Journal of Thermal Analysis and Calorimetry, Vol. 68 (2002) 983–995

STUDIES OF Mn(II), Co(II), Ni(II) AND Cu(II) CHELATES WITH 3-PHENYL-4-(*p*-METHOXY-PHENYLAZO)-5-PYRAZOLONE

S. A. Abdel-Latif[1] *and H. B. Hassib*[2]

[1]Chemistry Department, Faculty of Science, Helwan University, Cairo, Egypt
[2]Chemistry Department, Faculty of Science, Cairo University, Giza, Egypt

(Received April 23, 2001; in revised form January 3, 2002)

Abstract

Mn(II), Co(II), Ni(II) and Cu(II) chelates with 3-phenyl-4-(*p*-methoxyphenylazo)-5-pyrazolone have been synthesized and were characterized by elemental and thermal analyses as well as by IR, UV-VIS, ^{1}H NMR, conductometric and magnetic measurements. The first stage in the thermal decomposition process of these complexes shows the presence of water of hydration, the second denotes the removal of the coordinated water molecules. The final decomposition products were found to be the respective metal oxides. The data of the investigated complexes suggest octahedral geometry with respect to Co(II) 1:1, tetrahedral for Ni(II) 1:1 and 2:3; square planar for Cu(II) 1:1 and 2:3; the complexes with no coordinated water molecules (2:3) Co(II) and Mn(II) complexes are tetrahedral.

Keywords: azo dyes, chelates, cobalt, copper, manganese, nickel, pyrazolone

Introduction

Azo compounds containing a heterocyclic moiety have drawn the attention of many researchers. The importance of pyrazolone azo dyes in industry as well as their analytical applications and excellent ability to attract the attention of coordination chemists to study their reactions with transition metal ions. Pyrazolones and pyrazole derivatives such as 5-pryazolones are formed by reaction between hydrazines and β-ketonic esters, e.g. 3-methyl-1-phenylpyrazolone was prepared from phenylhydrazine and ethylacetoacetate. This, on methylation gives antipyrine (phenazone, 2,3-dimethyl-1-phenylpyrazole-5-one) which is used in medicine as an antipyretic [1]. Pyrazolin-5-ones are used as ligands for a large number of metal ions [2–4]. The metal chelates thus produced are well-known for their analytical and biological uses. The 4-position of a pyrazolin-5-one system is highly reactive and undergoes coupling reactions with diazonium salts to give 4-arylazo derivatives. These azo derivatives of 5-pyrazolones as well as their metal complexes have wide applications in the dye industry and as analytical reagents for the microdetermination of metals [5]. Different methods were reported for the synthesis of 4-arylazo-5-pyrazolones [6]. The mixed

1418–2874/2002/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

2,4-bipyridine-oxalato complexes with Mn(II), Co(II), Ni(II) and Cu(II) have been prepared and characterized [7]. Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes with 3-methylglutarates were prepared [8]. The complexes of 4-4'-bipyridine adducts of Mn(II), Co(II), Ni(II) and Cu(II) monochloroacetate were prepared [9] and characterized via IR, electronic spectra, conductivity measurements and thermal analyses. The thermal behaviour of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) complexes of uracil were studied by TG, DTG and DTA in a dynamic nitrogen atmosphere [10]. The thermal decomposition of Co(II), Ni(II) and Cu(II) complexes of 4-(3'-sulfonylazido-6'-methoxyphenylazo)-3-phenyl-3-methyl--2-pyrazolin-5-one were studied by thermogravimetry [11]. The first stage of decomposition is related to the elimination of water and nitrogen molecules with the formation of tetracoordinate complexes containing nitrene reactive species. The second stage represents the decomposition of the material to the metal oxide. The activation energies and other activation parameters were computed and related to the bonding and stereochemistry of the complexes.

In the present study 3-phenyll-4-(p-methoxyphenylazo)-5-pyrazolone as chelating agent for divalent Mn(II), Co(II), Ni(II) and Cu(II) ions was prepared and its complexes with these metal ions were isolated and subjected to several analytical techniques to throw some light on the bonds formed and on their structures.

