VERSITA

Chemical Papers 66 (3) 194–201 (2012)
DOI: 10.2478/s11696-011-0126-y

ORIGINAL PAPER

A new bis(azine) tetradentate ligand and its transition metal complexes: Synthesis, characterisation, and extraction properties

Sultan Kulaksızoğlu, Ramazan Gup

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

Received 4 July 2011; Revised 18 October 2011; Accepted 15 November 2011

A new bis(bidentate) azine ligand was prepared by linking (1*Z*,1′*Z*)-1,1′-{butane-1,4-diylbis[oxybenzene-4,1-diyl(1*Z*)ethyl-1-ylidene]}dihydrazine to salicylaldehyde. Two kinds of binuclear copper(II) and nickel(II) complexes with different stoichiometries were prepared. Reaction of bis(azine) ligand with Cu(II) and Ni(II) acetate at a 1 : 1 mole ratio gave double-stranded binuclear bis(azine) complexes with stoichiometry $[M(L)(H_2O)_2]_2$ containing $[M(II)N_2O_2]$ centres while at a 2 : 1 mole ratio, reaction of Cu(II) and Ni(II) chloride with bis(azine) resulted in dinuclear metal complexes with the general stoichiometry $[M_2(L)Cl_2(H_2O)_2]$. Structures of the bis(azine) ligand and its complexes were identified by elemental analysis, IR and UV-VIS spectra, magnetic susceptibility measurements, TGA, and powder XRD. Extraction properties of the bis(azine) ligand towards some transition metal cations and dichromate anions were also reported. It was found that the bis(azine) ligand does not extract cations but it has high extraction ability towards dichromate anions.

Keywords: bis(azine), complexes, extraction, heavy metals, dichromate anions

Introduction

Azines ($R_2C{=}N{-}N{=}CR_2$) are 2,3-diaza analogues of 1,3-butadiene. Their chemical properties have been extensively investigated in recent years because of their interesting physical and spectral properties (McLoughlin et al., 2007; El-Sayed et al., 2002). Azines are also potential ligands owing to the two imine groups. Therefore, they have recently been used as ligands in coordination chemistry (Chi et al., 2009; Davidson et al., 2006; Viñuelas-Zahínos et al., 2009). Azines can be considered as models of some biological systems (Abu-El-Wafa et al., 1985; Nour et al., 1988; Picón-Ferrer et al., 2009). Because they are considered to be nonlinear optical materials, physical properties of some substituted acetophenone azines have been recently studied (Chen et al., 1994, 1995).

Many heavy metals such as copper, mercury, chromium, lead, nickel, and cadmium are released into wastewaters during industrial processes (Dede et al., 2009, 2010; Hatay et. el., 2008; Gup & Giziroğlu, 2006). Chromium and its compounds are used in diverse industrial areas such as plating, leather tanning, dye and photographic industries, where large amounts of toxic pollutants are released to the environment (Raji & Anirudhan, 1998; Tabakci et al., 2007). Chromium can exist in several oxidation states: Cr(III) and Cr(VI). Cr(III) is reported to be biologically essential while Cr(VI) can be toxic since it diffuses as $Cr_2O_7^{2-}$ or $HCr_2O_7^{-}$ through cell membranes and oxidises biological molecules (Krishna et al., 2004). Therefore, heavy metal pollution is spread throughout the world with the expansion of industrial activities. A variety of techniques such as chemical precipitation, membrane filtration, coagulation, complexation, solvent extraction, ion exchange and adsorption are utilised to remove metals from wastewaters. Among them, the most widespread procedure is the solvent extraction method. Therefore, development of an efficient extractant is very important.

