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CHELATION BEHAVIOUR OF NITROSO-PYRAZOLONES WITH Mn(II), Co(II), Ni(II), Cu(II) AND Zn(II)

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Abstract

Infrared (IR), nuclear magnetic resonance (NMR), thermogravimetric analysis (TG), derivative thermogravimetric analysis (DTG), differential thermal analysis (DTA) and molar conductivity studies have been carried out on the chelates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with 3-methyl- and 3-phenyl-4-nitroso-5-pyrazolones. The solid chelates were synthesized, separated, analyzed and their structures were elucidated. The data obtained show that almost all of the prepared chelates contain water molecules in their coordination sphere. The initial stage in the thermal decomposition process of these chelates shows the presence of water molecule, the second denotes to the intermediate products. The final decomposition products were found to be the respective metal oxides. The NMR spectrum of 3-methyl-4-nitroso-5-pyrazolone ligand shows the existence of the oxime rather than the nitroso form. 3-phenyl-4-nitroso-5-pyrazolone acts as a neutral bidentate ligand whereas 3-methyl-4-nitroso-5-pyrazolone acts as monobasic bidentate ligand bonded to the metal ions through the two oxygen atoms of the carbonyl and nitroso groups. The solid chelates prepared behave as non-electrolytes in DMF solution. The coordination numbers of the obtained chelates using 3-methyl-4-nitroso-5-pyrazolone are four on applying the mole ratio 1:1 and six on using 1:2 mole ratio. In case of using the ligand 3-phenyl-4-nitroso-5-pyrazolone the coordination number is six in both cases.

Keywords: absorption spectra, conductivity, DTA, nitrosopyrazolones, NMR, TG, transition metals chelates

Introduction

Nitrosopyrazolones are widely used as analytical reagents. They are capable of forming chelates with a number of transition metal ions [1–3]. The formed chelates are characterized by their high stability resulting from the formation of six-membered rings. 3-methyl-4-carboxy-2-pyrazolin-5-one and 1-phenyl-3-methyl-4-carboxy-2-pyrazolin-5-one were screened for antifungal activity [4]. 4-nitroso-2-pyrazolin-5-one derivatives had significant activity against *Pyricularia oryzae* [5, 6]. Complexation behaviour of 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (L_I),

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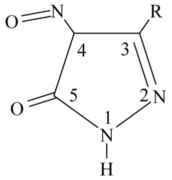
oximidobenzotetronic acid (L_{II}) and 4-nitroso-3-methyl-1-phenyl-2-pyrazolin-5-one (L_{III}) each containing the same NO coordination group is reported [7] with some transition metal ions. Thermogravimetric data were used to evaluate the kinetic parameters of the solid state reactions. L_{II} and L_{III} complexes have a chelate ring and are more stable. New complexes of $CuL_2\cdot2H_2O$, $CoL_2\cdot3H_2O$, $MnL_2\cdot2H_2O$ and $FeL_3\cdot2H_2O$, *L*=γ-*L*-glutamyl-5-(*p*-nitroanilide) were synthesized [8] and characterized by their spectral, magnetic and thermal properties. The thermal stabilities of the synthesized complexes were examined in the temperature range 20–500°C. New complexes of non-natural amino acid (*p*-iodo-phenylalanine) with divalent cobalt and nickel ions have been synthesized [9]. The crystal structure belongs to orthorhombic system. The first stage in the thermal decomposition process of the complex shows the presence of water of crystallization. The mixed 2,4-bipyridine-oxalato complexes of Mn(II), Co(II), Ni(II) and Cu(II) have been prepared and characterized [10]. Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes with 3-methylglutarates were prepared [11]. The complexes of 4,4'-bipyridine adducts of Mn(II), Co(II), Ni(II) and Cu(II) monochloroacetate were prepared [12] and characterized via the 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 [13]. 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 [14].

