Synthesis and structures of Octaaza Ni^{II} and Cu^{II} macrocyclic complexes containing biimidazole

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Abstract—The reactions of *bis*-(ethylenediamine)MX$_2$, M(en)$_2$X$_2$, *bis*-(1,3-propylenediamine)MX$_2$, M(1,3-DAP)$_2$X$_2$, and *bis*-(2,2-dimethyl-1,3-propylenediamine)MX$_2$, M(2,2-DM-1,3-DAP)$_2$X$_2$ complexes, [M = Cu^{II} or Ni^{II} and X = Cl$^-$ or ClO$_4^-$], after adjusting the pH values to 5, with 1,1-diacetyl-2,2'-biimidazole (Ac$_2$BiIm) afforded octaazamacrocyclic Cu^{II} complexes (1–6) and Ni^{II} complexes (7–12). The solid complexes were characterized by elemental analysis, molar conductivities, IR, UV–vis, EPR, NMR and atomic absorption spectra, back titration, TGA and DTA. © 1997 Elsevier Science Ltd

There is considerable current interest in the synthesis and investigation of macrocyclic ligands and their metal complexes especially those with pendant arms [1–12]. Such complexes are implicated in a number of metal-catalyzed and enzymatic reactions [13,14]. The preparation and spectral characterization of the new 16-membered macrocyclic complexes based on the reaction of 1,1'-diacetyl-2,2'-biimidazole (Ac$_2$BiIm) with Ni^{II}, Cu^{II} and Pd^{II} triethylene-tetramine complexes have been reported [15].

In this study we describe the synthesis and characterization of new octaazamacrocyclic complexes of Cu^{II} and Ni^{II}, which were prepared from aliphatic diamine complexes and Ac$_2$BiIm. The structures of these macrocyclic complexes were verified by elemental analysis, IR, UV–vis, EPR and NMR spectroscopy, as well as conductivity, magnetic susceptibility, DTA and TGA measurements.

EXPERIMENTAL

Preparation of Ac$_2$BiIm

Ac$_2$BiIm was prepared from 2,2'-biimidazole according to the published procedure [16]. The Ac$_2$BiIm, (1), has the following formula;

(I)
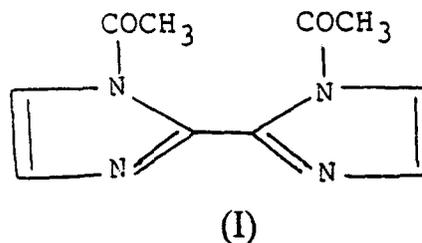
The structure of 1 was characterised by elemental analysis; Found: C, 55.3; H, 4.5; N, 25.6. Calc. for C$_{10}$H$_{10}$N$_4$O$_2$: C, 55.0; H, 4.6; N, 25.7%; IR spectra ($v_{C=O}$ = 1740, $v_{C=N}$ = 1630, δ_{CH} = 1130, 1100, and 1030 cm^{-1}) and m.p. 203–204°C.

Preparation of simple aliphatic diamine complexes

Simple aliphatic diamine complexes M(en)$_2$X$_2$, M(1,3-DAP)$_2$X$_2$ and M(2,2-DM-1,3-DAP)$_2$X$_2$, where; en = 1,2-diaminoethene, 1,3-DAP = 1,3-diaminopropane, 2,2-DM-1,3-DAP = 2,2-dimethyl-1,3-diaminopropane; X = Cl or ClO$_4$ and M = Cu^{II} and Ni^{II}, were prepared according to the published procedure [17]. These complexes were characterised by elemental analysis, IR, UV–vis and EPR spectroscopy. The data were in good agreement with those previously reported.

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Preparation of copper(II) chloride macrocyclic complexes

1.2727 g (0.005 mole) of Cu(en)$_2$Cl$_2$ was dissolved in 30 cm^3 of distilled water and stirred at room temperature. This solution was degassed by passing purified nitrogen in a three-necked flask and the pH was adjusted to 5 by adding few drops of dilute hydrochloric acid. To this solution, 2.18 g (0.01 mole) of I dissolved in a degassed 30 cm^3 of 1,4-dioxane, was added with vigorous stirring. The reaction mixture was gently heated under reflux for 36 h. The resulting macrocyclic complex, 1, was cooled, filtered off and dried *in vacuo* over P$_2$O$_5$.

