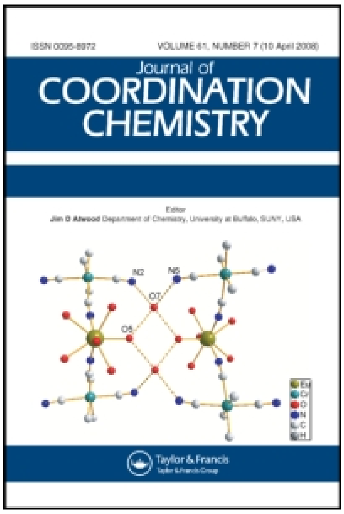


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Preparation and characterization of new nickel(II), cobalt(II) and copper(II) complexes of 3,11-diacetyl-2,12-dioxo-5,9-diazatrideca-3,11-diene; reactivity towards ammonia, 1,2-diaminopropane, hydroxylamine and copper(II) acetylacetonate compounds

Abdou S. El-Tabl[a]; Raafat M. Issa[b]
[a] Department of Chemistry, Faculty of Science, Menoufia University, Shebin El-Kom, Egypt [b] Department of Chemistry, Faculty of Science, Tanta University, Tanta, Egypt

To cite this Article El-Tabl, Abdou S. and Issa, Raafat M.(2004) 'Preparation and characterization of new nickel(II), cobalt(II) and copper(II) complexes of 3,11-diacetyl-2,12-dioxo-5,9-diazatrideca-3,11-diene; reactivity towards ammonia, 1,2-diaminopropane, hydroxylamine and copper(II) acetylacetonate compounds', Journal of Coordination Chemistry, 57: 6, 509 — 524

To link to this Article: DOI: 10.1080/00958970410001696816

URL: http://dx.doi.org/10.1080/00958970410001696816

J. Coord. Chem., Vol. 57, No. 6, 15 April 2004, pp. 509–524

Taylor & Francis
Taylor & Francis Group

PREPARATION AND CHARACTERIZATION OF NEW NICKEL(II), COBALT(II) AND COPPER(II) COMPLEXES OF 3,11-DIACETYL-2,12-DIOXO-5,9-DIAZATRIDECA-3,11-DIENE; REACTIVITY TOWARDS AMMONIA, 1,2-DIAMINOPROPANE, HYDROXYLAMINE AND COPPER(II) ACETYLACETONATE COMPOUNDS

ABDOU S. EL-TABL[a,]* and RAAFAT M. ISSA[b]

[a]*Department of Chemistry, Faculty of Science, Menoufia University, Shebin El-Kom, Egypt;*
[b]*Department of Chemistry, Faculty of Science, Tanta University, Tanta, Egypt*

(Received 6 August 2003; In final form 3 March 2004)

The interaction of the potentially binucleating enaminoketone, ligand 3,11-diacetyl-2,12-dioxo-5,9-diazatrideca-3,11-diene, towards nickel(II), cobalt(II) and copper(II) ions yields square planar complexes. The interaction of the complexes with ammonia, 1,2-diaminopropane, hydroxylamine and copper(II) acetylacetonate has been investigated. The complexes have been characterized by elemental analyses, UV-vis and IR spectroscopy, molar conductances, mass spectra, ^{1}H NMR, D.T.A., magnetic and ESR measurements. The molar conductances in DMF indicate that the complexes are non-ionic. Exposing nickel(II) complex (**2**) in CD_3OD/D_2O (10%) to ^{60}Co γ-rays at 77 K using a 0.2216 M rad h^{-1} dose, yields a nickel(I), d^9 species with a $d_{x^2-y^2}$ ground state. The spectrum shows that annealing above 77 K leads to a low-spin, nickel(III), d^7 species with a d_{z^2} ground state. The cobalt(II) complex (**3**) shows a spectrum with $g_\perp > g_{||}$, indicating a d_{z^2} ground state; however, the copper(II) complex (**4**) shows a spectrum with $g_{||} > g_\perp$, indicating a $d_{x^2-y^2}$ ground state. The redox properties of the copper(II) complexes (**4** and **13**) are discussed.

Keywords: β-Diketones; Ni; Co; Cu

INTRODUCTION

The preparation and reactions of synthetic β-diketones and macrocyclic ligands have been topics of growing importance in coordination chemistry. Metal complexes of macrocyclic ligands are found to be stabilized thermodynamically and kinetically relative to those of corresponding acyclic complexes. Further, they can provide a specific

---

*Corresponding author.

ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/00958970410001696816

geometrical environment for the bound metal ion and hence influence its physicochemical properties. Condensation of N_2O_2 quadridentate ketoenamine metal complexes with diamines yields tetraaza-macrocyclic metal complexes, which are used as model compounds for active sites in enzymes comprising corrin or porphyrin moieties. Also, various uses have been proposed for such complexes, including the selective extraction of metal ions from solution and the production of novel catalysts for diverse reactions such as the hydrolysis or oxidation of organic substrates [1–3].

Binuclear metal complexes are of interest in connection with spin exchange and charge transfer between the metal ions and in the domain of metalloenzymes and homogeneous catalyses. Binuclear copper(II) complexes obtained from the reaction of aromatic diamines and salicylaldehyde or 2-hydroxynaphthaldehyde have been synthesized and characterized [4]. The present study involves the preparation and characterization of nickel(II), cobalt(II) and copper(II) complexes of 3,11-diacetyl-2,12-dioxo-5,9-diazatrideca-3,11-diene and also, their reactivity towards ammonia, 1,2-diaminopropane, hydroxylamine and copper(II) acetylacetonate compounds.

EXPERIMENTAL

All chemicals and solvents were reagent grade commercial materials and used as received. C, H and N analyses were determined at the Analytical Unit of Cairo University, Egypt. Metal analyses were made on a Shimadzu AA-660 atomic absorption/flame emission spectrophotometer. All complexes were dried *in vacuo* over P_2O_5. IR spectra (as KBr or CsBr pellets and as nujol mull) were recorded on a Perkin-Elmer 681 spectrophotometer. Electronic spectra were recorded on a Perkin-Elmer 550 spectrometer. ^{1}H NMR spectra were obtained on a Bruker AM 300 MHz instrument with Me_4Si as internal reference. Mass spectra were recorded with a micromass 18 B mass spectrometer. Magnetic susceptibilities were measured at 25°C by the Gouy method with mercuric tetrathiocyanatocobaltate(II) as the magnetic susceptibility standard. Diamagnetic corrections were made using Pascal's constant [5]. Magnetic susceptibilities were measured at 25°C from the equation: $\mu_{\text{eff}} = 798(\chi_{\text{m}}T)^{1/2}$. Molar conductances were measured on a tacussel-type CD6NG conductivity bridge using 10^{-3} M DMF solutions. Differential thermal analysis (DTA) was carried out in air (20–800°C) using a Shimadzu DT-30 thermal analyzer. Cyclic voltammetry was measured in 2×10^{-3} M DMF solution containing 0.1 M as supporting electrolyte, using a gold working electrode. All ESR measurements from 77 K up to 300 K were carried out using a Varian E-109, X-band spectrometer (Leicester University, England). Complex **2** was irradiated in a Vickrad ^{60}Co source at 77 K with dose rate 0.2216 M rad h^{-1}. The spectrometer was calibrated using standard samples, such as the stable radical, α,α-diphenyl β-picryl hydrazyl (DPPH) [6]. X-ray powder diffraction patterns were carried out using a Shimadzu XD-3 diffractometer. TLC of all complexes confirmed their purity.

