Available online at www.sciencedirect.com
SCIENCE DIRECT
Spectrochimica Acta Part A 64 (2006) 809–815
SPECTROCHIMICA ACTA PART A
www.elsevier.com/locate/saa

Synthesis and spectroscopic studies of mixed-ligand and polymeric dinuclear transition metal complexes with bis-acylhydrazone tetradentate ligands and 1,10-phenanthroline

Ramazan Gup *, Bülent Kırkan

Department of Chemistry, Mugla University, Kampus-Kotekli, 48000 Mugla, Turkey

Received 4 July 2005; received in revised form 8 August 2005; accepted 16 August 2005

Abstract

Two types of dinuclear copper(II) and nickel(II) complexes with two tetradentate N_2O_2 donor ligands 1,4-bis(1-anthranoylhydrazonoethyl) benzene (L^1), 1,4-bis(1-salicyloylhydrazonoethyl)benzene (L^2) and *N*,*N*′-bidentate heterocyclic base [1,10-phenonthroline (phen)] have been synthesized and characterized by elemental analysis, infrared spectra, UV–vis electronic absorption spectra and magnetic susceptibility measurements. The reaction of metal(II) acetates with the solution containing ligand and 1,10-phenonthroline in methanol gives mixed-ligand dinuclear metal(II) complexes with general formula $[M_2L(phen)_2]Cl_2$ ($L = L^1$ or L^2), whereas, the ligands react with metal(II) acetates to form polymeric dinuclear complexes with general formula $[(M_2L_2)_n]$ ($L = L^1$ or L^2). In the complexes, the ligands act as dianionic tetradentate and coordination takes place in the enol tautomeric form with the enolic oxygen and azomethine nitrogen atoms while the phenolic hydroxyl and amino groups of aroylhydrazone moiety do not participate in coordination. The effect of varying pH and solvent on the absorption behavior of both ligands and complexes has been investigated.

Keywords: Schiff base; bis-Acylhydrazone; Mixed-ligand; Polymeric complexes; IR and electronic spectra; Copper(II) and nickel(II) ions

1. Introduction

The chemical properties of aroylhydrazones have been extensively investigated in the past decades because of their strong tendency to chelate transition metals and their pharmacological applications [1–9]. A number of hydrazones and their transition metal complexes have been reported to exhibit biological activity so far [10–15]. The copper(II) complex of salicylaldehyede benzoylhydrazone was found to be a potent inhibitor of DNA synthesis and cell growth. The copper(II) complex of salicylaldehyede acetylhydrazone has shown biological activity [16].

Aroylhydrazones are potential ligands due to having a number of bonding sites. They can act a neutral or monoanionic bidentate or tridentate ligand depending on the substituents and the reaction conditions. Furthermore, abilities to coordinate to metals either in keto(I) or enol(II) tautomeric form make them attractive as ligands (Fig. 1). 1,10-Phenanthroline (phen) is widely used as a classical *N*,*N*′-bidentate ligand to prepare mixed-ligand complexes in coordination chemistry. The presence of mixed-ligand can infer differences in bonding, spectral properties and geometry in coordination compounds.

Intensive investigations of the coordination chemistry of dinuclear metal complexes with chelating ligands continue to be stimulated by interest for metallobiomolecules [17], the search for appropriate systems for binding and activating simple molecules [18], catalysis [19] and magnetic interactions [20]. In spite of the greatest effort and success in the study of dinuclear copper(II) complexes, such complexes have still attracted much attention due to their interesting properties and the relative simplicity of their synthesis.

In our previous work, we reported the synthesis and spectroscopic studies of mononuclear copper and nickel complexes of Schiff base prepared by condensing aroylketones with anthranilhydrazide and salicylohydrazide [21]. Herein, we report the synthesis and spectroscopic studies of dinuclear copper(II) and nickel(II) polymeric complexes containing 4-bis(1-anthranoylhydrazonoethyl)benzene (L^1), 1,4-bis(1-salicyloylhydrazonoethyl)benzene (L^2) as well as mixed-ligand complexes with 1,10-phenanthroline. The effect of varying pH

---

* Corresponding author. Tel.: +90 252 2111496; fax: +90 252 2238656.
E-mail address: rgup@mu.edu.tr (R. Gup).