Also, by the same procedures, 2.18 g (0.01 mole) of 1 was added to a 1.4127 g (0.005 mole) of Cu(1,3-DAP)$_2$Cl$_2$ and also 2.18 g (0.01 mole) of 1 was added to a 1.6927 g (0.005 mole) of Cu(2,2-DM-1,3-DAP)$_2$Cl$_2$. The macrocyclic products 3 and 5, respectively, were cooled, filtered off and dried *in vacuo* over P$_2$O$_5$.

Preparation of copper(II) perchlorate macrocyclic complexes

1.9127 g (0.005 mole) of Cu(en)$_2$(ClO)$_2$ was dissolved in 20 cm^3 isopropanol and stirred at room temperature. This solution was degassed by passing purified nitrogen in a three-necked flask and the pH was adjusted to 5 by addition of dilute HClO$_4$ acid (0.1 mole). To the stirred solution 2.18 g (0.01 mole) of 1 suspended in a degassed 30 cm^3 of 1,4-dioxane, was added with vigorous stirring. The reaction mixture was gently heated under reflux for 36 h. The macrocyclic product, 2, was cooled, filtered off and dried *in vacuo* over P$_2$O$_5$. Also by the same procedures, 2.18 g (0.01 mole) of 1 was added to 2.0527 g (0.005 mole) of Cu(1,3-DAP)$_2$ (ClO$_4$)$_2$. The macrocyclic products 4 and 6, respectively, were cooled, filtered off and dried *in vacuo* over P$_2$O$_5$.

Preparation of nickel(II) chloride macrocyclic complexes

The Ni^{II} chloride macrocyclic complexes were prepared by the same procedures of Cu^{II} chloride macrocyclic complexes. Addition of 2.18 g (0.01 mole) of 1 suspended in 30 cm^3 1,4-dioxane to 1.2485 g (0.005 mole) of Ni(en)$_2$Cl$_2$, 1.3885 g (0.005 mole) of Ni(1,3DAP)$_2$Cl$_2$ and 1.6685 g (0.005 mole) of Ni(2,2-DM-1,3-DAP)$_2$Cl$_2$, lead to isolation of 7, 9 and 11 macrocyclic complexes, respectively. The products were cooled, filtered off and dried *in vacuo* over P$_2$O$_5$.

Preparation of nickel(II) perchlorate macrocyclic complexes

The Ni^{II} perchlorate macrocyclic complexes were prepared by the same procedures of Cu^{II} perchlorate macrocyclic complexes. Additions of 2.18 g (0.01 mole) of 1 suspended in 30 cm^3, 1,4-dioxane to; 1.885 g (0.005 mole) of Ni(en)$_2$(ClO$_4$)$_2$, 2.0285 g (0.005 mole) of Ni(1,3-DAP)$_2$(ClO$_4$)$_2$ and 2.3085 (0.005 mole) of Ni(2,2-DM-1,3-DAP)$_2$(ClO$_4$)$_2$ in 1,4-dioxane-H$_2$O (1 : 1) mixture, lead to isolation of 8, 10 and 12 macrocyclic complexes. The products were cooled, filtered off and dried *in vacuo* over P$_2$O$_5$.

Preparation of the isothiocyanate derivatives of Cu^{II} and Ni^{II} macrocyclic complexes

Aqueous solutions of KSCN were added to methanolic solutions of the chloride macrocyclic complexes 1, 3, 5, 9 and 11 to give the corresponding isothiocyanate macrocyclic complexes.

Physical measurements

IR spectra were recorded in a Perkin–Elmer 1430 spectrophotometer in a KBr matrix in the 4000–200 cm^{-1}. Ultraviolet and visible absorption spectral measurements were recorded as DMSO solutions and in the solid state as Nujol mulls on a Shimadzu UV–vis 240 spectrophotometer. EPR spectra were recorded on a JEOL-FE 2XG spectrometer using DPPH as a reference. The conductivity measurements were made at 25°C using a CRISON portable 523 conductometer. ^{1}H NMR spectra were recorded on a JEOL JNMPMX 60 NMR spectrometer. DTA were carried out using a Dupont 900 thermal analysis in the range of 50 mv/cm with scan rate 20°C/min. TGA were carried out using a Shimadzu thermogravimetric analyzer TG-50 H. The elemental analysis was performed on a Perkin–Elmer 2400 automatic elemental analyzer. The percentage of the metal was determined by two methods; atomic absorption using a Perkin–Elmer 2380 spectrophotometer, and back titration [18].