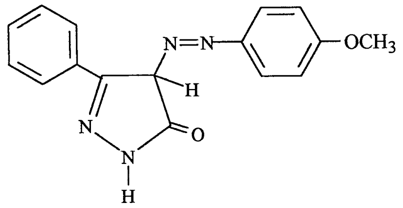
Experimental

All chemicals used were of the highest purity available from BDH. These included $MnCl_2\cdot4H_2O$, $CoCl_2\cdot6H_2O$, $NiCl_2\cdot6H_2O$ and $CuCl_2\cdot2H_2O$, NH_4OH, disodium salt dihydrate EDTA. The solvents used were ethanol, dimethylformamide (DMF), cyclohexane and deuterated dimethylsulfoxide (DMSO). These solvents were purified by distillation [12]. The water used was doubly distilled.

A mixture of ethylbenzoylacetate (9.6 g) and hydrazine hydrate (1.6 g) was heated at 120°C (oil bath, temp. 120–130°C) for 1 h. The resulting oil was cooled and stirred with diethyl ether (50 mL) until solidification occurred and the crude product was then filtered off. The final product was crystallized from 50% aqueous ethanol and collected as white powder of 3-phenyl-5-pyrazolone [13]. A well stirred solution of *p*-anisidine (0.01 mol) in 2 M HCl was cooled in an ice bath salt and diazotised with (20 mL) sodium nitrite solution (0.01 mol). The cooled diazonium solution was added slowly to a well stirred solution of 3-phenyl-5-pyrazolone in ethanol (100 mL) containing sodium hydroxide (10 g). The reaction mixture was stirred for 1 h at room temperature, then acidified with diluted HCl to neutralize the reaction mixture. The product was recrystallized from ethanol to give 3-phenyl-4-(*p*-methoxyphenylazo)-5-pyrazolone as reddish orange crystals (*m. p.* 197°C) [14].

Elemental analyses were carried out on the resulting compound (C% calc. 65.3; found 65.8, H% calc. 4.8; found 4.7, N% calc. 19.0; found 18.9).

The prepared metal ions 10^{-3} M stock solutions for conductometric titration were standardized against EDTA [15]. The 1:1 solid chelate were synthesized by mixing a hot alcoholic solution of the investigated ligand with the equivalent amount



of metal ion solution. The reaction mixture was heated on a steam bath, with occasional stirring till dryness. The solid product was washed several times with ethanol till a colourless filtrate was obtained. The solid was dried by suction and finally kept in a vacuum desiccator. In a trial to prepare 1:2 (*M:L*) solid complexes, $2\cdot10^{-3}$ mol of the metal was mixed with $4\cdot10^{-3}$ mol of the ligand following the described procedure and the corresponding 1:1 complexes obtained. The metal contents of the prepared solid complexes were then determined [16] after wet digestion, using atomic absorption spectrometry.

IR spectra were recorded on Shimadzu FTIR 8201 PC spectrophotometer applying the KBr disc technique. The electronic spectra were obtained using a Perkin Elmer λ 4B UV-VIS recording spectrophotometer. NMR spectra were measured by using a Varian EM 390 (200 MHz) spectrometer. The solvent used was deuterated dimethylsulphoxide (DMSO) and the spectra recorded from 1–15 ppm using TMS as internal standard. Conductometric titration was done with an YSI scientific field/laboratory conductance meter. Thermal analyses (TG and DTA) were obtained using a type-50 Shimadzu Derivatograph, and DTA-50. Magnetic susceptibility values were obtained using Sherwood scientific magnetic susceptibility balance.

Results and discussion

The solid chelates of the divalent transition metal ions (Mn, Co, Ni and Cu) with 3-phenyl-4-(*p*-methoxyphenylazo)-5-pyrazolone were prepared, separated, analyzed and their structures elucidated by elemental analysis for C, H, N, Cl and metal content, infrared spectral studies, magnetic susceptibility, thermogravimetric analysis, differential thermal analysis and electronic spectral studies. The results of elemental analysis are given in Table 1 and are in good agreement with the proposed formulae where in all cases 1:1 which is formed through the formation of Cl and OH bridges and 2:3 (*M:L*) solid complexes are proposed with the exception of Mn(II) where only 2:3 (*M:L*) solid complex was separated.