1386-1425/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.saa.2005.08.008

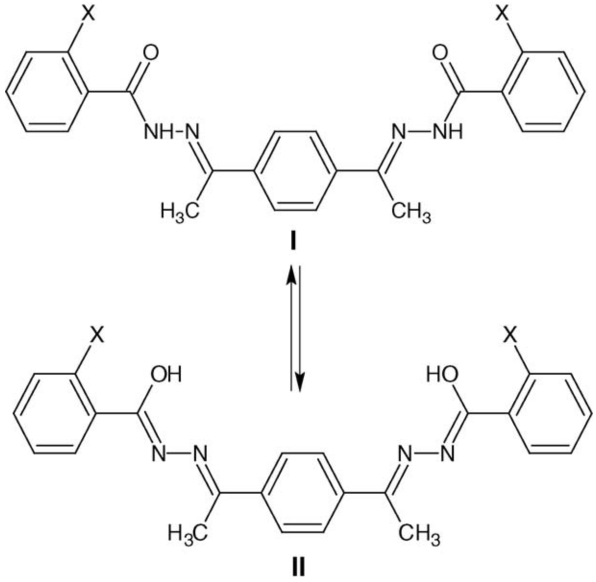


Fig. 1. Tautomeric forms of the ligands.

and solvent upon the absorption ability of bis-acylhydrazones and their complexes is also discussed in more detail.

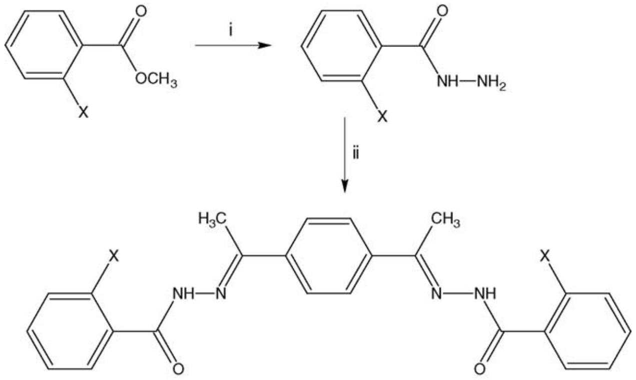
2. Experimental

2.1. Reagents

All the chemicals used were of A.R. grade. 1,4-Diacetylbenzene, ethyl anthranilate, ethyl salicylate, hydrazine monohydrate were purchased from Merck and Aldrich and used without further purification.

2.2. Apparatus

^{1}H NMR spectra were recorded on a Bruker 200 MHz spectrometer in DMSO_d_6 with TMS as the internal standard. IR spectra were recorded on a Perkin-Elmer 1605 FTIR spectrometer as KBr pellets. The electronic spectra of the ligands and complexes were recorded on a UV-1601 Shimadzu spectrophotometer in various solvents. Magnetic susceptibility measurements were performed at room temperature by Faraday method using Hg[Co(SCN)$_4$] as a calibrent. Atomic absorption spectrophotometer used to determine metal ion concentration in the aqueous phase was DV 2000 Perkin-Elmer ICP-AES. Melting points were determined on an Electrothermal IA 9100 digital melting point apparatus and are uncorrected.



Scheme 1. (i) $NH_2NH_2{\cdot}H_2O$ reflux 4 h; (ii) 1,4-diacetylbenzene, EtOH, CH_3COOH, reflux 1 h. Ligands referred to here are L^1: X = —NH_2, L^2: X = —OH.

2.3. Synthesis of ligands

Salicyloylhydrazine and anthranoylhydrazine were prepared by refluxing ethyl salicylate (10 mmol, 1.48 mL) or ethyl anthranilate (10 mmol, 1.48 mL) with hydrazine hydrate (2.5 mL) for 4 h, respectively [21–23]. The compounds precipitated on standing over night, filtered and washed with distilled water. The pure hydrazines were obtained by recrystalliztion from hot ethanol.

The ligands synthesized in this work are shown in Scheme 1 and their syntheses are described as follows.

Anthranoylhydrazine (10 mmol, 1.51 g) or salicyloylhydrazine (10 mmol, 1.52 g) dissolved in hot ethanol (30 mL) was added to solution of 1,4-diacetylbenzene (5 mmol, 0.81 g) with three drops of glacial acetic acid in ethanol (20 mL). The reaction mixture was stirred while refluxing for 1 h. The compounds which precipitated during refluxing were filtered off and washed several times with water and hot ethanol, and dried in air at room temperature. Some properties of the synthesized ligands and complexes are given in Table 1.