Synthesis of the Compounds

3-(Ethoxyvinylidene)-2,4-pentanedione and Compound **1** were prepared according to literature methods [7,8].

Preparation of Complexes 2, 3 and 4

To the ligand (0.017 mol) dissolved in ethanol (50 cm^3) was added the appropriate salt dissolved in ethanol (30 cm^3): 4.2 g $Ni(OAc)_2 \cdot 4H_2O$ for Complex **2**, 4.21 g $Co(OAc)_2 \cdot 4H_2O$ for Complex **3**; 3.4 g $Cu(OAc)_2 \cdot H_2O$ for Complex **4**. The mixture was heated at reflux for 1 h. On cooling to room temperature and reducing the volume, a precipitate appeared which was filtered off, washed with ethanol and subsequently dried over P_2O_5.

Preparation of Complexes 5, 6 and 7

In a 100-cm^3 short-necked round-bottomed flask, Complex **2** (0.006 mol) was taken in ethanol (30 cm^3) and to this was added 0.42 g 1,2-diaminopropane for Complex **5**, 0.2 g NH_4OH for Complex **6** or 0.57 g acetylacetone for Complex **7**, each dissolved in ethanol (20 cm^3). The reaction mixture was heated under reflux for 3 h, then it was cooled and coloured complexes were filtered off, washed with ethanol and dried over P_2O_5.

Preparation of Complexes 8, 9 and 10

Hydroxylamine hydrochloride (0.01 mol) was dissolved in pyridine (20 cm^3) under reflux on a water bath. To this solution was added 0.005 mol of Complex **2**, **3** or **4** in ethanol (25 cm^3) to give the corresponding Complex **8**, **9** or **10**, respectively. The mixture was heated on a water bath for 5 h. The solution was cooled to room temperature and the complexes were precipitated by addition of water, filtered off, washed with water and ethanol and then dried over P_2O_5.

Preparation of Complexes 11, 12 and 13

To a boiling solution of appropriate salt (0.03 mol) [$Ni(OAc)_2 \cdot 4H_2O$, (8.0 g) for Complex **11**, $Co(OAc)_2 \cdot 4H_2O$, (8.0 g) for Complex **12** and $Cu(OAc)_2 \cdot H_2O$ (6.4 g) for Complex **13**] and 3-(ethoxy-vinylidene)-2,4-pentanedione (10.0 g, 0.06 mol) in ethanol (30 cm^3) an ethanolic solution (20 cm^3) of 1,3-diaminopropane (2.4 g, 0.03 mol) was added slowly with constant stirring. The mixture was boiled under reflux for 4 h. On cooling, the complexes separated out. They were filtered off, washed with ethanol and dried over P_2O_5.

Preparation of Complexes 14, 15 and 16

To a boiling solution of copper(II) acetylacetonate complex (0.005 mol) in ethanol (25 cm^3), an ethanolic solution (30 cm^3) of equimolar amounts of **8** for Complex **14**, **9** for Complex **15** and **10** for Complex **16** was added slowly with constant stirring and the mixture was boiled under reflux for 5 h. On cooling, the complexes separated out. They were filtered off, washed with ethanol and dried over P_2O_5.

RESULTS AND DISCUSSION

All the newly synthesized complexes [9,10] are coloured crystalline solids, stable in air and not decomposing after prolonged storage (nine months). The complexes are soluble in chloroform, acetonitrile, DMF and DMSO, moderately soluble in ethanol and methanol and practically insoluble in carbon tetrachloride and benzene. The analytical and physical data (Table I) and spectral data (Tables II and III) are compatible with the supposed structures (Fig. 1). The elemental analyses were found to be in close agreement with the calculated values for the assigned molecular formulas. The mass fragmentation spectral data of the compounds are consistent with the proposed structures. The observation of the molecular ion allows an unambiguous identification. The most intense m/z peaks of Compound **1** are listed in Table IV.

The molar conductances in DMF solution are in the 7.1–25.4 $\Omega^{-1}\,cm^2\,mol^{-1}$ range (Table I), commensurate with non-electrolytic behaviour [8,11] and consistent with the expectation of a neutral complex formed by a dianionic ligand with a dipositive metal ion.

The ^{1}H NMR spectra of Compounds **1** and **8** in CD_3Cl show the expected chemical shifts. Strong resonances at 2.2 and 2.15, 2.4 and 2.26 ppm are ascribed to the protons of terminal methyl groups (c) and (d) respectively (Fig. 1). Two further peaks at 3.4 and 2.31 (b), 7.8 and 7.72 ppm (a), are due to the protons of methylene and ethylene groups. Another peak at 2.0 and 1.96 ppm (e) is assigned to the middle methylene group. The spectra also shows resonances at 10.8 and 11.45 ppm (f), due to the NH and NOH groups [8,12]. However, Complex **7** gives resonances at 2.01 and 3.02 ppm due to CH_3 and CH_2 protons of the acetylacetone molecule [13]. Complexes **11**, **12** and **13** were prepared by reaction of 3-ethoxyvinylidene-2,4-pentandeione with 1,3-diaminopropane in the presence of $M(OAc)_2 \cdot nH_2O$, 2 : 1 : 1 ratios in ethanol [$M = Ni(II)$, $n = 4$, **11**; $M = Co(II)$, $n = 4$, **12**; $M = Cu(II)$, $n = 1$, **13**]. However, the other complexes were prepared according to Scheme 1.