The present study deals with the preparation of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) chelates with 3-methyl- and 3-phenyl-4-nitroso-5-pyrazolones. The chelates obtained were characterized by elemental analysis, IR, proton NMR, TG, DTG, DTA molar conductance and electronic spectra to throw some light on the bonds formed and on their structures.

Experimental

All chemicals used in the present work were chemically pure, obtained from BDH chemicals. These include $MnCl_2\cdot4H_2O$, $CoCl_2\cdot6H_2O$, $NiCl_2\cdot6H_2O$, $CuCl_2\cdot2H_2O$ and $ZnCl_2$, NH_4OH, sodium nitrite; also the solvents used were ethanol, deuterated dimethyl sulfoxide (d_6-DMSO) and dimethyl formamide (DMF); ethylacetoacetate, ethylbenzoylacetate, hydrazine hydrate and sodium methoxide. 3-methyl-5-pyrazolone was prepared as reported [15]; *m.p.* 222°C. 3-phenyl-5-pyrazolone was described by Fitton [16]; *m.p.* 250°C.

3-methyl-4-nitroso-5-pyrazolone; *m.p.* 205°C and 3-phenyl-4-nitroso-5-pyrazolone; *m.p.* 190°C ligands were prepared [17] as follows, the nitrosation reaction were carried out by acidifying the cooled aqueous solution of 3-methyl- and 3-phenyl-5-pyrazolones (0.2 mol) at 0°C in sodium hydroxide solution containing equivalent amount of sodium nitrite (0.2 mol) with hydrochloric acid. The precipitated compounds were filtered off, washed several times with water and recrystallized from ethanol. The purity of these ligands were determined from the results of elemental analysis (Table 1), IR, ^{1}H NMR. The resulting nitroso compounds have the following general structure:



R=CH_3 (I_a), 3-methyl-4-nitroso-5-pyrazolone
R=C_6H_5 (I_b), 3-phenyl-4-nitroso-5-pyrazolone

Scheme 1

The 1:1 and 1:2 chelates were prepared by mixing a hot alcoholic solution of the ligands under investigation (1 or 2 mol) with the calculated (1 mol) of metal salt solution. The reaction mixture was refluxed for 4 h. The pH of the solution was maintained at a value of 5.0–6.0 by the addition of dilute ammonia solution (1:10). The solid product was dried on a steam bath with stirring, then filtered and washed several times with ethanol till a colourless filtrate was obtained. The solid was dried by suction and finally kept in a vacuum desiccator.

The IR spectra were recorded on a Jasco FTIR spectrophotometer applying the KBr disc technique. The ^{1}H NMR spectra were measured using Varian Gemini 200–200 MHz NMR spectrometer and the spectra were recorded from 0–15 ppm using TMS as internal standard and dimethylsulfoxide (d_6-DMSO) as the solvent. Thermal analyses (TG, DTG and DTA) were obtained in a nitrogen atmosphere using a type TGA 50 Shimadzu derivatograph thermal analyzer. The molar conductivities were carried out using a Jenway conductivity meter 4310. The electronic spectra were recorded using Jasco V-530 UV-Vis spectrophotometer.

Results and discussion

The results of elemental analysis (Table 1) are in good agreement with those calculated by the proposed formulae for 1:1 and 1:2 (M:L) solid chelates.

Infrared spectra

The IR spectral bands of all chelates display interesting changes that may give a reasonable idea about the functional groups of these chelates. These changes are interpreted in relation to elemental analysis (Table 1), the results of thermogravimetric analyses, ^{1}H NMR, molar conductance and electronic spectra, in order to deduce the structure of the solid chelates obtained. In the IR spectra of the chelates, the band observed within the range 1338–1476 cm^{-1} [17] assigned to ν(N=O) in the free ligands were shifted to lower wavenumber (1275–1383 cm^{-1}) indicating coordination of the NO group through its oxygen atom to the central metal ion. Also the band observed within the range 1707–1713 cm^{-1} assigned to ν(C=O) in the free ligands were also