Table 1
Characterization of the ligands and of the complexes

Complex	Empiric formula	m.p. (°C)	Yield (%)	B.M. μ_{eff}	Elemental analyses (%) (calcd./found)			
					C	H	N	M
L^1	$C_{24}H_{24}N_6O_2$	293–295	89	–	67.29/67.43	5.61/5.50	19.63/19.78	–
1	$C_{48}H_{44}N_{12}O_4Cu_2$	>300	85	2.27	58.84/59.10	4.49/4.28	17.16/17.34	12.97/12.80
2	$C_{48}H_{38}N_{10}O_2Cl_2Cu_2$	>300	88	2.30	58.54/58.83	3.86/4.01	14.23/14.01	12.91/13.22
3	$C_{48}H_{44}N_{12}O_4Ni_2$	>300	90	3.48	57.36/57.51	4.60/4.46	15.44/15.28	10.85/11.01
4	$C_{48}H_{38}N_{10}O_2Cl_2Ni_2$	>300	89	3.34	59.11/58.88	3.90/4.09	14.37/14.23	12.05/11.91
L^2	$C_{24}H_{22}N_4O_4$	307–308	85	–	66.98/67.04	5.12/5.01	13.02/12.88	–
5	$C_{48}H_{40}N_8O_8Cu_2$	>300	90	2.33	58.60/58.44	4.07/4.29	11.39/11.14	12.92/13.11
6	$C_{48}H_{36}N_8O_4Cl_2Cu_2$	>300	86	2.25	58.42/58.79	3.65/3.32	11.36/11.69	12.88/13.08
7	$C_{48}H_{40}N_8O_8Ni_2$	>300	88	3.43	59.17/59.38	4.11/3.96	11.51/11.28	12.06/11.83
8	$C_{48}H_{36}N_8O_4Cl_2Ni_2$	>300	84	3.52	58.99/59.23	3.69/3.50	11.47/11.78	12.02/12.39

Table 2
^{1}H NMR spectral data for the ligands (δ, ppm)

Complex	OH	NH	Aromatic proton	$-NH_2$	$-CH_3$
L^1	–	10.57 (s, 2H)	7.89 (s, 4H), 6.54–7.90 (m, 8H)	6.22 (s, 4H)	2.45 (s, 6H)
L^2	12.15 (s, 2H)	11.40 (s, 2H)	7.96 (s, 4H), 6.93–8.02 (m, 8H)	–	2.38 (s, 6H)

2.4. Synthesis of complexes

2.4.1. Synthesis of $[(M_2L_2)_n][M = Ni(II)$ or $Cu(II)$, $L = L^1$ or $L^2]$

The complexes $[(M_2L_2)_n]$ were prepared by the following general method. To hot solution of the ligand (L^1 or L^2) (5 mmol) in 20 mL of methanol, the metal(II) acetate (10 mmol) in 10 mL of methanol were added. The reaction mixture was heated under reflux for 4 h then the volume was reduced to half of the initial volume under reduced pressure. The precipitate was filtered off, washed with water and ethanol, and then dried in air at room temperature.

2.4.2. Synthesis of $[M_2L(phen)_2]Cl_2$ $[M = Ni(II)$ or $Cu(II)$, $L = L^1$ or $L^2]$

The complexes $[M_2L(phen)_2]Cl_2$ were prepared by the following general method. To a solution of $CuCl_2{\cdot}2H_2O$ or $NiCl_2{\cdot}6H_2O$ (10 mmol) in methanol (10 mL), a solution of 1-10-phenanthroline (phen) (10 mmol) in 10 mL methanol was added dropwise with constant stirring. The resulting colored solution, which was a suspension in the case of copper complexes, was stirred and heated for 15 min. 5 mmol of ligand dissolved in same solvent (25 mL) was added and refluxed for 3 h. The precipitate was filtered, washed with water and ethanol, and then dried in at room temperature.

3. Results and discussion

Hydrazones such as synthesized in this work may exist in the keto(I) or in the enol(II) tautomeric form in the solid state (Fig. 1). The observation of strong ν(C=O) absorption bands around 1641–1667 cm^{-1} in the infrared spectra of the ligands suggest that the ligands are in the keto form in the solid state [3,5,11,21,24]. The tautomeric keto forms of compounds were also indicated by ^{1}H NMR spectroscopy since the enolic OH signals of enol forms of ligands were not observed while amide NH signal of keto forms appeared around 10.47–11.01 ppm.

3.1. ^{1}H NMR and IR spectra of the ligands

In the ^{1}H NMR spectra of 4-bis(1-anthranoylhydrazonoethyl)benzene (L^1) the proton of amide group (NH) appears as a singlet at 10.57 ppm. The ring proton resonance of the 1,4-diacetylbenzene moiety of this ligand is observed as a singlet at 7.89 ppm while that of the anthranilic acid moiety appears as multiplet peaks. In the ^{1}H NMR spectra of 1,4-bis(1-salicyloylhydrazonoethyl)benzene (L^2) the phenolic OH and amide NH resonances appear as singlets at δ 12.15 and 11.40 ppm, respectively. The shift of phenolic OH and amide NH proton absorptions to lower frequency can be explained by strong intramolecular hydrogen bonding in this compound [21,23,25]. The other obtained values for ^{1}H NMR chemical shifts of these compounds are given Table 2. These data are in agreement with that previously reported for similar compounds [2,3,5,21,25–27].