IR Spectra

Spectral data of the compounds are given in Table II. Compound **1** reveals intense bands at 1657 and 1630 cm^{-1}, assigned to the terminal and chelate carbonyl groups [8,14]. Two $\nu(NH)$ bands appear at 3475 and 3421 cm^{-1}. Another band at 1575 cm^{-1} is assigned to the $\nu(C{=}C)$ vibration of aliphatic group [15]. Upon coordination the chelate $\nu(C{=}O)$ of Compound **1** is shifted (Table II) in the Complexes **2**, **3** and **4**. Such a pronounced downward shift (ca. 15 cm^{-1}) in the $\nu(C{=}O)$ implies strong metal–ligand bonding in the complexes under discussion [16]. The value of the terminal $\nu(C{=}O)$ remains unaltered during complexation, thus ruling out the possibility of coordination of the terminal carbonyl group to the metal ions. The strong, broad band in the 3650–3075 cm^{-1} range confirms the presence of water in all the complexes except **2**, **5**, **7** and **11**. In addition, the disappearance of the two $\nu(NH)$ bands (Table II) except for Complexes **6**, **12** and **13** is presumably due to the coordination to the metal ion. The band observed in the 1590–1555 cm^{-1} range is assigned to $\nu(C{=}C)$ of the aliphatic group. In Complex **5**, the band due to chelate carbonyl groups (1615 cm^{-1}) disappeared and a new band was observed at 1603 cm^{-1}, corresponding to the imino-groups (Table II); the $\nu(M–O)$ band also disappeared (570 cm^{-1}) and a new band was observed at 635 cm^{-1}, which is assigned to $\nu(M–N)$. These results are consistent

TABLE I Analytical and physical data of the ligand and its metal(II) complexes

Comp. No./ Suggested formula	*Color*	*Yield (%)*	*μ_{eff} (BM)*	*M.P. (°C)*	*Molar conductance (Ω^{-1} cm^2 mol^{-1})*	*Found (Calcd.) (%)*				
						C	*H*	*N*	*M*	
1 [$C_{15}H_{22}N_2O_4$]	yellow white	85	–	160	7.1	61.5 (61.5)	7.6 (7.4)	9.7 (9.5)	–	
2 [$C_{15}H_{20}N_2O_4Ni$]	red	77	diamag.	203	11.6	51.2 (51.3)	5.8 (5.8)	8.0 (8.0)	16.6 (16.7)	
3 [$C_{15}H_{20}N_2O_2Co \cdot 2H_2O$]	brown	73	2.2	220	13.2	47.3 (47.1)	6.2 (6.3)	7.2 (7.3)	15.4 (15.5)	
4 [$C_{15}H_{20}N_2O_2Cu \cdot H_2O$]	greenish blue	80	1.82	210	16.2	45.8 (64.0)	5.9 (6.1)	6.8 (7.1)	16.0 (16.2)	
5 [$C_{18}H_{26}N_4O_2Ni$]	brown	78	diamag.	220	11.9	55.3 (55.5)	6.6 (6.7)	14.2 (14.4)	15.0 (15.2)	
6 [$C_{12}H_{16}N_2O_4Ni \cdot 3\frac{1}{2}H_2O$]	yellowish brown	72	diamag.	215	13.0	38.8 (38.5)	5.9 (6.1)	7.5 (7.4)	16.1 (15.8)	
7 [$C_{20}H_{28}N_2O_6Ni$]	yellowish green	79	2.83	230	16.1	53.1 (53.2)	6.3 (6.2)	5.9 (6.2)	12.9 (13.1)	
8 [$C_{15}H_{22}N_4O_4Ni \cdot H_2O$]	dark orange	72	diamag.	275	18.9	45.0 (45.1)	6.0 (6.0)	13.8 (14.0)	15.0 (14.8)	
9 [$C_{15}H_{22}N_4O_4Co \cdot H_2O$]	dark brown	75	2.1	293	22.6	44.9 (45.0)	6.0 (5.9)	13.9 (14.0)	14.9 (14.8)	
10 [$C_{15}H_{22}N_4O_4Cu \cdot H_2O$]	dark green	81	1.79	290	19.6	44.8 (44.6)	6.0 (5.9)	14.0 (13.9)	15.8 (15.6)	
11 [$C_{15}H_{20}N_2O_4Ni]_n$	brown	80	diamag.	215	19.8	51.1 (51.1)	5.8 (5.9)	8.0 (7.9)	16.6 (16.7)	
12 [$C_{30}H_{42}N_4O_8Co \cdot \frac{1}{2}H_2O$]	green	80	2.0	205	23.0	54.8 (55.0)	6.7 (6.6)	8.7 (8.6)	9.1 (9.0)	
13 [$C_{30}H_{42}N_4O_8Cu \cdot 2H_2O$]	green	81	1.71	225	23.5	51.6 (51.8)	6.8 (6.8)	8.5 (8.3)	9.4 (9.3)	
14 [$C_{25}H_{36}N_4O_8NiCu \cdot H_2O$]	green	78	1.91	227	21.2	40.8 (40.7)	5.8 (5.9)	8.4 (8.3)	Ni 8.7 (8.5)	Cu 9.5 (9.3)
15 [$C_{25}H_{36}N_4O_8CoCu \cdot H_2O$]	violet	76	1.15	220	25.4	42.0 (41.8)	5.6 (5.8)	8.4 (8.5)	Co 9.0 (8.9)	Cu 9.7 (9.5)
16 [$C_{25}H_{36}N_4O_8Cu_2 \cdot 2H_2O$]	blue	75	1.2	230	24.1	40.6 (40.5)	5.7 (5.9)	8.4 (8.2)	18.8 (18.5)	

TABLE II IR spectra (cm^{-1}) of the ligand and its metal complexes

Comp. No.	*Assignment (cm^{-1}) $\nu(H_2O/H\text{-bonding})$ $\nu(N\text{–}H)$*	*$\nu(C{=}O)$*	*$\nu(C{=}N)$*	*$\nu(C{=}C)$*	*$\nu(NO)$*	*$\nu(MO)$*	*$\nu(M\text{–}N)$*
1	3600–3100 3475, 3421	1657 1630	–	1575	–	–	–
2	–	1657 1615	–	1572	–	570	630
3	3620–3200	1657 1618	–	1570	–	580	668
4	3620–3250	1657 1615	–	1570	–	550	620
5	–	1655	1603	1570	–	–	625 635
6	3625–3180 3365, 3320	1650	1630	1590	–	535	655
7	–	1655 1645 1620 1615	–	1557	–	530 570	655
8	3620–3210 3410	1655	1556	1575	–	650 632	1168 932
9	3600–3175 3400	1655	1570	1575	–	662 645	1172 930
10	3600–3180 3395	1655	1580	1575	–	645 638	1185 925
11	–	1657 1615	–	1565	–	560	630
12	3600–3280 3170–3275	1655 1618	–	1565	–	580	670
13	3625–3120 3260, 3170	1657 1615 1610	–	1566	–	560	615
14	3600–3200	1655 1645 1618 1615	1550	1575 1560	1290 952	595 550 515	615
15	3650–3075	1655 1645 1618 1615	1548	1570 1555	1283 961	545 520	615
16	3650–3150	1655 1645 1620 1615	1538	1560	1275 955	557 548	660

