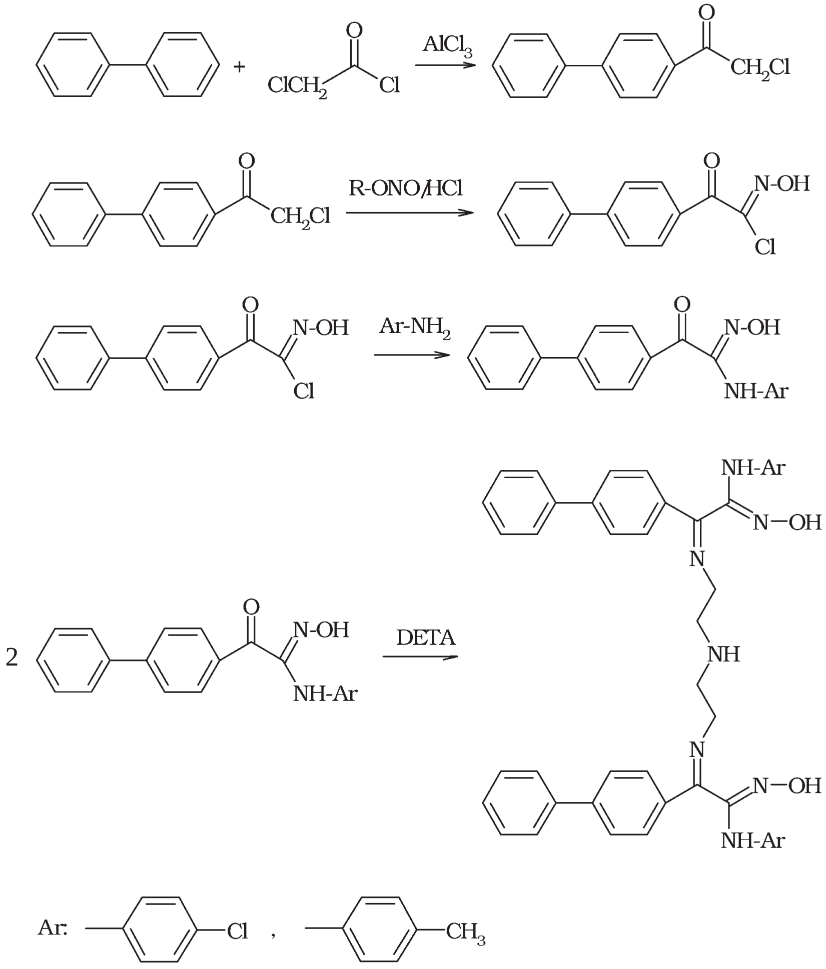
noted in two areas: (i) the research of the magneto–structural relationship and (ii) the characterization of active sites in multicopper proteins[10]. Copper(II) complexes show a wide range of biological activities. Some of these complexes have been known as antitumour, antiviral, and anti-inflammatory agents. In addition, since copper(II) complexes, especially with Schiff base or oxime ligands, are models of physical and chemical behavior of biological copper systems, they have received considerable attention[11,18–21]. The copper(II) complex of 1,10-phenanthroline has been the first synthetic transition metal complex effectively exhibiting nucleolytic activity[22].

In a previous study[9] we investigated the syntheses, characterization and optical properties of mono- and trinuclear copper(II) complexes of a novel tetradentate Schiff base. In the present work we report the syntheses and characterization of homodi-, homotrinuclear Cu(II) and heterodinuclear Cu(II)–Mn(II), Cu(II)–Co(II) complexes with 2,2′-[iminobis(ethylenenitrilo)]bis[2-(biphenyl-4-yl)-*N*-(4-chlorophenyl)-*N*′-hydroxyacetimidamide] (**1**; H_2L^1) and 2,2′-[iminobis(ethylenenitrilo)]bis[2-(biphenyl-4-yl)-*N*′-hydroxy-*N*-(4-methylphenyl)acetimidamide] (**6**; H_2L^2), see Scheme 1 and Figs 1–3.