In the IR spectra of bis-acylhydrazone compounds, the bands appearing at 1649 and 1641 cm^{-1} for L^1 and L^2, respectively, are attributed to the characteristic amide I band. The absorption band of the C=N group is observed at 1608 and 1606 cm^{-1} for L^1 and L^2, respectively. In the case of 1,4-bis(1-salicyloylhydrazonoethyl)benzene a very broad peak is observed in the 3285–2578 cm^{-1} region which is assigned to the intramolecular H–bonding vibration (O–H···O) [23,21]. Also the amide NH stretching band of this compound is not observed in the IR spectra probably because of overlapping with intramolecular hydrogen bonded OH stretching frequency. In the case of IR spectra of bis-anthranoylhydrazone derivative, the peaks observed at 3467 and 3354 cm^{-1} are attributed to symmetric and asymmetric stretching vibrations of the NH_2 group. The amide NH stretching vibration is observed around 3185 cm^{-1}. The other characteristic IR peaks of hydrazone compounds synthesized in this work are given in Table 3. These values are in accord with that previously reported hydrazone derivatives [1–6,21,23–25].

3.2. IR spectra of the complexes

Table 3 collects the characteristic IR frequency values of the ligands and their complexes. The IR spectra of the complexes show significant differences from the free ligand. The bands due to amide I, ν(C=O), ν(C=N$_{\text{imine}}$) and amide ν(NH) are absent in the IR spectra of the complexes, but two new bands appear between 1607 and 1626 cm^{-1} and ~1160 cm^{-1} probably due to C=N–N=C and C–O stretching, respectively, suggesting that the NH proton is likely lost via deprotonation induced by the metal and the resulting enolic oxygen and the azomethine nitrogen take place in coordination [3–7,21]. The shift of ν(N–N) stretch of the complexes to higher energy by ~20–25 cm^{-1} comparing to that of free ligand can be another evidence for the involvement of azomethine nitrogen in coordination. The symmetric and asymmetric stretching vibrations of amino group $\nu(NH_2)$ of L^1 is observed almost at the same frequencies as that of the free ligand indicating their non-involvement on coordination [2,7,21]. The IR spectra of complexes derived from L^2 shows a broad band around 3415 cm^{-1}, which can be attributed to the free OH stretching mode indicating non-participation of phenolic OH group in coordination.

Table 3
IR spectral data for the ligands and complexes (KBr, cm^{-1})

Complex	NH_2/OH	NH	C=O	C=N	C=N—N=C	C—N/C—O	N—N
L^1	3467, 3354	3185	1649	1630	–	1324	1028
1	3446, 3363	–	–	–	1614	1314/1157	1044
2	3466, 3378	–	–	–	1614	1315/1160	1043
3	3458, 3367	–	–	–	1626	1310/1159	1050
4	3468, 3389	–	–	–	1617	1313/1153	1048
L^2	2578–3285	–	1641	1628	1606	1233	1021
5	3414	–	–	–	1617	1256/1163	1044
6	3414	–	–	–	1609	1255/1161	1042
7	3412	–	–	–	1607	1257/1161	1043
8	3422	–	–	–	1606	1258/1162	1039

3.3. Magnetic studies

The room temperature magnetic moments of the complexes (Table 1) show both nickel(II) and copper(II) complexes are paramagnetic. The magnetic moment values of the copper(II) complexes are in the region of 2.27–2.33 μ_B while those of the nickel(II) complexes are in the region of 3.34–3.52 μ_B at 303 K. It can be observed that these magnetic moment values of both copper and nickel complexes are slightly higher than the theoretical value of 1.73 μ_B for one d^9 copper ion and 2.82 μ_B for one d^8 nickel ion. However, these magnetic moment values are lower than that expected for dinuclear copper(II) and nickel(II) complexes. These subnormal magnetic moment values of the dinuclear complexes may be explained by weak antiferromagnetic intramolecular interaction since this situation can occur when two equivalent metal ions are coupled via on exchange interaction in a polynuclear complex [28–30].

3.4. Electronic absorption spectra

The electronic absorption spectra for the hydrazone ligands recorded in various solvents such as MeOH, DMF, DMSO and $CHCl_3$ are given in Table 4. The effect of pH change, by adding two drops of 0.1 M HCl and KOH, for absorption spectra was also observed. The electronic spectral data of the ligand exhibit two to three bands in the UV region. The absorption bands appearing in the range of 240–277 nm are attributed to $\pi \rightarrow \pi^*$ transition of the benzenoid moiety of the compounds and intraligand $\pi \rightarrow \pi^*$ transition. The other two bands observed in the region of 321–329 and 335–355 nm are most probably due to $n \rightarrow \pi^*$ electronic transitions of imine and carbonyl groups [2,21,31–33].