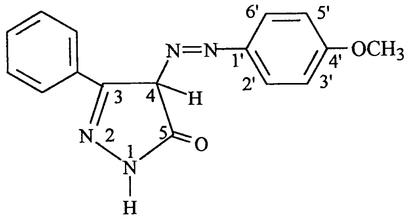
Nuclear magnetic resonance spectra

Nuclear magnetic resonance was used for the purpose of establishing the possible azo–hydrazo [17] or keto–enol tautomerism. The ^{1}H NMR spectra of the investigated ligand and 1,3-diphenyl-4-phenylazo-5-pyrazolone were recorded in DMSO as a solvent and tetramethylsilane as an internal standard. In each case, D_2O was then added to check for exchangeable protons. The chemical shifts of the different types are re-

Table 1 Elemental analysis and magnetic moments of 3-phenyl-4-(*p*-methoxyphenylazo)-5-pyrazolone complexes with Mn(II), Co(II), Ni(II) and Cu(II) ions

Metal ion	(*M*:*L*)	Formula	C/%		H/%		N/%		Cl/%		M/%		$\mu_{\text{eff.}}$/ B.M.
			calc.	found	calc.	found	calc.	found	calc.	found	calc.	found	
Mn(II)	(2:3)	[$Mn_2C_{48}H_{40}O_7N_{12}$]	57.20	57.5	3.97	4.7	16.68	16.4	–	–	10.92	10.67	5.38
Co(II)	(1:1)	[$Co_2C_{32}H_{34}O_8N_8Cl_2$]	45.30	44.9	4.01	3.8	13.21	13.4	8.38	8.0	13.39	13.37	3.73
	(2:3)	[$Co_2C_{48}H_{40}O_7N_{12}$]	56.75	56.8	3.94	4.1	16.55	16.8	–	–	11.63	11.57	3.60
Ni(II)	(1:1)	[$Ni_2C_{32}H_{31}O_7N_8Cl$]	48.45	48.5	3.91	4.2	14.13	13.9	4.47	5.0	14.81	15.23	2.91
	(2:3)	[$Ni_2C_{48}H_{44}O_9N_{12}$]	54.84	54.6	4.19	4.5	15.99	16.0	–	–	11.18	12.04	3.01
Cu(II)	(1:1)	[$Cu_2C_{32}H_{31}O_7N_8Cl$]	47.86	47.9	3.86	4.2	13.96	13.5	4.42	4.4	15.83	16.70	1.44
	(2:3)	[$Cu_2C_{48}H_{41}O_7N_{12}Cl$]	54.32	54.8	3.87	4.2	15.84	15.6	3.35	4.0	11.98	12.00	1.64

corded. The ^{1}H NMR spectrum of the investigated ligand exhibits a sharp singlet at 2.51 ppm which is assigned to the aliphatic proton H^4 and that observed at 2.32 ppm is assigned to the OCH_3 protons. The signals observed at 8.1–7.06 ppm are assigned to the aromatic protons. The integration curve shows 9 protons for this ligand. A signal observed down-field at 12.06 ppm, is assigned to the NH proton. The keto structure of the free ligand was confirmed by the absence of a singlet at 12.06 ppm upon investigating the ^{1}H NMR spectrum of 1,3-diphenyl-4-phenylazo-5-pyrazolone.



Electronic absorption spectra of the ligand

The electronic absorption spectra of the investigated ligand was scanned in ethanol (D=24.3) and cyclohexane (D=2.01). In ethanol the spectrum shows four bands in the region 242–430 nm. These bands are referred to A (430 nm), B (292 nm), C (276 nm) and D (242 nm). According to previously reported results [18] on similar compounds, the two bands C and D are assigned to π–π^* transitions within the pyrazolone and the phenyl rings, respectively. Band B is ascribed to n–π^* transition of the carbonyl and azo (N=N) within the system. The broad absorption band observed at wavelength 430 nm (A) arises from a transition involving electron migration along the entire conjugate system of the ligand i.e. it comprises charge transfer (C.T.) from the substituted phenyl ring to the carbonyl group by resonance and from hetero-ring by induction.