Table 1 Analytical data of the ligands and their Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) chelates

Ligands and complexes	*M*:*L*	Colour	*m.p.*/ °C	C/%		H/%		N/%		*M*/%		Λ_m
				found	calcd.	found	calcd.	found	calcd.	found	calcd.	
$C_4H_5N_3O_2\cdot 1/2H_2O$ (**I**$_a$)	–	yellow	205	35.0	35.29	4.2	4.41	30.2	30.00	–	–	–
$C_9H_7N_3O_2\cdot 2H_2O$ (**I**$_b$)	–	yellow	190	47.4	48.00	4.8	4.80	18.5	18.60	–	–	–
[Mn(**I**$_a$)(OH)$\cdot H_2O$]	1:1	pale brown	320	22.3	22.23	3.7	3.24	19.1	19.45	25.2	25.42	32.40
[Mn(**I**$_a$)$_2\cdot 2H_2O$]	1:2	dark brown	325	28.2	27.99	3.8	3.49	24.6	24.49	16.1	16.01	9.38
[Co(**I**$_a$)(OH)$\cdot H_2O$]	1:1	brown	347	22.1	21.82	3.5	3.18	19.1	19.09	26.5	26.78	–
[Co(**I**$_a$)$_2\cdot 2H_2O$]	1:2	brown	343	28.5	27.67	4.1	3.45	24.6	24.21	17.1	16.97	8.60
[Ni(**I**$_a$)(OH)$\cdot H_2O$]	1:1	greenish yellow	341	21.9	21.84	3.1	3.18	19.2	19.11	26.4	26.71	–
[Ni(**I**$_a$)$_2\cdot 2H_2O$]	1:2	dark green	330	27.8	27.68	3.5	3.46	24.3	24.22	17.1	16.93	35.50
[Cu(**I**$_a$)(Cl)$\cdot H_2O$]	1:1	black	286	19.9	19.75	2.5	2.46	17.4	17.28	26.3	26.13	9.58
[Cu(**I**$_a$)$_2\cdot 2H_2O$]	1:2	black	301	27.5	27.31	3.6	3.41	23.9	23.89	18.7	18.65	–
[Zn(**I**$_a$)(OH)$\cdot H_2O$]	1:1	yellow	336	21.6	21.21	3.0	3.09	18.4	18.55	29.1	28.85	8.76
[Zn(**I**$_a$)$_2\cdot 2H_2O$]	1:2	yellow	350	27.7	27.17	3.7	3.39	23.8	23.77	18.6	18.48	9.59