3.4.1. Solvent and pH effects on the electronic spectra of the ligands

The electronic absorption spectra of the compounds were studied in organic solvents having various polarities, MeOH, DMF, DMSO and $CHCl_3$. It can be seen from Table 4 that the absorption spectra of bis-acylhydrazones are considerably influenced by changing the solvent. In the case of the electronic spectra of L^1, the bands appearing ~320 and ~345 nm in MeOH and $CHCl_3$ are shifted to high wavelength in DMF and DMSO. The λ_{max} of 1,4-bis(1-salicyloylhydrazonoethyl)benzene (L^2) shows regular red shift with change in the polarity of the solvents. The highest red shift is observed in DMSO; for example, 323 nm in $CHCl_3$, 329 nm in MeOH, 335 nm in DMF and 336 nm in DMSO. Both types of ligands have more red shift in DMF and DMSO than other solvents. This phenomenon can be explained by the high proton accepting character and the low ionization potential of these solvents.

The effect of pH change on the electronic absorption spectra of the ligands was studied in MeOH solution by adding a small amount of 0.1 M HCl and KOH. The λ_{max} of L^1 in methanolic solution is not effected by adding a small amount of 0.1 M KOH. However, the electronic absorption spectra of this compound shows considerable hypsochromic effect when adding a small amount of 0.1 M HCl in methanolic solution (Fig. 2). After adding two drops of 0.1 M HCl to methanolic solution of

Table 4
Electronic spectral data (nm) of bis-acylhydrazones and their complexes

Complex	MeOH	MeOH + HCl	MeOH + KOH	$CHCl_3$	DMF	DMSO
L^1	251, 321, 347	253, 311	251, 323, 346	241, 319, 344	267, 328 s, 353	258, 328 s, 355
1	–	–	–	–	244, 267, 318 s, 358	243, 260, 319 s, 360
2	–	–	–	–	266, 330 s, 359	260, 325 s, 357
3	–	–	–	–	256, 265, 323 s, 363	260, 327 s, 366
4	–	–	–	–	266, 324 s, 362	259, 323 s, 364
L^2	240, 329	241, 299, 323	292, 324, 364	241, 323	260, 266, 335	241, 336
5	–	–	–		266, 342	260, 344
6	–	–	–		256, 267, 297, 345	277, 300, 346
7	–	–	–		266, 341	259, 343
8	–	–	–		267, 300, 340	275, 297, 339

s: shoulder.

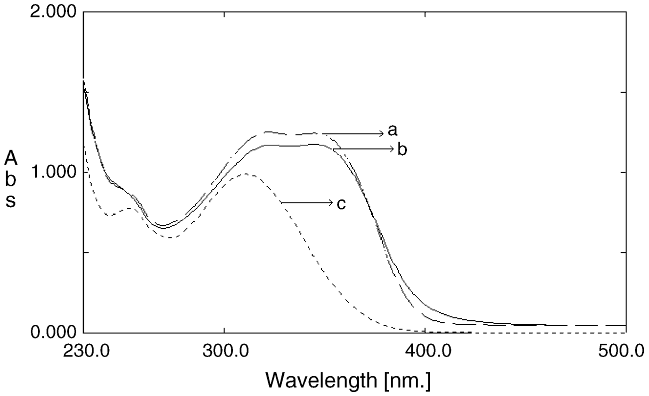


Fig. 2. Electronic absorption spectra of L^1 in: (a) MeOH; (b) MeOH + KOH; (c) MeOH + HCl.

this ligand, the bands appearing 321 and 347 nm in the spectra of the neutral methanolic solutions of L^1 disappears and a new broad band is observed at 311 nm indicating that 1,4-bis(1-anthranoylhydrazonoethyl)benzene exists in the cationic form in acidic solution probably due to protonation of the amino group.

The absorption spectra of L^2 are little influenced by adding 0.1 M HCl with respect to the absorption spectra in methanol. After adding two drops of 0.1 M HCl, the λ_{max} of L^2 shifts slightly to lower wavelength and a shoulder at 299 nm, which cannot be seen clearly in neutral MeOH solution of this ligand becomes much clear in the acidic solution. On the other hand, the electronic absorption spectra of 1,4-bis(1-salicyloylhydrazonoethyl)benzene shows considerable bathochromic effect when adding a small amount of 0.1 M KOH in methanolic solution (Fig. 3). After adding two drops of 0.1 M KOH to methanolic solution of this ligand, the band appearing at 329 nm in neutral solution shows a slight blue shift and a new shoulder at 299 nm, which cannot be seen clearly in neutral MeOH solution of this ligand becomes much clear in the basic solution. Furthermore, a new broad band appears at 364 nm indicating that 1,4-bis(1-salicyloylhydrazonoethyl)benzene exists in the anionic form in basic solutions probably due to phenolic or enolic groups.