with the formation of a macrocyclic complex. Complex **6** shows bands at 1630 and 1343 cm^{-1}, assigned to ν(C=N) and ν(C–O) groups respectively [15,16]. However, Complexes **8**, **9** and **10** show a band at 1655 cm^{-1}, assigned to ν(C=O) of the terminal group. Bands around 3395 cm^{-1} (Table II) are due to ν(OH) of the oxime group. The lowering of the ν(OH) frequencies corresponds to hydrogen bonding of the oxime group OH. Bands observed in the 1185–1168 and 932–925 cm^{-1} ranges are assigned to ν(NO) vibrations [17]. It is noteworthy that the chelate ν(C=O) band (Table II) disappears with the appearance of a new band around 1556 cm^{-1} which is assigned to ν(C=N) of the oxime group. The lowering of this band is associated with ν(C=N) of the N-coordination oximato group. The locations of these bands are identical with those reported for the metal(II) complexes of dioxime ligands [18,19]. In Complexes

14, **15** and **16**, the bands due to the hydrogen bonds in Complexes **8**, **9** and **10** disappear completely, suggesting the cleavage of hydrogen bonds in the parent complexes. The significant IR spectral bands in the binuclear complexes are 1550–1538 and 1290–1275 cm^{-1} ranges, assigned to ν(C=N) of the oxime group and ν(NO) stretches, which are shifted from the original complexes, indicating that the dioxime oxygen atoms have been coordinated to the copper(II) ion. Complexes **7**, **14**, **15** and **16** show bands at 1655, 1645 and 1620, and 1618 and 1615 cm^{-1} (Table II), corresponding to terminal C=O groups and coordinated C=O of acetyl groups [17,20–22]. The complexes show bands in the 670–615 and 595–515 cm^{-1} ranges due to ν(M–N) and ν(M–O) vibrations respectively [15,20,23]. If the molecular geometry of the ligand does not allow formation of a stable ring involving the metal ion, then polymeric Complex **11** is formed in the solid state [23,24].

Electronic Spectra

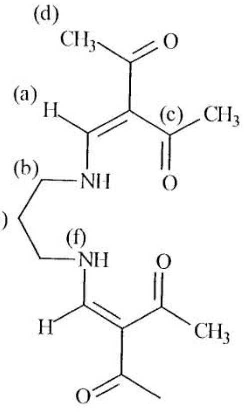
The electronic spectra of the compounds in nujol mull and chloroform solution are summarized in Table III. The electronic spectrum of Compound **1** in chloroform shows peaks at 323 nm ($\varepsilon = 2.8 \times 10^{-4}\,\mathrm{m^2\,mol^{-1}}$) and 236 nm ($\varepsilon = 3.0 \times 10^{-4}\,\mathrm{m^2\,mol^{-1}}$),

TABLE III Electronic spectra of the ligand and its metal(II) complexes

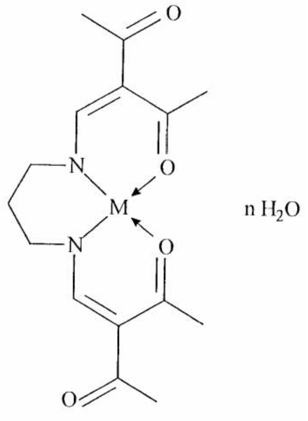
Comp. No.	*Medium*	$\lambda_{\max}$ *(nm)*
1	DMF	323 nm ($\varepsilon = 284.7 \times 10^{-2}\,\mathrm{m^2\,mol^{-1}}$)
	$CHCl_3$	236 nm ($\varepsilon = 292.6 \times 10^{-2}\,\mathrm{m^2\,mol^{-1}}$)
2	N.M.	572, 480, 370
	$CHCl_3$	565, 465, 355
3	N.M.	495, 382, 320
	$CHCl_3$	470, 365, 310
4	N.M.	535, 450, 310
	$CHCl_3$	515, 425, 300
5	N.M.	550, 485, 350
	$CHCl_3$	540, 470, 340
6	N.M.	540, 470, 365
	$CHCl_3$	525, 460, 345
7	N.M.	650, 435, 330
	$CHCl_3$	615, 428, 310
8	N.M.	552, 465, 372
	$CHCl_3$	525, 432, 355
9	N.M.	530, 410, 365
	$CHCl_3$	515, 390, 328
10	N.M.	560, 495, 380
	$CHCl_3$	525, 472, 365
11	N.M.	570, 480, 350
	$CHCl_3$	555, 468, 335
12	N.M.	520, 415, 315
	$CHCl_3$	500, 390, 305
13	N.M.	625, 412, 351
	$CHCl_3$	605, 400, 335
14	N.M.	610, 550, 475, 350
	$CHCl_3$	595, 535, 465, 340
15	N.M.	640, 523, 410, 310
	$CHCl_3$	615, 505, 380, 300
16	N.M.	650, 580, 470, 360, 305
	$CHCl_3$	620, 560, 450, 340, 295

N.M. = nujol mull.

ascribed to intramolecular electronic transitions. In nujol mull, nickel(II) Complexes **2**, **5**, **6**, **8**, **11** and **14** show there are well-defined bands in the 540–572, 465–485 and 350–372 nm ranges; however, in chloroform, the peaks appear in the 525–565, 432–470 and 335–355 nm ranges, assigned to ${}^1A_{1g} \rightarrow {}^1A_{2g}$, ${}^1A_{1g} \rightarrow {}^1A_{1g}$ and ${}^1A_{1g} \rightarrow {}^1E_g$ transitions respectively, consistent with square-planar geometry [21]. However, complex **7** in nujol mull shows two well-defined bands at 650 and 435 nm. In chloroform, the peaks appear at 615 and 428 nm assigned to the ${}^3A_{2g} \rightarrow {}^3T_{2g}(\nu_1)$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}(\nu_2)$ transitions respectively in an octahedral structure. The third d–d transition band (ν_3), which may lie obscured by the more intense charge-transfer band is calculated theoretically to lie at 330 nm (nujol) and 310 nm ($CHCl_3$). The ν_2/ν_1 value of 1.5 lies in the