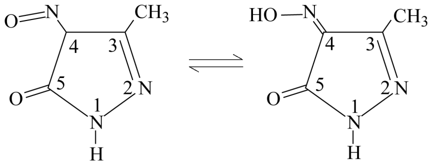
Table 1 Continued

Ligands and complexes	*M*:*L*	Colour	*m.p.*/ °C	C/%		H/%		N/%		*M*/%		Λ_m
				found	calcd.	found	calcd.	found	calcd.	found	calcd.	
$[Mn(\mathbf{I}_b)(OH)_2\cdot 2H_2O]$	1:1	greenish brown	340	34.5	34.40	3.9	4.14	13.6	13.38	17.6	17.48	6.10
$[Mn(\mathbf{I}_b)_2(OH)_2]$	1:2	greenish brown	315	47.6	46.26	3.8	3.42	20.4	20.56	11.9	11.75	11.52
$[Co(\mathbf{I}_b)(OH)_2\cdot 2H_2O]$	1:1	brown	325	34.1	33.97	4.0	4.08	13.2	13.21	18.4	18.52	–
$[Co(\mathbf{I}_b)_2(OH)_2]$	1:2	brown	330	44.4	45.86	3.8	3.39	17.6	17.83	12.3	12.50	13.00
$[Ni(\mathbf{I}_b)(OH)_2\cdot 2H_2O]$	1:1	pale brown	347	33.6	33.99	4.3	4.09	13.3	13.22	18.5	18.47	–
$[Ni(\mathbf{I}_b)_2(OH)_2]$	1:2	brown	338	45.7	45.88	3.9	3.39	17.8	17.84	12.5	12.47	10.52
$[Cu(\mathbf{I}_b)(OH)_2\cdot 2H_2O]$	1:1	dark brown	279	33.6	33.48	4.0	4.03	13.4	13.02	19.5	19.68	–
$[Cu(\mathbf{I}_b)_2(OH)_2]$	1:2	dark brown	286	45.6	45.42	3.7	3.36	17.8	17.66	13.5	13.35	21.9
$[Zn(\mathbf{I}_b)(OH)_2\cdot 2H_2O]$	1:1	yellow	350	33.2	33.30	3.7	4.00	12.8	12.95	20.4	20.13	8.50
$[Zn(\mathbf{I}_b)_2(OH)_2]$	1:2	yellow	335	45.5	45.25	3.7	3.37	17.4	17.59	13.8	13.68	17.83

shifted to lower wavenumber (1620–1652 cm^{-1}) indicating the involvement of the (C=O) group in chelation. The strong band at 3524 cm^{-1} for $\mathbf{I}_a$ is assigned to ν(OH) of the oxime, whereas that observed at 3550 cm^{-1} is assigned to water of crystallization and the strong band observed at 1090 cm^{-1} is assigned to ν(N–O) [18]. For all investigated chelates, the broad bands observed within the range (3232–3450 cm^{-1}) were assigned to ν(OH) of coordination of water and OH^- group which is present to neutralize the charge on the metal ion [19]. The spectra of the metal chelates exhibit bands in the range 453–545 cm^{-1} that may be assigned to ν(M–O) stretching frequency [20]. These bands are not observed in the spectra of the free ligands and are possibly due to the formation of coordinate bond (M←O) or (M–O) [21].

Nuclear magnetic resonance spectra

Further support for the results obtained from the IR spectra is gained by considering the changes in the ^1H NMR spectra of the investigated chelates. The spectrum of the $\mathbf{I}_a$ exhibits a singlet at 14.05 ppm which is assigned to the oxime H-atom =N–OH which means that this ligand is involved in nitroso–oxime tautomer, such kind of equilibrium may be represented as:



Scheme 2

A singlet observed at 2.22 ppm is assigned to the CH_3 proton (integration curve shows three H-atoms). The presence of this CH_3 group which is an electron donating group assists the formation of oxime tautomer by increasing the electron density on the NO group, increasing its polarity. This facilitates the formation of =N–OH oxime group since the oxygen atom is more electronegative than the nitrogen atom. A singlet observed at 3.45 ppm is assigned to H-atoms of the water of crystallization (integration curve shows one H-atom, half water molecule). A singlet observed at 11.35 ppm is assigned to –NH H-atom (integration curve shows one H-atom) [19]. For $\mathbf{I}_b$ ligand a singlet observed at 3.47 ppm is assigned to water of crystallization (integration curve shows four H-atoms corresponding to two water molecules). The signals observed at 7.40–7.95 ppm are assigned to the aromatic H-atoms (integration curve shows five H-atoms). A singlet observed at 11.91 ppm is assigned to –NH H-atom (integration curve shows one H-atom) [19].