RESULTS AND DISCUSSION

Preparation of the Schiff base ligands 2,2′-[iminobis(ethylenenitrilo)]bis[2-(biphenyl-4-yl)-*N*-(4-chlorophenyl)-*N*′-hydroxyacetimidamide] (H_2L^1) and 2,2′-[iminobis(ethylenenitrilo)]bis[2-(biphenyl-4-yl)-*N*′-hydroxy-*N*-(4-methylphenyl)acetimidamide] (H_2L^2) was performed in four steps from biphenyl as shown in Scheme 1. 4-(Chloroacetyl)biphenyl was prepared from chloroacetyl chloride and biphenyl by Friedel–Crafts acylation in the presence of aluminum chloride[23]. 1-(Biphenyl-4-yl)-2-chloro-2-(hydroxyimino)ethan-1-one was obtained by reacting 4-(chloroacetyl)biphenyl with alkyl nitrite in the presence of dry HCl gas[23]. 1-(Biphenyl-4-yl)-2-(4-chloroanilino)-2-(hydroxyimino)ethan-1-one and 1-(biphenyl-4-yl)-2-(hydroxyimino)-2-(4-methylanilino)ethan-1-one were prepared by reaction of 1-(biphenyl-4-yl)-2-chloro-2-(hydroxyimino)ethan-1-one with 4-chloroaniline or 4-methylaniline[24].

Condensation of the 2-anilino-1-(biphenyl-4-yl)-2-(hydroxyimino)ethan-1-ones with diethylenetriamine gave the corresponding products that were identified by elemental and thermal analysis, IR, ^{1}H and ^{13}C NMR spectra. The replacement of the carbonyl by the imine group results in: (i) lower energy of the ν(C=O) stretching in the IR spectrum and (ii) a shift to higher field of the CH=N proton signal in the ^{1}H NMR spectrum. The mono- (Fig. 1),



1 **6**

SCHEME 1

Syntheses of the Schiff base ligands H_2L^1 (**1**) and H_2L^2 (**6**)

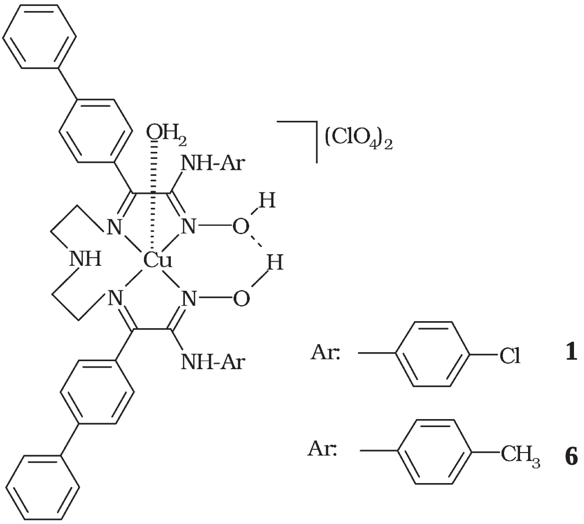


FIG. 1
Mononuclear copper(II) complexes of H_2L^1 and H_2L^2 (see Scheme 1)