In cyclohexane, all bands are blue shifted except band B where a counter shift is observed. The latter band is red shifted and overlaps with the descending portion of band A. The difference in absorbance and shape of band B in both solvents indicates a change in the structure of the pyrazolone moiety by changing the polarity of the solvent. This may be explained on the basis of a shift in the keto–enol tautomerism of the form, where the enol form is favoured in cyclohexane rather than keto form in ethanol.

Conductometric titrations

Conductometric titrations were performed to give a further insight into the nature and stoichiometry of the complex species formed in solution. This is particularly true for cases where the resulting complexes are stable, non-ionizable compounds or when the conductivity of the resulting ions as a result of complexation is fastly different from the initial mixture. Such is the case for reaction which result in the formation of hydrogen or hydroxide ions, since the mobilities of these ions are several times higher than other cationic or anionic species [19]. In these and similar cases, a break in the titration curve will occur as the system goes from one complex to the other and one can deduce the molar ratio of metal ions to ligand in the complexes formed i.e. the stoichiometry of the formed complexes. Corrections due to volume changes were made by multiplying the measured conductance by the ratio $(V+v)/V$, where V is the original volume of the titrant (50 mL) and v is the added volume of the titrant. The molar ratio $[L]/[M]$ was calculated for each increment of metal ions added and plotted *vs*. the corrected conductance values. The results indicated that the conductance increases with the addition of the metal ion solutions, presumably due to the release of the highly conducting hydrogen ions as a result of chelation. The initial low conductance of the ligand solution is primarily due to its weak acid nature. If one is adding metal ion to an excess of ligand, the process expected would be given by the following equations:

$$\underset{\text{(excess)}}{2HL}+M^{2+}\leftrightarrow ML_2+2H^+$$

$$ML_2+M^{2+}\leftrightarrow 2ML^+$$

At the beginning of the titration where large excess of the ligand is present, the ML_2 species predominates. As more metal ions are added the equilibrium is shifted towards the ML^+ species.

Inspection of the titration curves show the presence of two distinctive breaks in all curves at metal to ligand molar ratio of 1:2 and 1:1, which correspond to the above two equilibria, respectively. The plots, however, might indicate the presence of a third complex of $M:L$ molar ratio 2:3, indicating the formation of complex of formula M_2L_3 such a complex might occur by the association of the 1:1 and 1:2 complexes as follows:

$$ML^++ML_2\leftrightarrow M_2L_3^+$$

such a situation, however, cannot be confirmed from this or other solution data in this work and thus taking the conductometric data as evidence for 1:1 and 1:2 complex only.

IR spectra

The infrared spectrum of the investigated ligand shows the presence of a broad band at 3421 cm^{-1} which correspond to ν(OH) group [20]. The ν(NH) band appears as a medium broad one at 3124 cm^{-1}. The strong band appearing at 1654 cm^{-1} is assigned to the stretching frequency of the C=O group. The ν(N=N) band is observed in the region 1493 cm^{-1} conjugated with the aromatic ring skeletal vibrations (ν(C=C) 1546–1604 cm^{-1}) [21]. The strong band observed at 1242 cm^{-1} may be taken as indicative of keto–enol tautomerism within such compounds.

The infrared spectra of the solid complexes display interesting changes that may give a reasonable idea about the structure of these complexes. However, if these changes are interpreted in relation to elemental analysis (Table 1) and the results of thermogravimetric analysis (Table 3), the stereo geometry of the solid chelates may be clarified. The main IR bands of the solid complexes are given in Table 2. Comparison of the IR spectra of the metal complexes with that of the free ligand shows that ν(C=O) band completely disappeared on complex formation. The disappearance of C=O band indicates that it is a center of chelation as it loses its double bond character (–C–O–M). The OH stretching frequency appears in the spectra of all the complexes as a broad band within the range 3262–3417cm^{-1}. This is due to the presence of water of hydration and/or coordinated water molecules. In cobalt complex (1:1) a sharp band appears at 3550 cm^{-1} which is ascribed to chelated OH ion which neutralizes the charge on the metal ion. The ν(N=N) and ν(C–O) exhibit a shift to higher wavelength on complex formation indicating that they are the centers of chelation. The spectra of metal complexes exhibit bands in the ranges 501–567 and 409–426 cm^{-1}. This may be assigned to ν(M–N) and ν(M–O) stretching frequencies, respectively, in other words, these bands are possibly due to the formation of coordinate bonds between the donor atoms (O and N) and the central metal ion [20].