For Zn–$\mathbf{I}_a$ (1:2) chelate, a singlet observed at 2.23 ppm is assigned to CH_3 H-atoms (integration curve shows six H-atoms). A singlet observed at 3.39 ppm is assigned to H-atoms of water of coordination (integration curve shows four H-atoms corresponding to two water molecules). A singlet observed at 11.49 ppm is assigned to –NH H-atom (integration curve shows two H-atoms). A singlet observed at 14.05 ppm corresponding to =N–OH in the spectra of the free ligand disappeared or was not observed in the spectra of the chelate which means that the nitroso–oxime tautomer is a center of chelation. For Zn–$\mathbf{I}_b$ (1:2) chelate, a singlet observed at 3.37 ppm is assigned to water of coordination (integration curve shows eight H-atoms corresponding to four water molecules) two of these molecules being inside the coordination sphere and the other two outside this sphere. The signals observed at 7.30–8.11 ppm are assigned to the aromatic H-atoms (integration curve shows 10 protons). A singlet observed at 11.97 ppm is assigned to –NH H-atom (integration curve shows two H-atoms).

Thermogravimetric, derivative and differential thermal analysis

The aim of the thermal analysis is to obtain information concerning the thermal stability of the investigated chelates (Table 2), to decide whether the water molecules are inside or outside the coordination sphere, and to suggest a general scheme for the thermal decomposition of these chelates.

TG curves of Cu(II) chelates with the investigated ligands (1:1 and 1:2) were carried out (Figs 1 and 2). The mass loss, measured from ambient temperature to 800°C at a rate of 10°C min^{-1}, was used to calculate the number of coordinated water molecules. The investigated chelates show no hygroscopic water or moisture within the temperature range 25–100°C.

For the Cu–$\mathbf{I}_a$ (1:1) chelate, one water molecule is coordinated to the metal ion and expelled within the temperature range 230–323°C [22] in addition to the loss of C–CH_3, N–NH and CO groups corresponding to the loss of 41.61% (calcd. 41.97%). In the temperature range 388–673°C a mass loss of 25.49% is observed corresponding to the formation of intermediate species through the decomposition of the organic part with the loss of CN and Cl atom (calcd. 25.30%). At a temperature higher than 673°C and at the end of the process CuO was formed; the remainder is 30.89% (calcd. 31.70%). The data obtained are in good agreement with the calculated metal content obtained by determination of the metal ions applying the method described by Macdonald [23] and the results of elemental analysis (Table 1).

For Cu–$\mathbf{I}_b$ (1:1) chelate, a mass loss occurred within the temperature range 214–324°C corresponding to the loss of 81.15% (calcd. 82.28%) for two coordinated water molecules, two OH groups, one phenyl group, NO group, CO group, N–NH and two carbon atoms which were oxidized by the atmospheric oxygen to CO_2 [19]. After this temperature and in the range 324–800°C, the CuO residue was obtained 18.74% (calcd. 17.71%).

For Ni–$\mathbf{I}_a$ (1:2) chelate, a mass loss occurred within the temperature range 100–150°C corresponding to the loss of 10.12% (calcd. 10.38%) for two water molecules and at the temperature range 150–254°C corresponding to a loss of 9.99% (calcd. 9.65%) for two methyl groups. At a temperature range 254–350°C a loss of 73.62% (calcd. 73.38) corresponding to a loss of the organic part as intermediate species. At high temperature more than 350°C and at the end of the process NiO is formed, the remainder is 21.79 (calcd. 21.54).

Table 2 Thermogravimetric analysis results of some metal(II)–nitrosopyrazolone chelates

Chelate	Temperature/°C			Mass loss/%		Assignment
	TG range of thermal steps	DTA	DTG	found	calculated	
[Cu(**I**$_a$)(Cl)·H_2O]	230–323	258, 410	275	41.61	41.97	C–CH_3, N–NH, CO, H_2O
	388–673			25.49	25.30	CN, Cl
	673–800			30.89	31.70	CuO
[Cu(**I**$_b$)$(OH)_2$·$2H_2O$]	214–324	296, 446	273	81.15	82.28	$2H_2O$, 2C, 2OH, N–NH, C_6H_5, NO, CO
	324–800			18.74	17.71	CuO
[Ni(**I**$_a$)$_2$·$2H_2O$]	100–150	297, 387	290	10.12	10.38	$2H_2O$
	150–254			9.99	9.65	$2CH_3$
	254–350			73.62	73.38	2CO, 2NO, 2N–NH, 4C
	350–800			21.79	21.54	NiO
[Zn(**I**$_b$)$_2$·$(OH)_2$]	100–250	412, 501	420	7.14	7.12	2OH
	250–462			51.41	51.88	$2C_6H_5$, $2N_2$, CO
	462–550			14.99	14.75	NO
	550–800			17.03	17.40	ZnO