RESULTS AND DISCUSSION

The reaction of the Cu^{II} and Ni^{II} isolated diamine complexes with 1 led to the isolation of different coloured macrocyclic complexes [1–12]. The molecular formula of these coloured macrocyclic were supported by elemental and metal analysis, Table 1. The conductivity measurements of these macrocyclic complexes in DMSO at 25°C, Table 1, gave the values 220, 210, 208, 212, 223 and 216 S cm^2 mole^{-1} for the complexes 2, 4, 7, 8, 10 and 12, respectively, indicating that these complexes are 2 : 1 electrolytes [19], while the other macrocyclic complexes behave as non-electrolytes.

The presence of coordinated chloride ions was confirmed by the addition of methanolic solution of KSCN to methanolic solutions of the chloride macro-

Table 1. The molecular formula, elemental analysis and molar conductance of Cu^{II} and Ni^{II} macrocyclic complexes

Complex	Molecular formula	Elemental analysis			Calc. Cl	(Found)% M	(25°C) Scm^2 mol^{-1}
		C	H	N			
1	$C_{24}H_{28}N_{12}Cl_2Cu \cdot 3H_2O$	42.82	5.1	25.0	10.6	9.5	—
		(42.7)	(5.3)	(24.7)	(10.8)	(9.2)	
2	$C_{24}H_{28}N_{12}Cl_2O_8Cu \cdot 2H_2O$	36.8	4.1	21.5	9.1	8.1	220
		(36.8)	(4.1)	(21.2)	(9.15)	(8)	
3	$C_{26}H_{32}N_{12}Cl_2Cu \cdot 2H_2O$	45.7	5.3	24.6	10.4	9.3	—
		(45.4)	(5.3)	(24.9)	(10.3)	(9.1)	
4	$C_{26}H_{32}N_{12}Cl_2O_8Cu \cdot 2H_2O$	38.5	4.44	20.7	8.8	7.8	210
		(38.4)	(4.5)	(20.7)	(8.4)	(7.8)	
5	$C_{30}H_{40}N_{12}Cl_2Cu \cdot 2H_2O$	48.7	5.1	22.8	9.61	8.1	—
		(48.5)	(5.7)	(22.6)	(9.4)	(7.9)	
6	$C_{30}H_{40}N_{12}Cl_2O_8Cu \cdot 3H_2O$	40.7	5.20	18.1	8.03	7.2	—
		(40.5)	(5.4)	(19.2)	(7.9)	(6.1)	
7	$C_{24}H_{28}N_{12}Cl_2Ni \cdot H_2O$	45.6	4.8	26.6	11.24	9.3	208
		(45.2)	(4.4)	(26.1)	(11.1)	(8.1)	
8	$C_{24}H_{28}N_{12}Cl_2O_8Ni \cdot 4H_2O$	35.4	4.42	20.7	8.72	7.22	212
		(35.3)	(4.5)	(20.4)	(8.5)	(6.9)	
9	$C_{26}H_{32}N_{12}Cl_2Ni \cdot 2H_2O$	46.04	5.31	24.8	10.5	8.7	—
		(45.8)	(5.1)	(24.4)	(10.2)	(8.2)	
10	$C_{26}H_{32}N_{12}Cl_2O_8Ni \cdot 2H_2O$	38.7	4.5	20.9	8.8	7.3	223
		(38.9)	(4.7)	(20.8)	(8.2)	(7)	
11	$C_{30}H_{40}N_{12}Cl_2Ni \cdot 2H_2O$	49.1	5.1	22.9	9.7	8	—
		(49.4)	(5.7)	(22.5)	(9.31)	(7.9)	
12	$C_{30}H_{40}N_{12}Cl_2O_8Ni \cdot 2H_2O$	41.8	5.10	19.5	8.2	6.8	216
		(41.5)	(5)	(19.1)	(8.4)	(6.5)	

cyclic complexes 1, 3, 5, 9 and 11 which gave the corresponding isothiocyanate macrocyclic complexes.