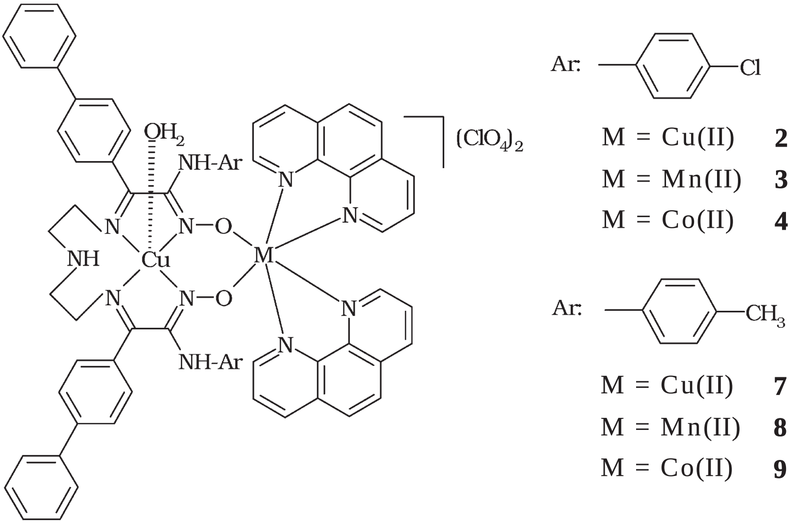


FIG. 2
Studied homodinuclear Cu(II) complexes **2** and **7**, Cu(II)–Mn(II) complexes **3** and **8**, and Cu(II)–Co(II) complexes **4** and **9**

homodi- (Fig. 2), homotri- (Fig. 3), and heterodinuclear Cu(II)–Mn(II) and Cu(II)–Co(II) complexes (Fig. 2) were prepared by the reaction of a ligand solution in acetone with copper(II), manganese(II) or cobalt(II) salts. The details are given in Experimental. The resulting solids were intensely colored and stable in air. Characterization of all the compounds studied is given in Table I.

NMR Spectra

^{1}H NMR spectra of the free ligands H_2L^1 (**1**) and H_2L^2 (**6**) were recorded in $CDCl_3$. The chemical shifts, expressed in ppm downfield from tetramethylsilane, are given in Table II. The ^{1}H NMR spectra of the ligands exhibited a broad singlet at 8.22 and 8.18 ppm for the OH protons of the oxime groups. In the region of 7.18–7.81 and 7.11–7.97 ppm, chemical shifts for aromatic hydrogens were assigned. The chemical shifts of the aromatic amine protons of H_2L^1 and H_2L^2 appeared at 6.84 and 6.94 ppm as singlets. Furthermore, the triplets in the range 1.04–2.41 ppm have been assigned to protons of the methylene groups of the triamine. The other obtained values of ^{1}H NMR chemical shifts of these compounds are given in Table II.

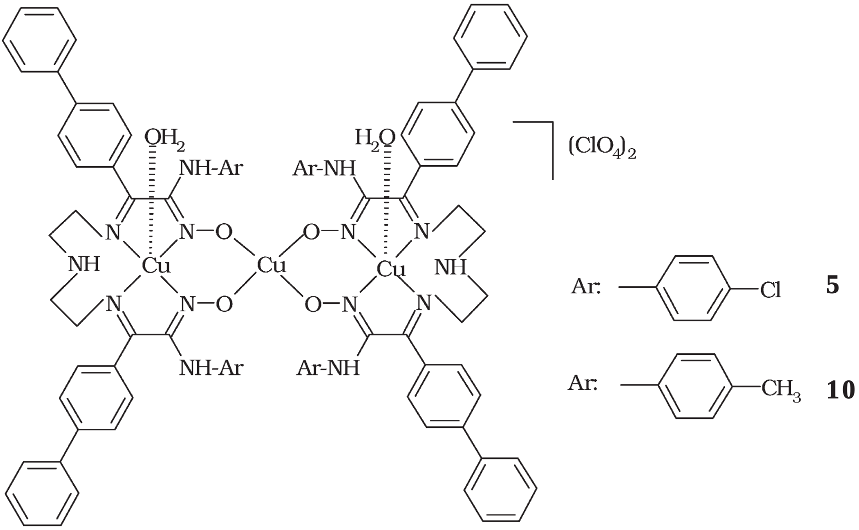


Fig. 3

Studied homotrinuclear Cu(II) complexes **5** and **10**

TABLE I
Physical properties and elemental analyses of the Schiff base ligands and complexes under study