Table 2 IR-spectral bands of divalent transition metal ion complexes with 3-phenyl-4-(*p*-methoxyphenylazo)-5-pyrazolone

Metal ion (*M:L*)	ν_{OH}	$\nu_{C=N}$	$\nu_{C=C}$		$\nu_{N=N}$	$\nu_{C–O}$	$\nu_{M–N}$	$\nu_{M–O}$
Mn(2:3)	3375v.b.	1605 s	1579 s,	1529 s	1504 m	1248 w	505 w	413 m
Co(1:1)	3263v.b.	1603 s	1585 s,	1531 s	1504 m	1248 s	567 w	426 m
(2:3)	3417v.b.	1605 m	1565 s,	1529 s	1529 m	1249 s	513 m	413 w
Ni(1:1)	3375v.b.	1603 m	1583 s,	1531 s	1504 s	1250 s	501 m	412 w
(2:3)	3375v.b.	1603 w	1581 s,	1530 s	1504 m	1248 m	503 m	409 s
Cu(1:1)	3415v.b.	1603 s	1587 s,	1537 s	1504 m	1250 m	507 w	412 s
(2:3)	3415v.b.	1605 s	1587 s,	1540 s	1504 s	1248 s	505 m	412 m

v.b.: very broad, b: broad, s: strong, w: weak, m: medium

Thermogravimetric and differential thermal analysis

The aim of the thermal analysis is to open up new possibilities for the investigation of metal complexes and to obtain information concerning the thermal stability of the divalent transition metal-3-phenyl-4-(*p*-methoxyphenylazo)-5-pyrazolone complexes, establish whether the water molecules are inner or outer sphere and suggest a general scheme for the thermal decomposition of these complexes. The TG curve follows the decrease in sample mass with the linear increase in temperature. In the present investigation, heating rates were suitably controlled at 10°C min^{-1} and the mass loss followed up to 800–1000°C. From the TG curves obtained (Fig. 1), the mass loss for each complex was calculated within the temperature range at which the water molecules were expelled. The experimentally found and theoretically calculated mass losses are collected in Table 3. Inspection of the TG curve for 1:1 complex of Co(II) with the investigated ligand reveals an initial mass loss occurring at temperature less than 160°C and this is attributed to loss of water of hydration during the drying of the complex. At higher temperature more than 230°C loss of coordinated water occurs. On further heating, the TG curve shows the decomposition of the organic moiety of the chelates and this continues till a constant mass is obtained where the metal oxide residue is formed as the final product. For 1:1 complexes of Co(II), Ni(II) and 2:3 complexes of Co(II) and Ni(II) with the investigated ligand loss of water of hydration is depicted in Table 3 followed by decomposition of the organic part of the chelates till a constant mass where the metal oxide residue is formed as the final product. The curves of Co(II) and Mn(II) (2:3) (*M:L*) complexes contain no water of hydration and water of coordination. This behaviour is consistent with elemental analysis (Table 1). The DTA curves (Fig. 1) of Co(II) (1:1), Ni(II) (1:1) and (2:3) and Cu(II) (1:1) and (2:3) complexes are characterized by the presence of a small endothermic peak in the temperature range 30–169°C that is believed to be due to the elimination of water of crystallization. Since coordination water molecules occupy definite positions in the coordination sphere of the central metal ion, and are more bound to the central metal ion than water of hydration, their elimination will take place at higher temperature