Infrared spectra

The IR spectral data of these macrocyclic complexes show the expected vibrations attributable to simple diamine complexes [17] and biimidazole components [20], with the absence of the band at 1740 cm^{-1} due to $\nu_{C=O}$ and the bands at 3300 and 3205 cm^{-1} corresponding to the $\nu_{NH_{y2}}$ of the diamine base, Table 2. The spectra of these macrocyclic complexes exhibit a broad band in the 3420–3460 cm^{-1} region attributable to the stretching vibrations of the water molecules. The values of the vibrational modes in the macrocyclic complexes resulting from the imidazole rings at 1400–1460 cm^{-1} show no significant change when compared to the similar absorptions for 1 [21]. This suggests that the biimidazole is not involved in metal ion complexation. The appearance of a new strong absorption band in the 1615–1695 cm^{-1} region attributable to the characteristic stretching frequencies of the imino linkage, $\nu_{C=N}$, and the absence of the stretching and deformation frequencies of the amino and the carbonyl groups in the IR spectra of these macrocyclic complexes provide strong evidence for the presence of cyclic products containing Schiff base linkages. The IR spectra of the perchlorate macrocyclic complexes 2, 4, 8, 10 and 12 exhibit a very strong unsplit band around 1105–1110 cm^{-1} which is

characteristic to the noncoordinated ClO_4^- anion [22], while the perchlorate macrocyclic complex 6 has a very strong splited band at ca 1100–1130 cm^{-1} characteristic to a ClO_4^- anion coordinated to the central Cu^{II} atom [22]. The IR spectra of the isothiocyanate complexes reveal new strong bands in the 2060–2090 cm^{-1} and 780–800 cm^{-1} regions attributable to $\nu_{C\equiv N}$ and $\nu_{C=S}$, respectively. These bands indicate that the coordination of the NCS moiety involves the nitrogen atom [19]. Further support for complex formation is gathered from the presence of the strong bands at ca 330–415 cm^{-1} due to ν_{Cu-N} and at ca 320–435 cm^{-1} due to ν_{Ni-N}, while the shift of these bands to lower frequencies than those of the corresponding bands of the aliphatic diamine complexes reflect the formation of macrocyclic ring.

Electronic absorption spectra

The electronic absorption spectra of these complexes in DMSO and in the solid state as Nujol mulls were measured at room temperature over the 200–850 nm range, Table 3. The spectra of the Cu-macrocyclic complexes 1–6 in DMSO solutions exhibit five absorption bands at 620–690, 530–580, 410–460, 350–390 and 280–290 nm regions. These spectra are characteristic to a pseudo-octahedral structure [23]. The first three low energy bands have low intensity and broad shape so that the second band is not observed in the DMSO solution spectrum of 1 or in the spectrum of

Table 2. The IR spectral data for AC$_2$ BiIm and Cu^{II}, Ni^{II} macrocyclic complexes