Compd	m.p. °C	Yield %	Color	μ_{eff} (μ_B)	Λ_M[b]	Calcd (Found), % C	H	N	Metal
1	180	93	yellow	–	–	68.75 (68.72)	5.11 (5.17)	12.75 (12.69)	–
2	217[a]	52	brown	1.75	182	55.52 (55.47)	3.77 (3.79)	10.47 (10.36)	Cu: 8.64 (8.57)
3	260[a]	40	brown	3.64	167	55.84 (55.81)	3.79 (3.86)	10.53 (10.41)	Cu: 4.34 (4.38); Mn: 3.76 (3.82)
4	234[a]	53	green	2.49	173	55.69 (55.57)	3.78 (3.90)	10.51 (10.45)	Cu: 4.33 (4.41); Co: 4.02 (4.15)
5	204[a]	45	brown	1.86	186	53.95 (53.82)	4.01 (4.26)	10.01 (10.17)	Cu: 9.73 (9.89)
6	164	82	yellow	–	–	75.90 (75.73)	6.23 (6.15)	13.47 (13.56)	–
7	202[a]	65	green	1.82	181	58.78 (58.75)	4.30 (4.43)	10.77 (10.74)	Cu: 8.88 (8.82)
8	300>	48	green	3.72	163	59.14 (59.03)	4.32 (4.24)	10.84 (10.70)	Cu: 4.47 (4.56); Mn: 3.86 (3.92)
9	198[a]	75	green	2.40	155	58.97 (58.78)	4.31 (4.36)	10.81 (10.95)	Cu: 4.46 (4.40); Co: 4.13 (4.16)
10	205[a]	43	green	1.92	184	58.86 (58.84)	4.83 (4.95)	10.45 (10.32)	Cu:10.15 (10.24)

[a] Decomposition point. [b] Molar conductivity (S cm^{-1} mol^{-1}).

All the protons present in the Schiff bases exhibited signals in the expected regions. These data are in good agreement with those previously reported for similar compounds[25]. All the studied complexes are paramagnetic; therefore, the ^1H NMR spectra could not be obtained.

The ^{13}C NMR spectra of the free ligands were recorded in $CDCl_3$. The chemical shifts, expressed in ppm downfield from tetramethylsilane, are given in Table III. The chemical shifts of H_2L^1 and H_2L^2 for imine carbons (C=N) were found at 186.18 and 186.42 ppm, respectively. The carbon resonances of the oxime groups are found at 148.33 ppm for H_2L^1 and 149.22 ppm for H_2L^2, respectively[26,27]. All the signals in the 120.89–146.64 ppm range are assigned to the carbon atoms of the aromatic rings. In the ^{13}C NMR spectra, the methylene carbons appeared in the region 46.27–57.08 ppm. The carbon atom of the methyl group was observed at 20.74 ppm for H_2L^2.

TABLE II
^1H NMR chemical shifts (δ, ppm) for the Schiff base ligands H_2L^1 (**1**) and H_2L^2 (**6**)

Compd	$O\text{–}H_{(ox)}$	$C\text{–}H_{(arom)}$	N–H	$C\text{–}H_{(aliph)}$
1	8.22 (s, 2H)	7.18–7.81 (m, 26H)	6.22 (s, 1H) 6.84 (s, 2H) (Ar-NH-)	1.32 (t, 4H) 2.41 (t, 4H)
6	8.18 (s, 2H)	7.11–7.97 (m, 26H)	6.51 (s, 1H) 6.94 (s, 2H) (Ar-NH-)	2.45 (s, 6H) (Ar-NH-) 1.04 (t, 4H) 1.47 (t, 4H)

TABLE III
^{13}C chemical shifts (δ, ppm) for the Schiff base ligands H_2L^1 (**1**) and H_2L^2 (**6**)

Compd	C_{im}	C_{ox}	C_{arom}	C_{aliph}
1	186.18	148.33	122.37–146.16	46.67 56.82
6	186.42	149.22	120.89–146.64	20.74 (Ar-CH_3) 46.27 57.08

IR Spectra

IR spectroscopy is a powerful tool for structure determinations of ligands and metal chelates. The IR spectra of the free ligands and their complexes exhibit various bands in the 400–4000 cm^{-1} region (Table IV).