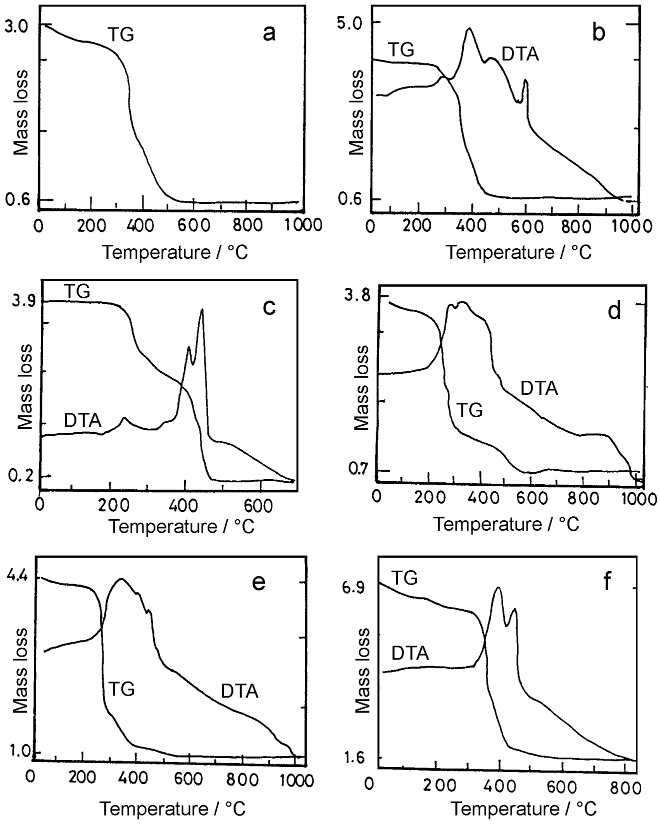


Fig. 1 Thermogravimetric and differential thermal analysis of a – Ni(II) (1:1); b – Ni(II) (2:3); c – Mn(II) (2:3); d – Cu(II) (1:1); e – Cu(II) (2:3); f – Co(II) (1:1) with 3-methyl-4-(*p*-methoxyphenylazo)-5-pyrazolone

Table 3 Thermogravimetric analysis results of metal chelates with 3-phenyl-4-(*p*-methoxyphenylazo)-5-pyrazolone

Complex (*M*:*L*)	Hygroscopic water				Coordinated water				Metallic residue/%	
	T_{upto}/ °C	Mass loss/%		H_2O molecules	T_{range}/ °C	Mass loss/%		H_2O molecules	calc.	found
		calc.	found			calc.	found			
Co–L (1:1) $[Co_2(L)_2 2Cl{\cdot}2H_2O]{\cdot}2H_2O$	100	4.24	4.07	2	100–230	4.24	4.39	2	17.73	17.75
Ni–L (1:1) $[Ni_2(L)_2OH{\cdot}Cl{\cdot}2(H_2O)]$	120	4.54	4.04	2	–	–	–	–	18.85	18.90
Ni–L (2:3) $[Ni_2(L)_3OH]{\cdot}2H_2O$	160	3.43	3.47	2	–	–	–	–	14.22	14.31
Cu–L (1:1) $[Cu_2(L)_2OHCl]{\cdot}2H_2O$	120	4.49	4.70	2	–	–	–	–	19.82	20.43
Cu–L (2:3) $[Cu_2(L)_3Cl]{\cdot}2H_2O$	150	1.73	1.91	2	–	–	–	–	–	–

and a sharp endothermic peak on the DTA curves is observed. Raising the temperature over 300°C results in the decomposition of the complex and its combustion, followed by decarbonization of the organic material in presence of oxygen and at the end a metallic residue in the form of metal oxide remains.

Electronic absorption spectra of the chelates

The electronic absorption bands of metal chelates can be classified into three types, depending on the nature of the electronic transition involved. These types are *L–L* transition, *d–d* transition, and *M–L* or *L–M* charge transfer transition. The electronic spectra of the free ligand and its metal complexes were recorded as Nujol mulls. The values of the band maxima are listed in Table 4. The free ligand, C.T. band appears in the region 446 nm. A shift to lower wavelength is observed on complex formation (405–418 nm). This is attributed to the *L*→*M* charge transfer. In almost all the spectra of the prepared complexes a band of low intensity compared with the previous one is observed in the range 543–600 nm which may be ascribed to *d–d* transition within the metal ion.