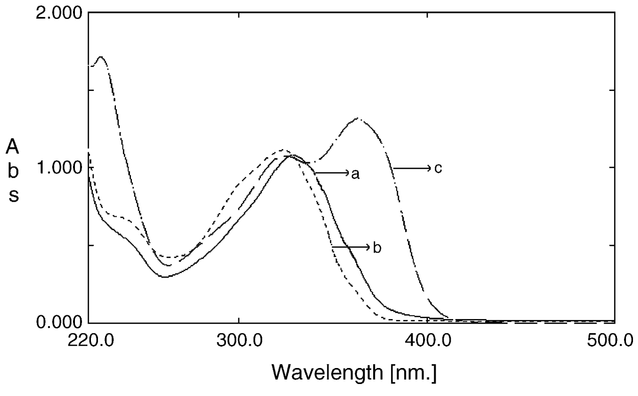


Fig. 3. Electronic absorption spectra of L^2 in: (a) MeOH; (b) MeOH + HCl; (c) MeOH + KOH.

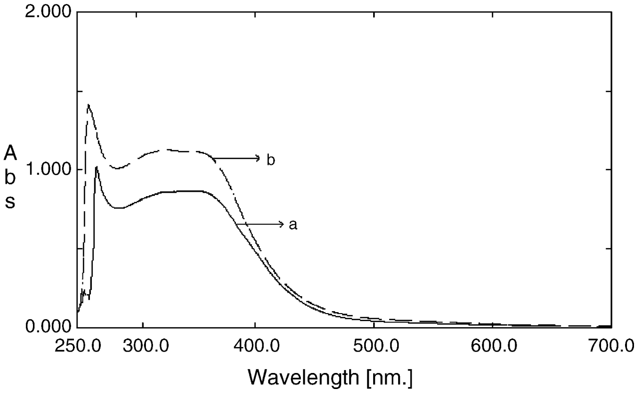


Fig. 4. Electronic absorption spectra of $[(M_2L_2)_n]$ complexes of L^1 in DMF: (a) $[(Cu_2L_2)_n]$ (1); (b) $[(Ni_2L_2)_n]$ (3).

3.5. Electronic absorption spectra of the complexes

Electronic absorption spectra of $[ML_2]$ and [ML(phen)]Cl complexes were recorded in DMF and DMSO solutions (Table 4). In the electronic spectra of all complexes there is a broad band around 339–366 nm tailing into visible region in the spectra of many complexes. This band is assigned as a CT transition [2,21,27,31].

Comparison of the electronic absorption of L^1 and its polymeric nickel(II) and copper(II) complexes, it is observed that the shoulder appearing around 328 nm for L^1 slightly decreases in intensity and shows slightly blue shift. In the case of L^2 and its polymeric complexes the broad band observed around 335 nm in free ligand becomes narrow with a slight red shift tailing in to visible region in the electronic spectra of polymeric complexes (Fig. 4). However, the electronic absorption spectra of the mixed-ligand dinuclear complexes of 1,4-bis(1-salicyloylhydrazonoethyl)benzene is considerably different from those of the free ligand and corresponding polymeric complexes (Fig. 5). Two new bands which cannot be seen in the free ligand appear around 267–277 nm and 297–300 nm. The first of these bands may be attributed $\pi \rightarrow \pi^*$ transition of phenatranoline moiety of the mixed-ligand complexes. The second band can be assigned to $n \rightarrow \pi^*$ electronic transition.

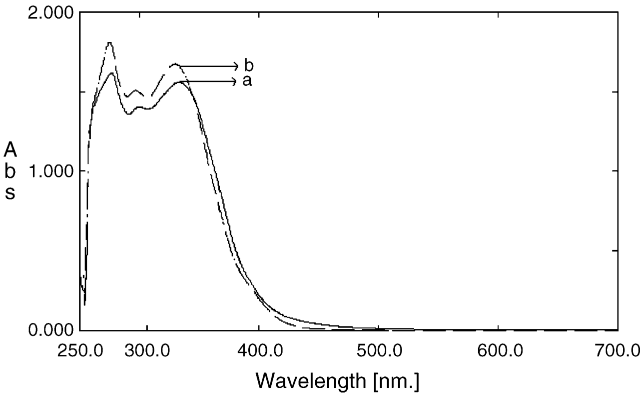


Fig. 5. Electronic absorption spectra of $[M_2L(phen)_2]Cl_2$ complexes of L^2 in DMSO: (a) $[Cu_2L(phen)_2]Cl_2$ (6); (b) $[Ni_2L(phen)_2]Cl_2$ (8).