H_2L (1)

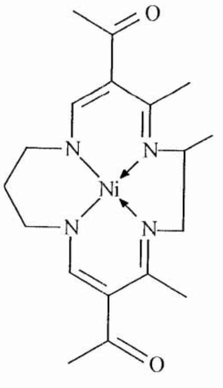


M = Ni(II) n = 0 H_2O **(2)**
M = Co(II) n = 2 H_2O **(3)**
M = Cu(II) n = 2 H_2O **(4)**

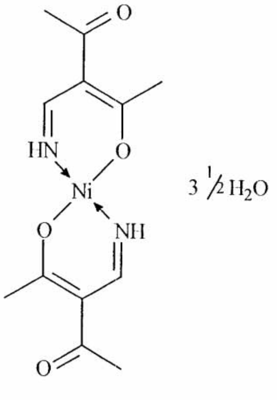
FIGURE 1

range expected for octahedral geometry [22,25]. The electronic spectra of cobalt(II) Complexes **3**, **9**, **12** and **15** in nujol mull show three bands at 310–365, 382–415 and 495–530 nm; however, in chloroform the bands appear at 300–328, 365–390 and 470–515 nm. The first two are within the ligand, and the third transition is characteristic of a square-planar environment and probably arises from the $^2A_{1g}$ transition with configuration $e_g^4b_2^2a_{1g}$ [22,26]. The copper(II) Complexes **4** and **10** give three bands in the nujol mull located at 310, 450, 535 and 380, 495, 560 nm. However, in chloroform, the bands appear at 300, 425, 515 and 365, 472, 525 nm. The first band is within the ligand and the other bands correspond to $^2B_{1g} \rightarrow {}^2E_g$ and $^2B_{1g} \rightarrow {}^2A_{1g}$ transitions respectively, assuming a square-planar configuration [27].

Complex **13** in nujol mull shows three bands at 351, 412 and 625 nm; however, in chloroform the peaks appear at 335, 400 and 605 nm. The first two are within the ligand and the third band corresponds to the $^2B_{1g} \rightarrow {}^2E_g$ transition of a copper(II) ion in a tetragonally distorted octahedral geometry [28]. Complexes **14**, **15** and **16** show an additional band in nujol mull at 610–650 nm; in chloroform it appears at



(5)



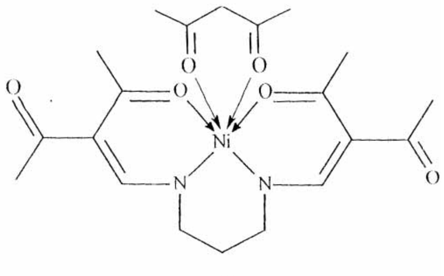
(6)

FIGURE 1 (continued).

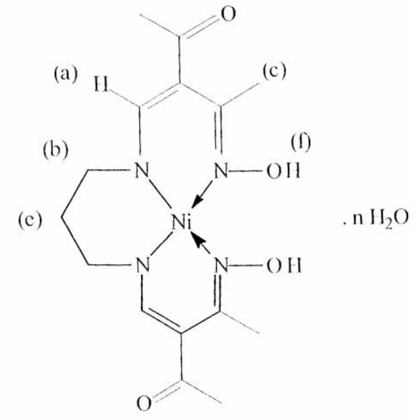
595–615 nm and is assigned to the $^2B_{1g} \rightarrow {}^2E_g$ transition in a tetragonally clongated octahedron [28].

Magnetic Moments

The magnetic moments for the compounds are shown in Table I. Nickel(II) complexes **2**, **5**, **6**, **8** and **11** are diamagnetic as expected for a square-planar geometry d^8 system. However, for Complex **7** the value of 2.83 BM shows octahedral geometry around the nickel(II) ion. The cobalt(II) Complexes **3**, **9** and **12** have values 2.2, 2.0 and 2.1 BM respectively, indicating square-planar geometry [29]. The copper(II) Complexes **4** and **10** show values 1.82 and 1.79 BM respectively, corresponding to one unpaired electron as expected for d^9 square-planar copper(II) complexes [30]. However, complex **13** has a value of 1.71 BM, confirming octahedral geometry [29]. Complexes **14**, **15** and **16** have values of 1.91, 1.15 and 1.2 BM respectively, as expected for the proposed structures. The low moments of Complexes **15** and **16** may be the result of dimerization and subsequent antiferromagnetic exchange between the metal(II) ions.



(7)

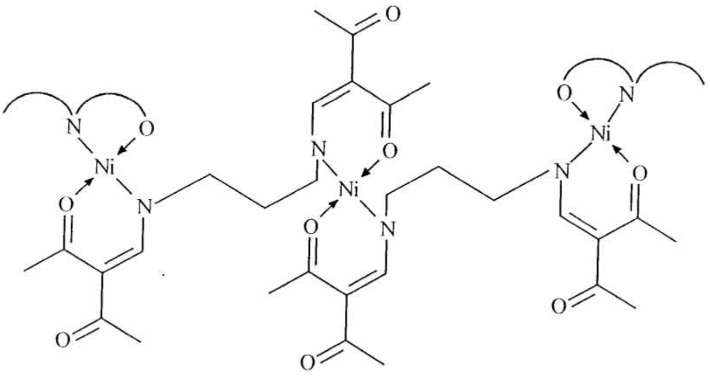


M = Ni(II) n = H$_2$O **(8)**
M = Co(II) n = H$_2$O **(9)**
M = Cu(II) n = H$_2$O **(10)**

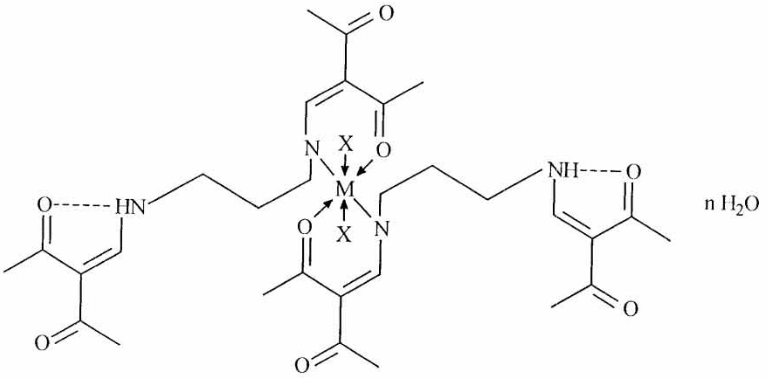
FIGURE 1 (continued).