The broad ν(OH) bands at 3367 and 3230 cm^{-1} observed in the IR spectra of the free ligands are absent in the IR spectra of their complexes with Cu(II), indicating deprotonation of the OH groups and formation of M–O bonds. This is supported by the appearance of a new band in the region 536–507 cm^{-1} assigned to ν(M–O) [28,29]. The IR spectra of the copper(II) complexes also showed a broad band in the 3502–3566 cm^{-1} region, in line with the presence of water molecules coordinated to the metal ion[28].

IR spectra of H_2L^1 and H_2L^2 exhibited fairly strong bands at 3383 and 3389 cm^{-1} attributable to the ν(NH) vibration of aromatic amine groups. The NO stretching vibrations of the ligands were observed as medium-intensity bands at 1364 and 1377 cm^{-1} (refs[30,31]).

Strong bands at 1657 and 1665 cm^{-1} in the IR spectra of the free ligands, assigned to modes involving the imine group (C=N), shifted[32–34] to the smaller wavenumbers in the spectra of the complexes. The ν(C=N) bands for the oxime groups lie at 1601 and 1602 cm^{-1}, as reported for similar ligands[35,36]. Coordination of the ligands to the metal ions through the azomethine nitrogen atom is expected to reduce the electron density at the azomethine link of the imine and oxime groups, and to lower the ν(C=N) frequency. In the IR spectra of all the new complexes, the band due to ν(C=N) appears at smaller wavenumbers, viz. 1639–1653 cm^{-1} (imine) and 1598–1600 cm^{-1} (oxime), being indicative of the coordination of the azomethine nitrogen to the metal centres[37,38]. This idea is supported by the appearance of a new band at 437–416 cm^{-1} assigned to ν(M–N) [28,29]. The complexes show also a medium broad band in the region 1187–1145 cm^{-1}, a strong band at 1109–1083 cm^{-1} and a weak band in the 626–617 cm^{-1} range; these features are typical for uncoordinated perchlorates[29,39,40]. Thus the IR spectra of the Schiff base ligands and their metal complexes provide strong evidence of the complexation of potentially multidentate ligands.

Molar Conductivity

The molar conductivity of the complexes was an aid in proposing their formulas. Conductivity measurements were carried out in 10^{-3} M *N*,*N*-dimethylformamide solutions at 20 °C. The complexes showed values between 155 and 186 S cm^{-1} mol^{-1} (Table I). The molar conductivities of the di- and

TABLE IV
IR spectral data for the Schiff base ligands and their complexes under study

Compd	ν(O–H)	ν(N–H)	ν(C=N)$_{im}$	ν(C=N)$_{ox}$	ν(N–O)	ν(C–N)	ν(ClO_4)	ν(M–O)	ν(M–N)
1	3367s	3389s	1657s	1601s	1364m	1503s	–		–
2	3502b	3387s	1645s	1598s	1404m	1485s	1089s, 1180w, 626w	536w	428w
3	3508b	3387s	1639s	1568m	1400m	1481m	1083m, 1180w, 617w	516w	418w
4	3547b	3387m	1645m	1598w	1425m	1514m	1089s, 1161w, 626w	513w	428w
5	3523b	3385s	1653s	1598s	1404m	1487s	1089m, 1186m, 618w	526w	418w
6	3230b	3383m	1665s	1602s	1377m	1518s	–		–
7	3516b	3227s	1649s	1600m	1398m	1506s	1107s, 1145w, 626w	516w	424w
8	3508b	3313s	1649s	1600m	1427m	1516m	1109s, 1145m, 626w	527w	426w
9	3566b	3396m	1654s	1598w	1431m	1516m	1089s, 1166m, 626w	507w	437w
10	3529b	3332m	1654s	1598s	1408m	1506s	1106s, 1187m, 626w	507w	416w

s, strong; m, medium; w, weak; b, broad.

trinuclear copper(II) complexes in DMF indicated that complexes of copper(II) containing perchlorate ions behave as 1:2 electrolytes[10,41].