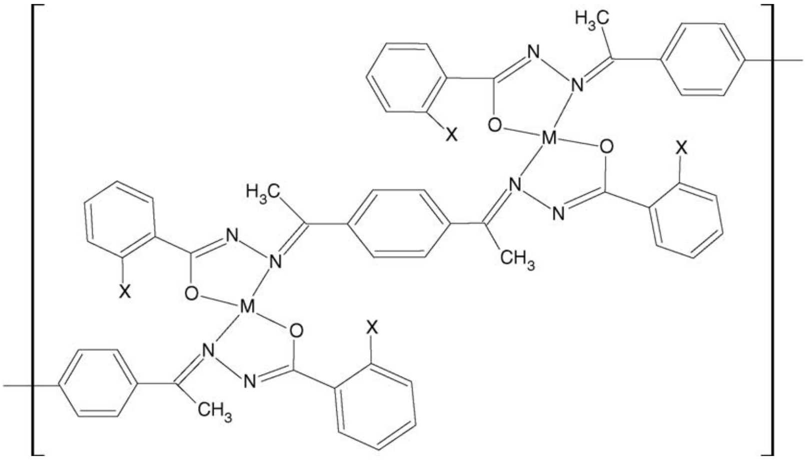


Fig. 6. Suggested structure for the polymeric dinuclear complexes $[\{Cu_2(L^1)_2\}_n]$ (1); $[\{Ni_2(L^1)_2\}_n]$ (3); $[\{Cu_2(L^2)_2\}_n]$ (5); $[\{Ni_2(L^2)_2\}_n]$ (7).

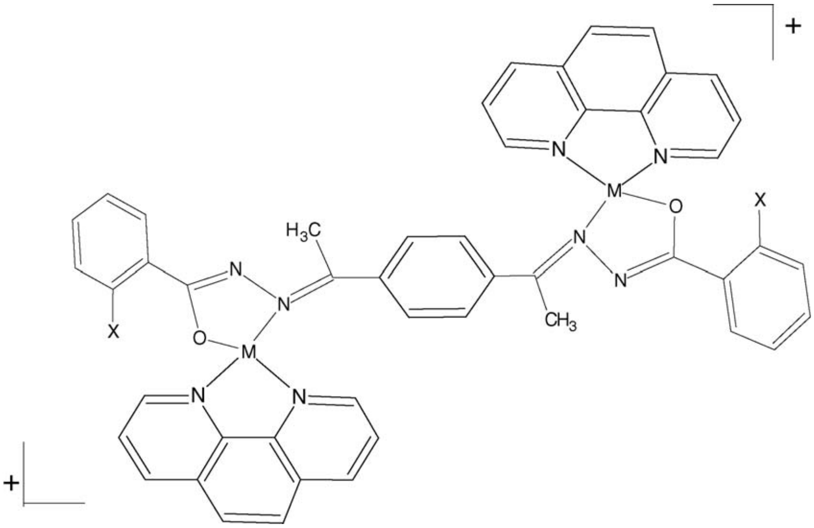


Fig. 7. Suggested structure for the mixed-ligand dinuclear complexes $[Cu_2(L^1)(phen)_2]Cl_2$ (2); $[Ni_2(L^1)(phen)_2]Cl_2$ (4); $[Cu_2(L^2)(phen)_2]Cl_2$ (6); $[Ni_2(L^2)(phen)_2]Cl_2$ (8).

Unfortunately the expected weak d–d transition in the visible region for all complexes cannot be detected even with concentrated solution. It may be lost in the low energy tail of the charge transfer transition [2,21,22,34,35].

4. Conclusion

The present paper reports on the synthesis, characterization and their electronic absorption spectra of bis-acylhydrazones and their copper(II) and nickel(II) complexes. In this investigation we also provide two types of copper and nickel complexes, mixed-ligand and polymeric, by using these synthesized Schiff base and bidentate 1,10-phenanthroline. On the basis of IR and ^{1}H NMR spectral data, bis-acylhydrazone ligands are in the keto tautomeric form in the solid state. However, in the IR spectra of the complexes ν(C=O), ν(C=N), and ν(N–H) stretching vibrations disappears but two new bands are observed due to C=N–N=N and C–O stretching, respectively, suggesting that the coordination takes place in enol tautomeric form. Furthermore, the observation of phenolic ν(O–H) and $\nu(NH_2)$ stretching vibration in the IR spectra of the complexes is concluded as non-involvements of these groups in coordination. Considering the elemental analysis results and spectral data, the structures proposed for polynuclear and mixed-ligand complexes are given in Figs. 6 and 7.

The results of the varying pH and solvents effect on the absorption ability of bis-acylhydrazones and their complexes are also discussed in this paper. The electronic absorption bands of the presented ligands exhibit solvent dependence behavior. The λ_{max} of bis-salicyloylhydrazone derivative is effected by both acidic and basic media while the basic media does not effect the λ_{max} of bis-anthranoylhyadrazone derivative. In the case of the electronic spectra the complexes, CT bands are observed around 339–366 nm. The polymeric and mixed-ligand dinuclear complexes exhibit slightly different CT pattern.

References

[1] T.R. Rao, S. Shrestha, A. Prasad, K.K. Narang, Synth. React. Inorg. Met.-Org. Chem. 32 (2002) 419.