Complex assignment	AC2BiIm	1	2	3	4	5	6	7	8	9	10	11	12
ν_{OH} of H$_2$O	—	3440(br)	3420(br)	3450(br)	3420(br)	3440(br)	3440(br)	3420(br)	3440(br)	3440(br)	3450(br)	3430(br)	3460(sh)
CH Str. of BiIm	3145(vs)	3140(s)	3140(w)	3120(w)	3140(sh)	3140(m)	3120(w)	3140(m)	3140(m)	3140(s)	3140(sh)	3140(sh)	3140(sh)
	3110(s)	3070(w)	3070(w)	3080(sh)	3070(w)	3070(m)	3070(m)	3070(m)	2070(m)	3110(s&p)	3060(m)	3100(sh)	3070(w)
$\nu_{C=O}$	1740(vs)	—	—	—	—	—	—	—	—	—	—	—	—
$\nu_{C=N}$	—	1680(s)	1670(s)	1615(b)	1620(b)	1670(br&s)	1680(br&s)	1685(s)	1685(s)	1695(s&br)	1680(s&br)	1620(br)	1680(s&p)
$\nu_{C=N}$ Str. of BiIm	1630(s)	1615(s)	1620(s)	—	—	—	—	—	—	1630(s)	—	—	—
BiIm. ring vibrations	1540(s)	1545(vs)	1545(vs)	1525(vs)	1545(vs)	1545(vs)	1545(vs)	1545(vs)	1545(vs)	—	1535(s&br)	1525(vs)	1535(vs&s)
	1455(s)	—	1460(w)	1460(sh)	—	—	1460(w)	1470(sh)	1475(sh)	1465(w)	1460(vs)	—	1455(sh)
	144(s)	1435(s)	1435(s)	1430(s)	1435(w)	1435(w)	1435(s)	1435(s)	1435(s)	1425(vs)	1420(s)	1425(vs)	1425(w)
	1425(s)	1400(vs)	1405(vs)	1425(s)	1425(s)	1405(s)	1400(vs)	1400(vs)	1405(vs)	—	1405(sh)	1385(sh)	1505(vs)
	1380(vs&sp)	—	—	—	—	—	—	—	—	—	—	—	—
ν_3 ClO$_4^-$	—	—	1110(vs)	1105(vs)	1105(vs)	—	1130	—	1100(vs)	—	1110(vs&br)	—	1100(vs)
	—	—	—	—	—	—	1100	—	620(br)	—	—	—	625(br)
$\nu_{M=N}$	—	410(w)	405(sh)	330(vs)	340(vs)	415(vs)	450(vs)	435(s)	430(s)	335(w)	370(w)	370(w)	345(s)
	—	340(br)	335(vs)	—	—	364(m)	330(vs)	353(m)	340(w)	330(sh)	315(sh)	340(w)	320(m)
	—	—	—	—	—	—	—	330(w)	320(w)	—	—	320(sh)	—

Table 3. The colour and UV–vis spectral data for Cu^{II} and Ni^{II} macrocyclic complexes

Complex	Colour	DMSO Solution	Nujol mull
1	Faint rose	620(br)	690(br)
		460(br)	460(br)
		350(br)	340(sh)
		280(s)	250(s)
2	Faint brown	620(br)	630(sh)
		540(br)	—
		410(br)	460(br)
		390(sh)	370(sh)
		290(s)	310(s)
3	Bright green	740(br)	—
		620(br)	640(br)
		540(br)	—
		—	440(br)
		390(sh)	—
		290(s)	290(s)
4	Grey	690(br)	650(br)
		530(br)	—
		410(br)	460(sh)
		390(sh)	—
		290(s)	300(s)
5	Brown	660(br)	620(br)
		540(br)	—
		410(br)	480(br)
		390(sh)	380(sh)
		280(s)	310(s)
6	Faint brown	680(br)	620(br)
		580(br)	—
		420(br)	480(br)
		360(sh)	370(sh)
		280(s)	300(s)
7	White	—	—
		—	—
		410(sh)	—
		350(S)	—
		—	300(S)
8	Yellow white	—	—
		—	—
		420(sh)	—
		360(sh)	390(sh)
9	Light blue	610(br)	—
		550(sh)	570(br)
		410(sh)	—
		340(sh)	380(sh)
		—	300(s)
10	Faint blue	610(br)	—
		550(sh)	560(br)
		420(sh)	—
		350(sh)	360(sh)
		—	300(s)
11	Light blue	610(br)	—
		550(br)	550(br)
		410(sh)	—
		—	350(sh)
		—	300(s)
12	Faint blue	610(br)	—
		550(br)	560(br)
		400(sh)	—
		—	360(sh)
		—	310(s)

the solid complex. They are assigned to $^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2E_g$ transitions, respectively [23]. In this case, the Cu^{II} macrocyclic complexes 1–6 will tend to form a *bis*-complex involving a tetragonal octahedral configuration by the four nitrogen atoms of the azomethine linkage and two equal longer bonds in the axial positions with the weakly coordinating anions present. The band in the 350–390 nm region can be attributed to a charge transfer transition which could arise from the transfer of an electron from an orbital largely belonging to a ligand to an orbital largely belonging to the central atom [24]. The highly intense band in the 250–290 nm region has been assigned to the π–π^* transitions of the azomethine groups [25].