Table 4 Electronic spectra of 3-phenyl-4-(*p*-methoxyphenylazo)-5-pyrazolone and some of its complexes

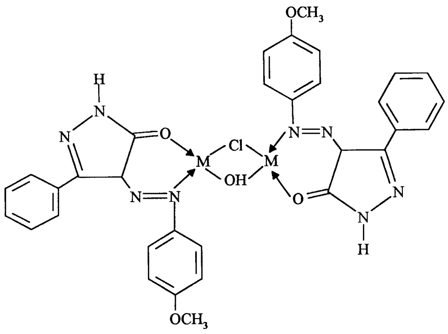
Free ligand	Co(II)		*M:L*	Mn(II)		*M:L*	Cu(II)		*M:L*
λ_{nm}	λ_{nm}			λ_{nm}			λ_{nm}		
446	418	558	1:1	412	600	2:3	418	556	1:1
–	405	543	2:3	–	–	–	–	–	–

Magnetic susceptibility measurements

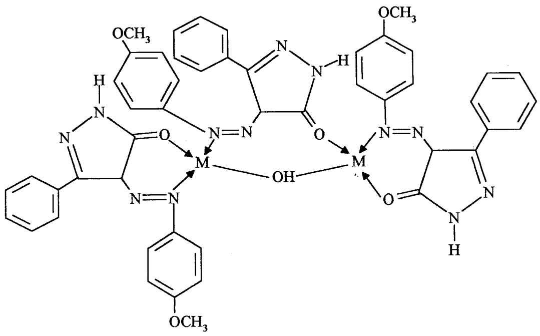
The magnetic moment (μ) of a transition metal ion can give important information about the number of unpaired electrons present in the metal ion and in some special cases help to indicate the structure of the complex. The results obtained show that the values of μ are in some cases higher than those calculated using the spin only approximation. Such as Co(II) complexes in which orbital contribution cannot be neglected which is the case of the first row transition metal ions. The calculated magnetic moments of 1:1 and 2:3 (*M:L*) complexes with Co(II) metal ion are in the range 3.51–4.11 B.M. indicating the presence of three unpaired electrons per metal ion. The magnetic moment values (Table 1) indicate the presence of one unpaired electron in Cu(II) complexes, while for 2:3 (*M:L*) Mn(II) complexes indicates that Mn(II) has five unpaired electrons in its *d* orbital ($\mu_{eff.}$ 5.38). The decrease in $\mu_{eff.}$ of the complexes is due to spin-spin coupling of the two metal ions present in the same complex molecule. Ni(II) complex 1:1 shows $\mu_{eff.}$=2.91 per mol of complex denoting two unpaired electrons and showing paramagnetic properties. All of the metal complexes show paramagnetic which means that the ligand has little or no effect on the metal ions field i.e. the ligand exhibits a weak field effect.

Based on the results of elemental analysis, IR, visible absorption spectra, thermal analyses and magnetic moment calculations. The divalent Mn, Co, Ni and Cu metal ion chelates with the investigated ligand may be formulated as for 1:1 complexes are $[M_2L_2OHCl{\cdot}xH_2O]{\cdot}yH_2O$ (M=(Ni(II) and Cu(II)) or $[M_2L_2Cl_2{\cdot}xH_2O]{\cdot}yH_2O$ (M=Co(II)), whereas for the 2:3 complexes the suggested formulae are $[M_2L_3OH]{\cdot}yH_2O$ (M=Mn(II)), Co(II) and Ni(II) or $[M_2L_3Cl]{\cdot}yH_2O$ (M=Cu(II)), where x and y are the number of inner and outer sphere water molecules, respectively and vary in the range 0–2 for each.

The proposed stereochemical structures for the investigated metal complexes suggest octahedral geometry with respect to Co(II) (1:1); tetrahedral for Ni(II) (1:1) and Ni(II) (2:3); square planar for Cu(II) (1:1) and (2:3); all complexes without coordinated water molecules (2:3); cobalt and manganese complexes with the investigated ligand are tetrahedral.



1:1 complex



2:3 complex

M=Mn(II), Co(II), Ni(II) and Cu(II)