Differential Thermal Analysis

Because the IR spectra indicate the presence of water molecules, thermal analyses were undertaken to ascertain their nature. DTA shows that all the complexes are thermally stable up to 70°C, when dehydration begins. This is characterized by endothermic peaks in the range 70–83°C, corresponding to the loss of hydrated water [31]. Complex **13** shows an exothermic peak at 208°C, corresponding to loss of coordinated water [31,32]. The existence of an exothermic peak in the DTA curve at the same temperature suggests that Complexes **3**, **4**, **6** and **12** all provide the same chemical environment [33].



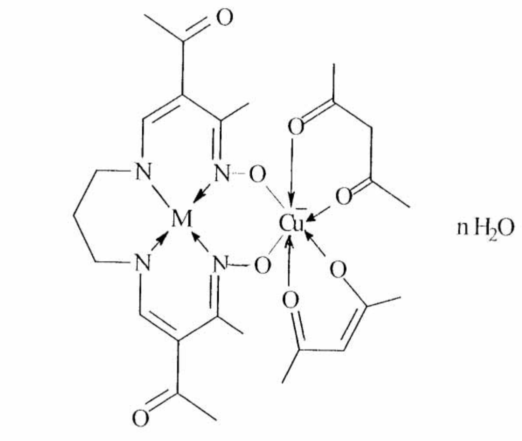
(11)



M = Co (II) X = 0 H_2O **(12)**
n = $\frac{1}{2}$ H_2O

M = Cu(II) X = H_2O **(13)**
n = 0 H_2O

FIGURE 1 (continued).



$M = Ni(II)$, $n = H_2O$ **(14)**

$M = Co(II)$, $n = 2H_2O$ **(15)**

$M = Cu(II)$, $n = 2H_2O$ **(16)**

FIGURE 1 (continued).

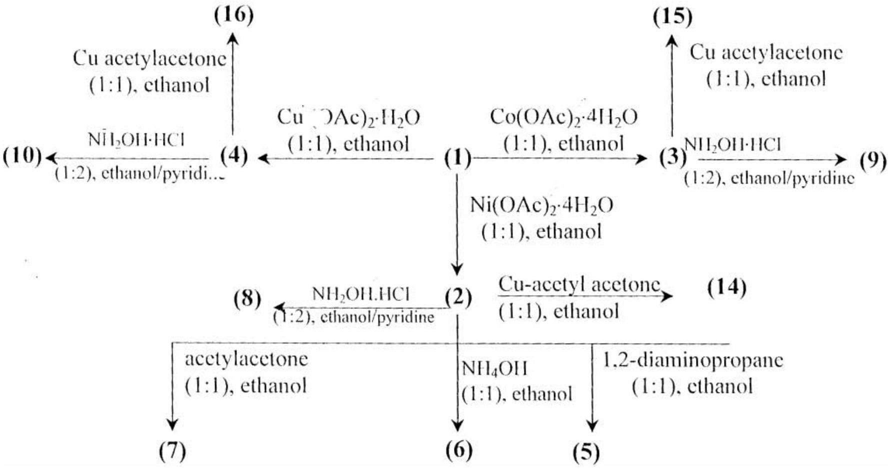
TABLE IV Mass fragmentation spectrum of Compound **1**

m/z	*Rel. abundance*	*Assignment*
43	100	$[C_2H_3O]^+$
98.5	60	$[C_2H_6O_2]^+$
127	100	$[C_6H_8O_2N]^+$
196	21	$[C_{10}H_{16}O_2N_2]^+$
208	100	$[C_{11}H_{16}O_2N_2]^+$
251	90	$[C_{12}H_{19}O_3N_3]^+$
294.7	100	$[C_{15}H_{21}N_2O_4]^+$

The complexes also show an endothermic peak at 205–230°C, the melting points of the complexes. The products are stable up to 485°C when the organic constituents of the complexes start decomposing, finally leaving the metal oxide (485–580°C). The D.T.A. data for the complexes are shown in Table V.

ESR Spectra

Nickel(II) Complex **2** has a diamagnetic, d^8 structure, so ESR spectroscopy has not been applied to the study of its electronic structure. In order to overcome this, the complex was dissolved in $CD_3OD + D_2O$ (10%) in liquid nitrogen and exposed to ^{60}Co γ-rays at 77 K using a 0.2216 M rad h^{-1} vicrad source for periods up to 5 h. Addition of an electron to the d^8 electronic configuration of the nickel(II) ion resulted in the formation of a d^9 nickel(I) complex. The signals detected from the spectrum is the $g_{\|}(= 2.17)$ in the low-field region and $g_{\perp}(= 2.06)$ in the high-field region. In addition, the free radical



SCHEME 1.

TABLE V DTA peaks and their assignments for the complexes

Comp. No	*DTA peaks (°C)* *Endo*	*Exo*	*Assignments*
3	75	–	Dehydration process
	220	–	M.P. of the complex
	–	510	Decomposition of the complex
4	80	–	Dehydration process
	210	–	M.P. of the complex
	–	485	Decomposition of the complex
6	80	–	Dehydration process
	215	–	M.P. of the complex
	–	518	Decomposition of the complex
7	230	–	M.P. of the complex
	–	530	Decomposition of the complex
8	85	–	Dehydration process
	275	–	M.P. of the complex
	–	300	Braking of H-bonding
	–	580	Decomposition of the complex
12	70	–	Dehydration process
	205	–	M.P. of the complex
	–	498	Decomposition of the complex
13	–	208	Thermal dissociation of coordinated water
	225	–	M.P. of the complex
	–	500	Decomposition of the complex
14	83	–	Dehydration process
	227	–	M.P. of the complex
	–	540	Decomposition of the complex
15	82	–	Dehydration process
	220	–	M.P. of the complex
		538	Decomposition of the complex
16	80	–	Dehydration process
	230	–	M.P. of the complex
		540	Decomposition of the complex

signal of the solvent was observed at ~ 2.0. This spectrum has axial-type symmetry with $g_{||} > g_{\perp} > 2.04$, suggesting a $d_{x^2-y^2}$ ground state [34,35], characteristic of square-planar geometry [36] for a d^9 nickel(I) complex. The complex was annealed above 77 K by decanting the liquid nitrogen from the dewar flask and continuously monitoring the ESR spectra. Whenever significant changes were observed, the complex was recooled to 77 K for study. Analysis at 77 K shows an axial-type spectrum with new features, at $g_{||}(=2.05)$ and $g_{\perp}(=2.12)$; $g_{\perp} > g_{||} > 2.0$. This observation is consistent with the existence of a low-spin nickel(III), d^7 system with the unpaired electron in the d_{z^2} orbital of a square-planar geometry [35,37]. The nickel(III) complex is formed by the reaction of the nickel(II) complex with solvent radicals, e.g.