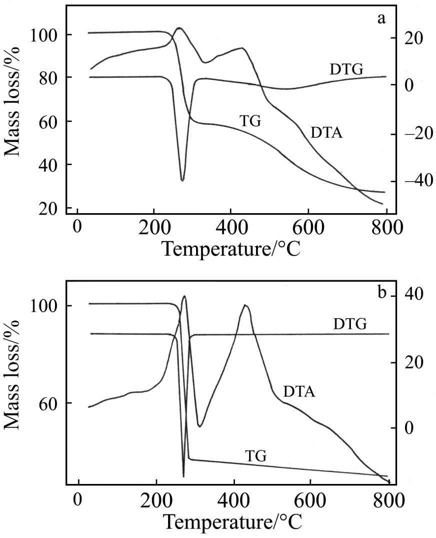


Fig. 1 Thermogravimetric, derivative and differential thermal analyses curves of Cu(II)–$\mathbf{I}_a$ (1:1) and Cu(II)–$\mathbf{I}_b$ (1:1) chelates

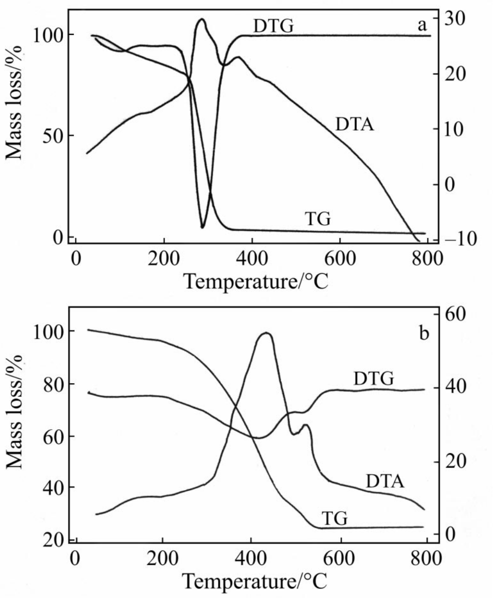


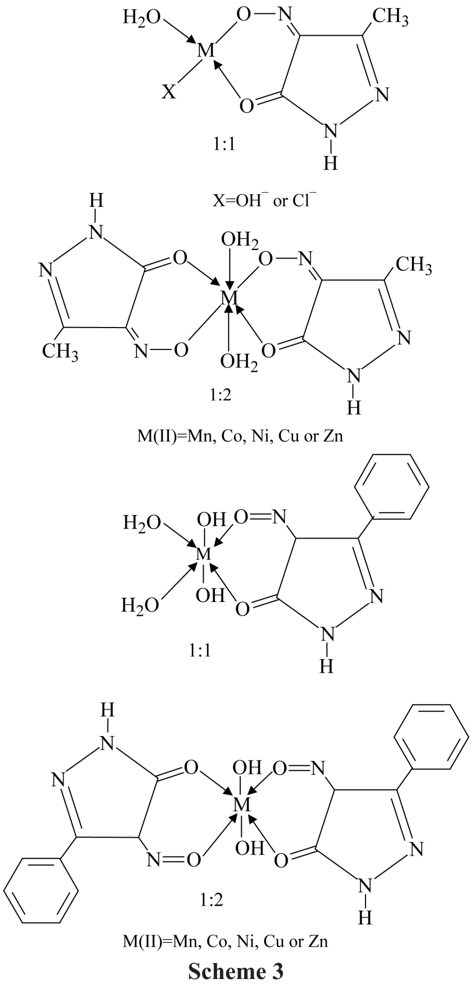
Fig. 2 Thermogravimetric, derivative and differential thermal analyses curves of Ni(II)–$\mathbf{I}_a$ (1:2) and Zn(II)–$\mathbf{I}_b$ (1:2) chelates