The spectra of the Ni^{II} macrocyclic complexes 9–12 show four absorption bands in the 610, 520–550, 400–490 and 340–360 nm regions in DMSO solution and three absorption bands at 550–570, 350–380 and 310 nm in Nujol mulls. The spectra reveal pseudo-octahedral symmetry [26,27]. The first three low energy bands are broad with low intensity and characteristic to the $^2A_{2g} \rightarrow {}^3A_{1g}$ (P) and $^3A_{2g} \rightarrow {}^3A_{1g}$ (F) transitions of octahedral symmetry, respectively [28,29]. The band at 310 nm with high intensity corresponds to the π–π^* transitions of the azomethine groups. On the other hand, the spectra of 7 and 8 exhibit two absorption bands in DMSO solution; 350–480 nm and one strong broad absorption band at 300–390 nm in Nujol mulls. The first low energy band corresponds to square planar configuration. Both spectra in Nujol mulls and DMSO solution reveal no change in the geometry of the complex on going from the solid state to the DMSO solution.

EPR spectra and magnetic susceptibility of Cu^{II} and Ni^{II} macrocyclic complexes

The X-band EPR spectra of the solid Cu^{II} macrocyclic complexes 1–6 at room temperature involve two g-values in the region 2.063–2.216 of the axial elongated symmetry with $g_{11} > g_\perp$ indicating normal tetragonal Cu^{II} ion environment (Table 4 and Fig. 1). The

G factors in the range 2.444–2.915 indicate some sort of exchange interaction between Cu^{II} macrocyclic complexes [30]. The average g-values were calculated according to the relation:

$$g_{av.} = 1/3g_{11} + 2/3g_\perp$$

and gave values in the range 2.093–2.116 which is in accordance with the orbitally non-degenerate $^2B_{1g}$ ground state.

The magnetic susceptibilities at 25°C of the Cu^{II} complexes are (1.59–1.96 B.M) mainly in agreement with an orbitally non-degenerate ground state giving a pseudo-octahedral structure. On the other hand, the Ni^{II} macrocyclic complexes 9–12 have magnetic susceptibilities of 2.65–2.86 (Table 4) confirming the octahedral structure of these complexes. However, complexes 7 and 8 are diamagnetic indicating that they have the square planar configuration.

Thermal analysis

The TGA results of the macrocyclic complexes 2, 4, 10 and 12 show that the coordinated water molecules could be eliminated from these complexes within the temperature range 120–270°C while in the case of other macrocyclic complexes, the lattice water molecules are removed at 60–120°C. The two perchlorate ions are removed at 370–480°C while the coordinated chloride ions could be removed within the temperature range 340–420°C. Above 500°C, and as the temperature is increased to 750°C complete decomposition of the organic moiety occurs to get the corresponding metal oxide. These results were further supported by the DTA measurements which show endothermic peaks at 65–125°C and exothermic peaks at 130–300°C corresponding to the lattice and the coordinated water molecules, respectively. Also, there are strong sharp exothermic peaks within the temperature range 300–500°C corresponding to the removal of perchlorate ions of the perchlorate macrocyclic complexes or of the chloride ions of the chloride macrocyclic complexes. The exothermic peaks appearing above 500°C correspond to the complete decomposition of the macrocyclic complexes.

NMR spectroscopy

Due to the sparing solubilities of the Cu^{II} and Ni^{II} macrocyclic complexes 1–6 and 9–12, in most common deuterated solvents, the 60 MHz ^{1}H NMR spectra of these complexes did not show any characteristic signals.

On the other hand, ^{1}H NMR spectra of the Ni^{II} macrocyclic complexes 7 and 8 in deuterated DMSO showed the aromatic imidazole protons at 6.76–7.33 ppm and the methyl protons at 2.00 ppm and methylene protons at 3.6–3.7 ppm [31, 32]. The number of methyl and methylene protons was varified by integration.