$$(\mathrm{Ni}^{2+})\mathrm{L} + {}^{\bullet}\mathrm{OH} \rightarrow (\mathrm{Ni}^{3+})\mathrm{L} + {}^{-}\mathrm{OH}$$

$$(\mathrm{Ni}^{2+})\mathrm{L} + {}^{\bullet}\mathrm{R} \rightarrow (\mathrm{R}^{-})\text{–}(\mathrm{Ni}^{3+})\mathrm{L}$$

The ESR spectra of solid Complex **3** at room temperature and 77 K show a broad signal, indicating that spin-exchange interactions take place between the cobalt(II) ions [38]. The ESR spectrum of this complex in CD_3OD/D_2O (10%) at 77 K is characteristic of a low-spin monomeric species, with d^7 configuration. The line widths are anisotropic. The spectrum exhibits two features assigned to $g_{||}(=2.03)$ and $g_{\perp}(=2.29)$, which are characteristic of square-planar geometry [39]; $g_{\perp} > g_{||} > 2.0023$, indicating a d_{z^2} ground state [40,41].

The ESR spectra of Complex **4** were recorded at both room and liquid nitrogen temperatures. These spectra show marked broadening and loss of hyperfine splitting, suggesting spin-exchange interactions between the copper(II) sites [42]. The shift of the signal in the low-field region to a slightly lower value at 77 K indicates stronger metal–ligand bonding, consistent with a flattening of any tetrahedral distortion present in this complex at room temperature [36]. However, in CD_3OD/D_2O (10%) at 77 K, the spectrum shows four lines in the low-field region and a broad line in the high-field region with $g_{||}(=2.18)$ and $A_{||}(200\,G)$ with $g_{\perp}(=2.06)$, $(g_{\mathrm{iso}}=2.1)$ indicating a $d_{x^2-y^2}$ ground state and an essentially square-planar geometry around the copper(II) ion [43]. The $g_{||}/A_{||}$ value can be used to determine the stereochemistry of the copper(II) complex [44]; the range reported for square-planar complexes is 105–135 cm^{-1} and for tetrahedrally distorted complexes 150–250 cm^{-1}. The $g_{||}/A_{||}$ value is 109 cm^{-1}, in the range expected for square-planar complexes. The g-values are related by the expression [32,44], $G = (g_{||} - 2)/(g_{\perp} - 2)$; if $G > 4.0$, local tetragonal axes are aligned parallel or only slightly misaligned; if $G < 4.0$, significant exchange coupling is present. In this case the G value is 3.0, indicating that a spin-exchange interactions take place. The $g_{||}$-value in copper(II) complexes can be used as a measure of the covalent character of the metal–ligand bond. If $g_{||} \geq 2.3$, the environment is essentially ionic and $g_{||} < 2.3$ indicates covalent bond character. The $g_{||}$ value indicates covalent bond character in this complex [45].

Electrochemistry

The redox properties of copper(II) Complexes **4** and **13** were examined by cyclic voltammetry in dimethylformamide solutions containing 0.1 M LiCl as supporting electrolyte at a gold electrode at scan rates varying from +0.4 to −1.50V. Complex **4** shows three reduction peaks at $E'_{\mathrm{Pc}} = -0.41$, $E^2_{\mathrm{Pc}} = -1.05$ and $E^3_{\mathrm{Pc}} = -1.26$V respectively, and two oxidation peak at $E^1_{\mathrm{Pa}} = +0.32$ and $E^2_{\mathrm{Pa}} = +0.05$ V. The two reduction peaks at -0.41 and -1.26 V may be attributed to $\mathrm{Cu^{II}/Cu^{I}}$ and $\mathrm{Cu^{I}/Cu}$ redox processes respectively, while the two oxidation peaks at $+0.05$ and $+0.32$ V correspond to the $\mathrm{Cu/Cu^{I}}$ and $\mathrm{Cu^{I}Cu^{II}}$ redox processes respectively. The huge difference between E_{Pc} and E_{Pa} in both cases suggests that a chemical change is occurring with electron transfer, possibly a structural reorganization of the copper coordination sphere [46,47]. The reduction peak at -1.05 V can be attributed to reduction of the ligand itself. However, the redox behaviour of the binuclear copper(II) Complex **13** has been investigated as a 2×10^{-3} M solution in dimethylformamide containing 0.1 M LiCl at a gold electrode. The behavior of this complex is typical of most binuclear complexes [42]. The scan from $+0.6$ to -0.6 V shows two cathodic peaks at $E^1_{\mathrm{Pc}} = -0.046$ and $E^2_{\mathrm{Pc}} = -0.32$ V and two anodic peaks at $E^1_{\mathrm{Pa}} = +0.31$ and $E^2_{\mathrm{Pa}} = +0.12$ V. These peaks can be assigned to the following processes:

$$[\mathrm{Cu^{II}Cu^{II}}] \xrightleftharpoons[+0.31]{-0.046} [\mathrm{Cu^{I}Cu^{II}}] \xrightleftharpoons[+0.12]{-0.32} [\mathrm{Cu^{I}Cu^{I}}]$$

However, the complete scan in the range of $+0.4$ to -1.7 V shows four cathodic peaks at $E^1_{\mathrm{Pc}} = -0.21$, $E^2_{\mathrm{Pc}} = -0.47$, $E^3_{\mathrm{Pc}} = -1.04$ and $E^4_{\mathrm{Pc}} = -1.40$ V. The cathodic peaks at -0.21, -0.47 and -1.40 V could be assigned to $[\mathrm{Cu^{II}Cu^{II}}]/[\mathrm{Cu^{I}Cu^{II}}]$, $[\mathrm{Cu^{I}Cu^{II}}]/[\mathrm{Cu^{I}Cu^{I}}]$ and $[\mathrm{Cu^{I}Cu^{I}}]/[\mathrm{Cu}]$ redox processes, respectively [46,48], while the peak at -1.40 V could be attributed to reduction of the ligand itself. Only one anodic peak at $E^1_{\mathrm{Pa}} = +0.21$ V was observed.

X-ray Diffraction

X-ray diffraction patterns were obtained for the ligand and its nickel complexes. The ligand pattern has strong lines, indicating a high degree of crystallinity. Comparing the patterns from the ligand and its complexes shows that the square-planar complexes are more highly crystalline than the distorted octahedral complexes. This can be inferred from the peak intensities [49]. The order of the degree of crystallinity is **1** > **11** > **6** > **2** > **8** > **14** > **7**.