Magnetic Studies

The magnetic moments of the complexes at room temperature (Table I) reveal that all the copper(II) complexes are paramagnetic. The measured magnetic moments of the trinuclear copper(II) complexes are 1.86 and 1.92 μ_B for **5** and **10**, respectively. The magnetic moments for the homodinuclear copper(II) complexes **2** and **7** are 1.75 and 1.82 μ_B, respectively, at 298 K. These values are only slightly lower than expected for dinuclear copper(II) complexes, with the theoretical value of 1.73 μ_B per one d^9 copper ion[10]. The strong antiferromagnetic coupling within the homodi- and trinuclear copper(II) complexes is explained by good superexchange properties of the oximato group[10]. Furthermore, the heterodinuclear complexes show μ_{eff} values of 3.64 (**3**), 2.49 (**4**), 3.72 (**8**) and 2.40 (**9**) μ_B. These subnormal magnetic moment values may be explained by weak intramolecular antiferromagnetic interactions[42,44].

Thermal Studies

The thermal behavior of all the complexes was almost the same. Therefore, only four of the complexes are discussed here in detail. In thermogravimetry (TG), the change in the weight of a complex is recorded as a function of temperature during heating. The TG curves give information on the thermal stability and the products formed on heating. The TG curve is also supported by the derivative thermogravimetry (DTG) curves.

It is noted from the TG analysis that the homodinuclear Cu(II) complex **2** loses 91% of its original weight between 190 and 840 °C and the 9% residue is metallic Cu. The sample decomposes in three stages. The first decomposition occurs between 190 and 210 °C with 1.40% weight loss, the second one between 210 and 455 °C with 37.80% weight loss and the third one between 455 and 840 °C with 51.80% weight loss.

The homotrinuclear Co(II) complex **5** shows a decomposition pattern of four stages. The first step with the estimated weight loss 1.70% was found within the temperature range 185–204 °C corresponding to the loss of two H_2O molecules. The second step with the estimated weight loss of 41.70%, found within the temperature range 204–410 °C, corresponds to the loss of two perchlorate and four biphenyl groups. The remaining decomposition

TABLE V

Thermoanalytical results (TG, DTG) for metal complexes under study

Compd	TG range °C	DTG_{max} °C	Estimated (calculated), %		Assignment	Metal residue
			Weight loss	Total weight loss		
2	190–210	205	1.40 (1.23)		loss of one H_2O molecule	
	210–455	260, 295	37.80 (38.04)		loss of two perchlorate and two phenanthroline groups	
	455–840	720	51.80 (52.09)	91.00 (91.36)	loss of other groups	2 Cu
5	185–204	201	1.70 (1.84)		loss of two H_2O molecules	
	204–410	260, 310	41.70 (41.73)		loss of two perchlorate and four biphenyl groups	
	410–955	515, 720	44.10 (44.55)	87.50 (87.52)	loss of other groups	3 CuO
7	175–202	190	1.50 (1.26)		loss of one H_2O molecule	
	202–495	260, 285	39.30 (39.10)		loss of two perchlorate and two phenanthroline groups	
	495–965	695, 845	50.10 (50.75)	90.90 (91.11)	loss of other groups	2 Cu
10	170–205	198	2.20 (1.92)		loss of two H_2O molecules	
	205–260	265, 310	3.85 (33.21)		loss of two perchlorate and four 4-methylphenyl groups	
	379–1000	720, 845	52.45 (52.16)	87.50 (87.29)	loss of other groups	3 CuO

steps (at 410–995 °C) with an estimated weight loss 44.10% due to the loss of the other groups, leave the CuO residue.