For Zn–$\mathbf{I}_b$ 1:2 chelate, a mass loss observed within the temperature range 100–250°C corresponding to a loss of 7.17% (calcd. 7.12) for two OH groups, at higher temperature range 250–462°C a loss occurred are corresponding to a loss of

51.41% (calcd. 51.88) for two phenyl, two nitrogen molecules and one CO group. At a temperature range 462–550°C a loss occurred corresponding to a loss of 14.99% (calcd. 14.75) for NO group. At a temperature more than 550°C and at the end of the process ZnO residue obtained is 17.40% (calcd. 17.03%).

The derivative thermogravimetric analyses curves show that peaks lie at temperatures of 273 and 420 for the investigated Ni, Cu, Zn–$\mathbf{I}_\mathrm{a}$ or $\mathbf{I}_\mathrm{b}$ 1:1 and 1:2 chelates indicating decomposition of the organic part at these temperatures.

From the DTA curves of the investigated Cu–$\mathbf{I}_\mathrm{a}$ and Cu–$\mathbf{I}_\mathrm{b}$ 1:1 chelates, two exothermic peaks were observed within the range 258 and 446°C, whereas for Ni–$\mathbf{I}_\mathrm{a}$ and Zn–$\mathbf{I}_\mathrm{b}$ 1:2 chelates, two exothermic peaks were observed within the temperature range 297 and 501°C. At these temperatures the chelates are no longer stable and a phase change in the crystal structure of the chelates are liable to occur i.e. crystallo-



Scheme 3

graphic phase transition. Above this temperature decomposition and combustion begins leaving a final residue of the metal oxide.

Molar conductivity measurements

The molar conductivity values of 1 mM in DMF of the given chelates show that the investigated chelates are neutral in nature since the values obtained are 6.10–35.5 $\text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$. These values were small to account for ionic chelates of the investigated divalent metal ions. These low conductivity values may be attributed to the coordination of chloride ions, if present, rather than the ionic association to the metal ions during chelate formation. This directly supports the fact that all of the investigated chelates are non-ionic in nature.

Electronic absorption spectra

The electronic spectra of the free ligands and some of their chelates were recorded in DMF. In the free ligands the C.T. band appears at 352 and 371 nm for $\mathbf{I}_a$ and $\mathbf{I}_b$, respectively. A shift to higher wavelength is observed on complex formation. This is attributed to the ($M \to L$) charge transfer spectra (C.T.). In all of the spectra of the prepared chelates a band of low intensity is observed at 460 and 458 nm for Mn and Co chelates with $\mathbf{I}_a$ (1:2); at 458 nm for Mn:$\mathbf{I}_b$ (1:1); 460, 458 and 458 nm for Co, Ni and Zn with $\mathbf{I}_b$, respectively. This may be ascribed to *d–d* transition within the metal ion indicating the presence of the metal ions in chelate formation.

Based on the above results the structure of the 1:1 and 1:2 (*M*:*L*) chelates formed between the metal ion and the ligands can be represented as follows in Scheme 3.