Acknowledgment

We are grateful to the Chemistry Department, Leicester University, England, for ESR measurements.

References

[1] L. Bouurget-Merle, M.F. Lappert and J.R. Severn, *Chem. Rev.* **102**, 3031 (2002).
[2] A.D. Garnovskii and I.S. Vasilchenko, *Russ. Chem. Rev.* **71**, 943 (2002).
[3] S. Chandra and K. Fupta, *Transition Met. Chem.* **27**, 196 (2002).
[4] N.D. Kulkarni and P.K. Bhattacharya, *Transition Met. Chem.* **14**, 303 (1989).
[5] P.W. Selwood, Magnetochemistry (Interscience, New York, 1956), p. 78.
[6] M.C.R. Symons, Chemical and Biochemical Aspects of Electron Spin Resonance (Van Nostrand Reinhold, Wokingham, 1978).
[7] J.H. Cameron and S. Graham *J. Chem. Soc., Dalton Trans.* 1599 (1989).
[8] A.S. El-Tabl and M.M. Abou-Sekkina, *Polish J. Chem.* **73**, 1937 (1999).

[9] N.V. Gerbeleu, V.B. Arion and J. Burgess, Template Synthesis of Macrocyclic Compounds (Wiley-VCH, Weinheim, 1999), p. 565.

[10] A.D. Garnovskii and B.I. Kharisov, Synthetic Coordination and Organometallic Chemistry (Marcel Dekker, New York-Basel, 2003), p. 520.

[11] R.C. Maurya, R. Verma and D. Sutradha, *Synth. React. Inorg. Met.-Org. Chem.* **33**, 435 (2003).

[12] M.M. Mostafa, K.M. Ibrahim and M.N. Moussa, *Transition Met. Chem.* **9**, 243 (1984).

[13] S. Jayasree and K.K. Aravidakshan, *J. Indian Chem. Soc.* **71**, 97 (1994).

[14] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds (J. Wiley & Sons, New York, 1986).

[15] A.S. El-Tabl and S.M. Imam, *Transition Met. Chem.* **22**, 259 (1997).

[16] P. Athappan and G. Rajafopal, *Transition Met. Chem.* **22**, 84 (1997).

[17] V.K. Sharma, O.P. Pandey and S.K. Sengupta, *Synth. React. Inorg. Met.-Org. Chem.* **21**, 1587 (1991).

[18] A.S.El-Tabl, *Transition Met. Chem.* **22**, 400 (1997).

[19] M.M. Aly, S.M. Imam and F.A. El-Saied, *Transition Met Chem.* **14**, 375 (1989).

[20] H.M. El-Tabl, F.A. El-Saied and M.I. Ayad, *Synth. React. Inorg. Met-Org. Chem.* **32**, 1247 (2002).

[21] H. Beraldo, L.P. Boyd and D.X. West, *Transition Met. Chem.* **23**, 67 (1998).

[22] A.S. El-Tabl, *Transition Met. Chem.* **27**, 166 (2002).

[23] A.Z. El-Sonbati, A.A.E. Bindary and E.M. Mabrouk, *Transition Met. Chem.* **17**, 66 (1992).

[24] A.S. El-Tabl, K.Y. Baradie and R.M. Issa, *J. Coord. Chem.* **56**, 1113 (2003).

[25] E. Gao, S. Bi, H. Sun and S. Liv, *Synth. React. Inorg. Met.-Org. Chem.* **27**, 115 (1997).

[26] A.Z. El-Sonbati, *Transition Met. Chem.* **16**, 45 (1991).

[27] K. Sakata, H. Taziri, F. Yamaura and M. Hashimoto, *Synth. React. Inorg. Met.-Org. Chem.* **20**, 757 (1991).

[28] S. Rao and H. Reddy, *Indian J. Chem.* **35A**, 681 (1996).

[29] A.S. El-Tabl, Ph.D. Thesis, Menoufia University, Egypt (1993).

[30] A.K. Saxena, S. Saxena and A.K. Ray, *Synth. React. Inorg. Met.-Org. Chem.* **20**, 21 (1990).

[31] M. Gaber and M.M. Ayad, *Thermochim. Acta* **176**, 21 (1991).

[32] P.P. Hankare and S.S. Chanan, *Synth. React. Inor. Met.-Org. Chem.* **33**, 423 (2003).

[33] A.S. El-Tabl, *Transition Met. Chem.* **21**, 428 (1996).

[34] R. Pognmi, GD.D. Lunga and R. Basosi, *J. Am. Chem. Soc.* **115**, 1540 (1993).

[35] A.S. El-Tabl and T.I. Kashar, *Polish J. Chem.* **72**, 519 (1998).

[36] A.S. El-Tabl, *J. Chem. Res.*, **1**, 19 (1981).

[37] A. Mcaul and S. Subramanian, *Inorg. Chem.* **29**, 2830 (1990).

[38] K.K. Sharma and S. Chandra, *Transition Met. Chem.* **9**, 401 (1984).

[39] M. Mahajan, K.N. Saxena and C.P. Saxena, *J. Inorg. Nucl. Chem.* **43**, 2148, (1981).

[40] T. Ozawa and A. Hanaki, *Inorg. Chim. Acta* **153**, 201 (1988).

[41] M.C.R. Symons, M.M. Aly and A.S. El-Tabl. *J. Chem. Soc.*, *Dalton Trans.* (in press).

[42] C. Nataragjan, P. Shanthi, P. Athappan and R. Murugesan, *Transition Met. Chem.* **17**, 39 (1992).

[43] R.K. Ray, *Inorg. Chim. Acta* **174**, 237, 257 (1990).

[44] A.S. El-Tabl, *Transition Met. Chem.* **23**, 63 (1998).

[45] A.S. El-Tabl, *J. Chem. Res.*, Issue 11, 529 (2002), (M), 1110 (2002).

[46] M.S. Mashuta, R.M. Buchanan and W. Pierce, *Inorg. Chim. Acta* **158**, 227 (1989).

[47] V.V. Pavlishchuk and A.W. Addison, *Inorg. Chim. Acta* **203**, 29 (1993).

[48] C.J. Mckenzie, H. Toftlund, M. Pietraszkiewics, Z. Stojek and K. Slowinski, *Inorg. Chim. Acta* **210**, 143 (1993).

[49] A.M. Donia, N.R. Radan and A.A. Atia, *J. Therm. Anal. Cal.* **61**, 249 (2000).