It was found from the TG analysis that the homodinuclear Cu(II) complex **7** starts losing weight at 175 °C, which ends at 965 °C after 90.90% weight loss, leaving a metallic Cu residue that corresponds to 9.10% of the total weight. The examination of the TG curve showed that the complex decomposes in three stages. The sample loses 1.50% of the weight between 175 and 202 °C, 39.30% between 202 and 495 °C, and 50.10% between 495 and 965 °C.

DTG/TG studies showed that the residual black solid was CuO, which corresponds to a theoretical weight of 12.50% of the homotrinuclear Cu(II) complex **10**. This Cu(II) complex decomposes in three stages by losing 2.20, 32.85 and 52.45% of its weight during pyrolysis. The temperature ranges of these decompositions are found at 170–205, 205–260 and 379–1000 °C, respectively.

The theoretical and experimental per cent weight losses obtained from these decomposition stages are in good agreement. The critical data and values deduced from the present study are summarized in Table V.

EXPERIMENTAL

Physical Measurements

All the solvents, amines and metal salts ($Cu(ClO_4)_2 \cdot 6H_2O$, $Mn(OAc)_2 \cdot 4H_2O$, $Co(OAc)_2 \cdot 4H_2O$) used for the syntheses and physical measurements were purchased from Aldrich, Baker and Merck, and used as received. ^1H NMR and ^{13}C NMR spectra of the ligands **1** and **6** were recorded in $CDCl_3$ solutions, with TMS as the internal standard in the Central Laboratory at METU-Ankara, Turkey. IR spectra (4000–400 cm^{-1}) were recorded on a Shimadzu IRPrestige-21 FT-IR spectrophotometer as KBr pellets. The thermogravimetric analyses (TG and DTG) of the complexes were measured in the Central Laboratory at METU-Ankara, Turkey. C, H and N microanalyses were determined on a LECO 932 CHNS analyzer. Mn, Co and Cu contents were measured on a Perkin–Elmer Optima 5300 DV ICP-OES spectrometer. Magnetic susceptibilities were obtained with a Sherwood scientific magnetic susceptibility balance (Model MX1) at room temperature. The conductivity measurements were carried out using an Optic Ivymen System conductivity meter. Melting points were determined with a digital instrument from Electrothermal model IA 9100.

Syntheses of Ligands H_2L^1 (**1**) and H_2L^2 (**6**)

2-Anilino-1-(biphenyl-4-yl)-2-(hydroxyimino)ethan-1-ones (HL^1 and HL^2) were prepared according to previously published procedures[24]. These precursors (30 mmol, 23.06 g HL^1 and 21.84 g HL^2) in absolute ethanol (10 ml) and added diethylenetriamine (1.547 g, 15 mmol) in absolute ethanol (10 ml) were stirred at room temperature for 2 h. The precipitate was filtered off and washed several times with diethyl ether and dried over P_2O_5.

Syntheses of Complexes

Caution: Perchlorate salts of metal complexes are potentially explosive and should be handled in small quantities.

$[Cu(H_2L^1)(H_2O)]ClO_4$ and $[Cu(H_2L^2)(H_2O)]ClO_4$. The copper(II) complexes were prepared in a similar manner[30]. A solution of $Cu(ClO_4)_2\cdot6H_2O$ (370 mg, 1 mmol) in acetone (25 ml) was added to the ligand solution (1 mmol) in acetone (30 ml). This mixture was refluxed for 1 h under stirring. After stripping off the excess solvent under reduced pressure, a crude oily product was obtained. The mononuclear copper(II) complexes were used without further purification.

$[Cu(L^1)(H_2O)Cu(phen)_2](ClO_4)_2$ (**2**) *and $[Cu(L^2)(H_2O)Cu(phen)_2](ClO_4)_2$* (**7**). The mononuclear copper complex (1 mmol) was added to Et_3N (101 mg, 1 mmol) in MeOH (25 ml) and the mixture was stirred for 0.5 h. The solutions of $Cu(ClO_4)_2\cdot6H_2O$ (370 mg, 1 mmol) in MeOH (10 ml) and 1,10-phenanthroline monohydrate (397 mg, 2 mmol) in MeOH (10 ml) were successively added to the resulting mixture, which was refluxed for 3 h. The product was filtered off, washed with H_2O, MeOH and Et_2O, and dried over P_2O_5.