[2] S. Naskar, S. Biswas, D. Mishra, B. Adhikary, L.R. Falvello, T. Soler, C.H. Schwalbe, S.K. Chattopadhyay, Inorg. Chem. Acta 357 (2004) 4264.

[3] R. Dinda, P. Sengupta, S. Ghash, T.C.M. Mak, Inorg. Chem. 41 (2002) 1684.

[4] A. Sreekanth, C.R.C.R. Nayar, M.R.P. Kurup, Polyhedron 23 (2004) 41.

[5] R. Dinda, P. Sengupta, S. Ghash, W.S. Sheldrick, Eur. Inorg. Chem. (2003) 363.

[6] R.M. Issa, S.A. Abdel-Latif, H.A. Abdel-Salam, Synth. React. Inorg. Met.-Org. Chem. 31 (2001) 95.

[7] P.B. Sreeja, M.R.P. Kurup, A. Kishare, C. Jasmin, Polyhedron 23 (2003) 575.

[8] S.K. Agarwal, R. Gupta, D. Kumar, Polish J. Chem. 63 (1989) 329.

[9] S. Ersan, S. Nacak, R. Berkem, Farmaco 53 (1989) 773.

[10] E.W. Ainscough, A.M. Brodie, A.J. Dobbs, J.D. Ranford, J.M. Waters, Inorg. Chim. Acta 267 (1998) 27.

[11] E.W. Ainscough, A.M. Brodie, W.A. Denny, G.J. Finlay, S.A. Gothe, J.D. Ranford, J. Inorg. Biochem. 77 (1999) 125.

[12] N. Nawar, M.A. Khattab, N.M. Hosny, Synth. React. Inorg. Met.-Org. Chem. 29 (1999) 1365.

[13] Z.H. Chohan, Synth. React. Inorg. Met.-Org. Chem. 31 (2001) 1.

[14] D. Van Reyk, S. Sarel, N. Hunt, N. Biochem. Pharmacol. 60 (2000) 581.

[15] M. Carcelli, P. Mazza, C. Pelizzi, G. Pelizzi, F. Zani, J. Inorg. Biochem. 57 (1995) 43.

[16] J.R. Dimmock, G.B. Baker, W.G. Taylor, Can. J. Pharm. Sci. 7 (1972) 100.

[17] K.D. Karlin, J. Zubieta, Copper Coordination Chemistry, Biochemical and Inorganic Perspectives, Adenine Press, New York, 1983.

[18] P.A. Vigato, S. Tamburini, D.E. Fenton, Coord. Chem. Rev. 106 (1990) 25.

[19] R. Eisenberg, D.E. Hendrikson, Adv. Catal. 28 (1979) 79.

[20] D. Gatteschi, O. Kahn, J.S. Miller, F. Palacio (Eds.), Molecular Magnetic Material, NATO ASI Series, Kluwer, Dordrecht, 1991.

[21] R. Gup, B. Kırkan, Spectrochim Acta A (2005) in press.

[22] S.G. Komurcu, S. Rollas, M. Ulgen, J. Gorrod, Boll Chim. Farmaccutico 134 (1995) 375.

[23] F.V. Bagrov, T.V. Vasil’eva, Russ. J. Org. Chem. 38 (2002) 1364.

[24] P.E. Lee, C.T. Yong, D. Fon, J.J. Vittal, J.D. Ranford, Polyhedron 22 (2003) 2781.

[25] L.L. Koh, O.L. Kon, Y.C. Loh, J.D. Ranford, A.L.C. Tan, Y.Y. Tjan, J. Inorg. Biochem. 72 (1998) 155.

[26] A.M. Khambekar, A.D. Sawant, Indian J. Chem. 36 (1997) 459.

[27] J.J. Norman, R.M. Heggie, J.B. Larose, Can. J. Chem. 40 (1962) 1547.

[28] J.D. Ranford, J.J. Vittal, Y.M. Wang, Inorg. Chem. 37 (1998) 1226.

[29] B. Moubaraki, K.S. Murray, J.D. Ranford, J.J. Vittal, X. Wang, Y. Xu, J. Chem. Soc., Dalton Trans. (1999) 3573.

[30] R. Gup, Russ. J. Coord. Chem. (2005) in press.

[31] J.W. Godhes, W.A. Armstrong, Inorg. Chem. 13 (1992) 368.

[32] D. Maiti, H. Paul, N. Chanda, S. Chakrabort, B. Mondal, V.G. Puranik, G.K. Lahiri, Polyhedron 23 (2004) 831.

[33] M.M. Rageh, Spectrochim. Acta A 60 (2004) 1917.

[34] E. Prenesti, S. Berto, P.G. Daniele, Spectrochim. Acta A 59 (2003) 201.

[35] S. Pang, Y. Liang, Spectrochim. Acta A 57 (2001) 435.