Conclusions

According to the results of elemental analysis, IR, electronic absorption spectra, thermal analyses and magnetic moment measurements. The divalent Mn, Co, Ni, and Cu metal ion chelates with the investigated ligand may be formulated, where 1:1 (M:L)

complexes are formed through the formation of Cl and OH bridges and 2:3 *(M:L)* solid complexes are proposed with the exception of Mn(II) where only 2:3 (*M:L*) solid complex was separated. The IR spectra of the metal complexes show that ν(C=O) band completely disappeared on complex formation. The disappearance of C=O band indicates that it is a center of chelation as it loses its double bond character (–C–O–M). The curves of the Co(II) and Mn(II) (2:3) (*M:L*) complexes show that they contain no water of hydration and water of coordination. The calculated magnetic moments of 1:1 and 2:3 (*M:L*) complexes with Co(II) metal ion are in the range 3.51–4.11 B.M. indicating the presence of three unpaired electrons per metal ion. The magnetic moment values indicate the presence of one unpaired electron in Cu(II) complexes, while for 2:3 (*M:L*) Mn(II) complexes indicate that Mn(II) has five unpaired electrons in its *d* orbital ($\mu_{\text{eff.}}$ 5.38). Ni(II) complex 1:1 shows $\mu_{\text{eff.}}=2.91$ per mole of complex denoting two unpaired electrons and showing paramagnetic properties. All of the metal complexes are paramagnetic which means that the ligand has no effect on the metal ions field i.e. the ligand exhibits a weak field effect. The proposed stereochemical structures for the investigated metal complexes suggest octahedral geometry with respect to Co(II) (1:1); tetrahedral for Ni(II) (1:1) and Ni(II) (2:3); square planar for Cu(II) (1:1) and (2:3); complexes of Co(II) and Mn(II) (2:3) are tetrahedral.

References

1 L. Finar, Organic Chemistry, The Fundamental Principles, 6th ed., Longmans, London 1973, p. 846.
2 M. Wisniewski and L. Pacak, Pol. J. Chem., 65 (1991) 2073.
3 P. Indrasenan and G. Rajendran, Synth. React. Inorg. Met.-Org. Chem., 22 (1992) 715.
4 E. C. Okafor, P. U. Adiukwu and B. A. Uzoukwu, Synth. React. Inorg. Met.-Org. Chem., 23 (1993) 97.
5 F. A. Adam, M. T. El-Haty, A. H. Amrallah and N. A. Abdalla, Bull. Soc. Chim. Fr., 4 (1988) 605.
6 A. Tantawy, F. Goda and A. M. Abdelal, Chin. Pharm. J., 47 (1995) 37.
7 D. Czakis-Sulikowska, J. Radwańska-Doczekalska and M. Markiewicz, J. Therm. Anal. Cal., 60 (2000) 145.
8 W. Brzyska and O. Ożga, J. Therm. Anal. Cal., 61 (2000) 135.
9 D. Czakis-Sulikowska, A. Czylkowska and J. Radwańska-Doczekalska, J. Therm. Anal. Cal., 63 (2001) 387.
10 H. Ölmez, O. Z. Yeşilel and H. Isbudak, J. Therm. Anal. Cal., 63 (2001) 105.
11 S. S. Kandil, F. I. Abdel-Hay and R. M. Issa, J. Therm. Anal. Cal., 63 (2001) 173.
12 A. I. Vogel, A Text Book of Practical Organic Chemistry, 5th ed., Longmans, London 1989, p. 169.
13 A. O. Fitton and R. K. Smalley, Practical Heterocyclic Chemistry, Academic Press, London 1968, p. 25.
14 S. A. Abdel-Latif, Synth. React. Inorg. Met.-Org. Chem., 31 (2001) 1355.

15 T. S. West, Complexometry with EDTA and Related Reagents, 3rd ed., BDH Chemical Ltd., Pool, London 1969, p. 179.

16 A. M. MacDonald and P. Sirichanya, Microchem. J., 14 (1969) 199.

17 K. Schofield, M. R. Grimmett and B. R. T. Keene, Heteroaromatic Nitrogen Compounds, the Azoles, Cambridge University Press, Cambridge 1984, p. 43.

18 G. A. El-Inany, S. A. El-Wahab and Y. M. Issa, Egypt. J. Chem., 25 (1982) 101.

19 A. I. Vogel, A Text Book of Quantitative Inorganic Analysis, 4th ed. Longmans, London 1978, p. 617.

20 A. A. A. Emara, Synth. React. Inorg. Met.-Org. Chem., 29 (1999) 87.

21 G. A. El-Inany, K. A. R. Salib, S. B. El-Maraghy and S. L. Stefan, Egypt. J. Chem., 27 (1985) 357.