$[Cu(L^1)(H_2O)Mn(phen)_2](ClO_4)_2$ (**3**) *and $[Cu(L^2)(H_2O)Mn(phen)_2](ClO_4)_2$* (**8**). The mononuclear copper complex (1 mmol) was mixed with Et_3N (101 mg, 1 mmol) in MeOH (20 ml) and stirred for 0.5 h. The solutions of $Mn(OAc)_2\cdot4H_2O$ (268 mg, 1 mmol) in MeOH (10 ml) and 1,10-phenanthroline monohydrate (397 mg, 2 mmol) in MeOH (10 ml) were successively added to the resulting solution. A stoichiometric amount of $NaClO_4$ (123 mg, 1 mmol) was then added to the resulting mixture that was refluxed for 3 h. The product was filtered off, washed with H_2O, MeOH and Et_2O, and dried over P_2O_5.

$[Cu(L^1)(H_2O)Co(phen)_2](ClO_4)_2$ (**4**) *and $[Cu(L^2)(H_2O)Co(phen)_2](ClO_4)_2$* (**9**). The mononuclear copper complex (1 mmol) was mixed with Et_3N (101 mg, 1 mmol) in MeOH (20 ml) and stirred for 0.5 h. The solutions of $Co(OAc)_2\cdot4H_2O$ (249 mg, 1 mmol) in MeOH (10 ml) and 1,10-phenanthroline monohydrate (397 mg, 2 mmol) in MeOH (10 ml) were successively added to the resulting solution. A stoichiometric amount of $NaClO_4$ (123 mg, 1 mmol) was then added to the resulting mixture which was refluxed for 5 h. The product was filtered off, washed with H_2O, MeOH and Et_2O, and dried over P_2O_5.

$[Cu_3(L^1)_2(H_2O)_2](ClO_4)_2$ (**5**) *and $[Cu_3(L^2)_2(H_2O)_2](ClO_4)_2$* (**10**). A mixture of mononuclear copper complex (2 mmol), $Cu(ClO_4)_2.6H_2O$ (370 mg, 1 mmol) and Et_3N (202 mg, 2 mmol) in acetone (25 ml) was refluxed for 2 h. The resulting solution was filtered while hot and concentrated slowly. As the solution cooled, a powder product precipitated. It was isolated by vacuum filtration, washed with Et_2O and dried over P_2O_5.

The colors, yields, melting points, elemental analyses, magnetic susceptibility and molar conductivity values of the oligonuclear complexes are given in Table I.

CONCLUSION

New Schiff base ligands **1** and **6** (Scheme 1) and their homodi- and homotrinuclear copper(II) and heterodinuclear copper(II)–manganese(II), copper(II)–cobalt(II) complexes were synthesized and characterized by elemental analyses, TG/DTG, ICP-OES, magnetic susceptibility, molar conductivity, and FT-IR, ^{13}C and ^1H NMR spectroscopies. Elemental analyses, stoichiometric and spectroscopic data of the metal complexes indicate that in the dinuclear complexes, in which the first Cu(II) ion is complexed by nitrogen atoms of the oxime and imine groups, the second ion (Cu(II), Mn(II), Co(II)) is ligated with dianionic oxygen atoms of the oxime groups and linked to the 1,10-phenanthroline nitrogen atoms. The trinuclear copper(II) complex was formed by coordination of the third Cu(II) ion by four dianionic oxygen atoms in the two mononuclear copper(II) complex moieties. All complexes of these ligands have a square-pyramidal or octahedral structure, except the second copper(II) in the trinuclear complexes. The thermal analyses of these chelates show that the complexes thermally decompose in 4–5 consecutive steps. The final decomposition products are the corresponding metal or metal oxides.

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