Conclusions

Based on the data obtained from elemental analysis, IR, ^{1}H NMR electronic absorption spectra, thermal analyses and molar conductivities measurements, the chelates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with $\mathbf{I}_a$ and $\mathbf{I}_b$ ligands may be formulated, where bonding in the case 1:1 and 1:2 chelates are formed through coordination with the oxygen of the carbonyl group and the oxygen of the nitroso–oxime tautomer. The chelates prepared contain water of coordination in their coordination sphere. $\mathbf{I}_b$ acts as neutral bidentate ligand whereas $\mathbf{I}_a$ acts as monobasic bidentate. The solid chelates prepared behave as non-electrolytes in DMF solution. The electronic spectra of the free ligands exhibit a C.T. band at 352 and 371 nm for $\mathbf{I}_a$ and $\mathbf{I}_b$, respectively. A shift to higher wavelength is observed on complex formation may be attributed to $M \to L$ charge transfer spectra. The bands observed at higher wavelengths which are not observed in the spectra of the free ligands may be ascribed to *d–d* electronic transition within the metal ions. The coordination numbers of the obtained chelates using $\mathbf{I}_a$ are four on applying the mole ratio 1:1 and six on using 1:2 mole ratio. In case of using the ligand $\mathbf{I}_b$ the coordination number is six in both cases.

References

1 B. Kuncheria and P. Indrasenan, Indian J. Chem., 27 (1988) 1005.
2 R. K. Agarwal and K. Arora, Synth. React. Inorg. Met-Org. Chem., 23 (1993) 653.
3 R. K. Agarwal and K. Arora, Pol. J. Chem., 67 (1993) 25.
4 S. Das and A. S. Mittra, J. Indian. Chem. Soc., 55 (1978) 520.
5 N. B. Das and A. S. Mittra, Indian J. Chem., 16B (1978) 638.
6 A. Nayak and A. S. Mittra, J. Indian Chem. Soc., 57 (1980) 643.
7 H. Singh, S. Srivastava and S. Maheshwari, Thermochim. Acta, 57 (1982) 369.
8 L. Ghizdavu, C. Bãlan, L. David, C. Bâtiu, O. Cozar and D. Ristoiu, J. Therm. Anal. Cal., 62 (2000) 729.
9 W. J. Wang, S. R. Luan, Y.R. Chen, L. Z. Cal, Y. Q. Jia, S. K. Ruan and J. F. Duan, J. Therm. Anal. Cal., 63 (2001) 823.
10 D. Czakis-Sulikowska, J. Radwañska-Doczekalska and M. Markiewicz, J. Therm. Anal. Cal., 60 (2000) 145.
11 W. Brzyska and W. Ozga, J. Therm. Anal. Cal., 61 (2000) 135.
12 D. Czakis-Sulikowska, A. Czylkowska and J. Radwañska-Doczekalska, J. Therm. Anal. Cal., 63 (2001) 387.
13 H. Ölmez, O. Z. Yesilel and H. Isbudak, J. Therm. Anal. Cal., 63 (2001) 105.
14 S. S. Kandil, F. I. Abdel-Hay and R. M. Issa, J. Therm. Anal. Cal., 63 (2001) 173.
15 A. I. Vogel, A Text Book of Practical Organic Chemistry. 5th Edn., Longman Scientific and Technical, England 1989, p. 807.
16 A. O. Fitton and R. K. Smalley, Practical Heterocyclic Chemistry. Academic Press, London 1968, p. 25.
17 Y. M. Issa and S. A. Abdel-Latif, J. Therm. Anal. Cal., 51 (1998) 449.
18 C. Bisi Castellani, O. Carugo and C. Tomba, Inorg. Chim. Acta, 145 (1988) 157.
19 S. A. Abdel-Latif, Synth. React. Inorg. Met-Org. Chem., 31 (2001) 1355.
20 H. Temel, Ü. Cakir, B. Otludil and H. I. Ugras, Synth. React. Inorg. Met-Org. Chem., 31 (2001) 1323.
21 A. A. A. Emara, Synth. React. Inorg. Met-Org. Chem., 29 (1999) 87.
22 I. Tossidis and A. Syngollitou-kourakou, J. Thermal Anal., 32 (1987) 491.
23 A. M. Macdonald and P. Sirichanya, Microchem. J., 14 (1969) 199.