Table 4. The EPR spectral data and magnetic susceptibility of the Cu^{II} and Ni^{II} macrocyclic complexes

Complex	g_{11}	$g_\perp$	$g_{av.}$	μ_{eff} B.M.
1	2.154	2.063	2.093	1.60
2	2.162	2.063	2.069	1.96
3	2.216	2.087	2.129	1.71
4	2.216	2.079	2.125	1.59
5	2.216	2.079	2.125	1.81
6	2.207	2.071	2.116	1.78
9				2.76
10				2.65
11				2.86
12				2.71
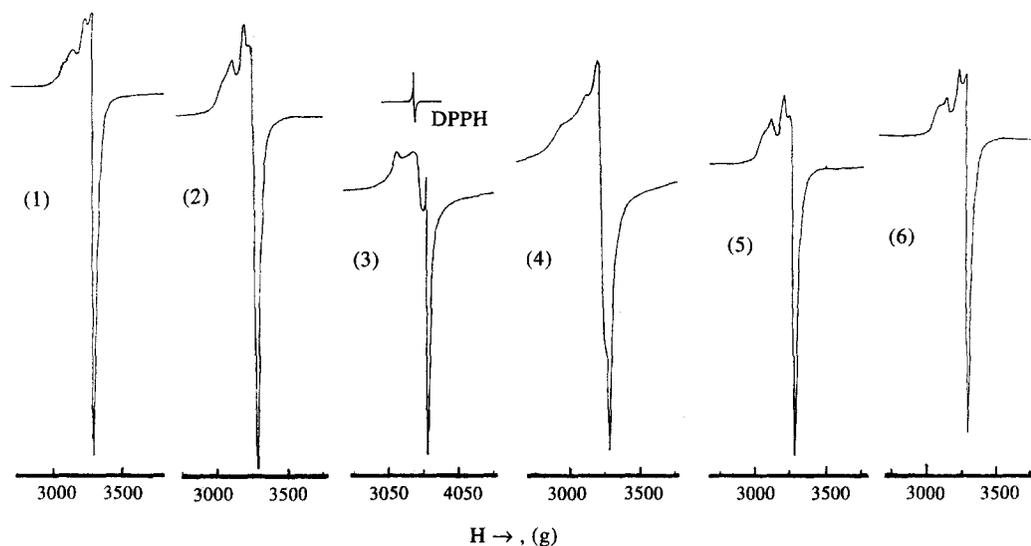
Fig. 1. EPR—Spectra of Cu^{II} macrocyclic complexes.
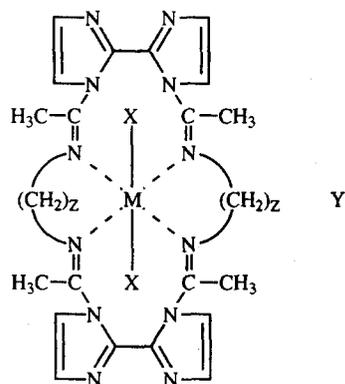
For 1: M=Cu, X=Cl, Y=3H$_2$O, Z=2
    2: M=Cu, X=H$_2$O, Y=2ClO$_4^-$, Z=2
    3: M=Cu, X=Cl, Y=2H$_2$O, Z=3
    4: M=Cu, X=H$_2$O, Y=2ClO$_4^-$, Z=3
    7: M=Ni, X=-, Y=2Cl.H$_2$O, Z=2
    8: M=Ni, X=-, Y=2ClO$_4^-$.3H$_2$O, Z=2
    9: M=Ni, X=Cl, Y=2H$_2$O, Z=3
    10: M=Ni, X=H$_2$O, Y=2ClO$_4^-$, Z=3

Scheme 1.
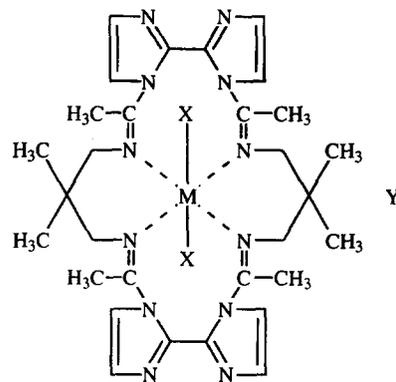
For 5: M=Cu, X=Cl, Y=2H$_2$O,
    6: M=Cu, X=ClO$_4$, Y=3H$_2$O,
    11: M=Ni, X=Cl, Y=2H$_2$O,
    12: M=Ni, X=H$_2$O, Y=2ClO$_4^-$.

Scheme 2.

The structures of the Cu^{II} and Ni^{II} macrocyclic complexes 1–12 are given in Schemes 1 and 2.

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