Although a lot of works were devoted to the study of the structure of azines (Chi et al., 2009; Davidson et

---

*Corresponding author, e-mail: rgup@mu.edu.tr al., 2009; Viñuelas-Zahínos et al., 2009; Abu-El-Wafa et al., 1985; Nour et al., 1988), studies concerning the complexes of azine compounds and their extraction abilities are rare. Therefore, we described the synthesis and characterisation of new symmetric azine and its binuclear Cu(II) and Ni(II) complexes. Extraction properties of the prepared azine towards the dichromate anion and some heavy metals were also studied by the solvent extraction technique.

Experimental

Materials and methods

All chemicals used were of the analytical reagent grade. $CuCl_2 \cdot 2H_2O$, $Cu(OAc)_2 \cdot H_2O$, $NiCl_2 \cdot 6H_2O$, $Ni(OAc)_2 \cdot 4H_2O$, 4-hydroxyacetophenone, 1,3-dibromopropane, salicylaldehyde, K_2CO_3, acetone, hydrazine monohydrate were purchased from Fluka and Sigma–Aldrich and used without further purification. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz spectrometer in DMSO-d_6 with TMS as the internal standard. IR spectra (in KBr pellets) were recorded on a Perkin–Elmer 1605 FTIR spectrometer. Electronic spectra of the ligand were recorded on a UV-1601 Shimadzu spectrophotometer. Elemental analyses were carried out on a LECO 932 CHNS analyser and metal contents were determined by an inductively coupled plasma atomic emission spectrometer DV 2000 Perkin–Elmer ICP-AES. Magnetic susceptibility measurements were carried out with powdered samples using a Sherwood Scientific MK1 Model Gouy Magnetic Susceptibility Balance at room temperature. Melting points were determined on an Electrothermal IA 9100 digital melting point apparatus. Thermogravimetric analysis was carried out in dynamic nitrogen atmosphere (20 mL min^{-1}) at the heating rate of 20 °C min^{-1} using a Perkin–Elmer Pyris 1 TGA thermal analyser. XRD analyses of the powder samples were recorded with a Rigaku corporation X-ray diffractometer (Model smartlab). All diffraction patterns were obtained using Cu$K\alpha$ radiation with a graphite monochromator at the scanning rate of 5° per minute. 1,1′-[Propane-1,3-diylbis(oxybenzene-4,1-diyl)]diethanone (*II*) and (1*Z*,1′*Z*)-1,1′-{propane-1,3-diylbis[oxybenzene-4,1-diyl(1*Z*)eth-1-yl-1-ylidene]} dihydrazine (*III*) were synthesised by a previously reported method (Kulaksızoğlu, 2011).

Picrate and/or dichromate extraction experiments were performed following the Pedersen's procedure (Pedersen, 1968). The volume of 10 mL of 2.5×10^{-5} M aqueous picrate solution (Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}) or of 10^{-4} M aqueous dichromate solution (pH of the dichromate solution was changed by an addition of 0.01 M KOH/HCl solution) and 10 mL of 10^{-3} M solution of bis(azine) in CH_2Cl_2 were vigorously agitated in a stoppered glass tube with a mechanical shaker for 2 min and then magnetically stirred in a thermostated water-bath at 25 °C for 1 h, and finally left standing for an additional 30 min. Concentration of the picrate/dichromate ions remaining in the aqueous phase was then determined spectrophotometrically as described previously (Tabakci et al., 2003). Blank experiments showed that no picrate/dichromate extraction occurred in the absence of bis(azine). Extractability was calculated using the following equation:

$$\text{Extractability (\%)} = [(A_0 - A)/A_0] \times 100 \qquad (1)$$

where A_0 and A are the initial and final concentrations of the metal picrate/dichromate before and after the extraction, respectively.

1,3-Bis{4-{(1E)-1-((2E)-(2-hydroxybenzene-2-ylmehylidene) hydrazonylidene)ethyl} phenoxy}propane (H_2L)

Salicyladehyde (4 mmol, 0.488 g) dissolved in ethanol (10 mL) was added dropwise to a solution of *III* (2 mmol, 0.68 g) with two drops of glacial acetic acid in hot ethanol (30 mL). The reaction mixture was stirred while refluxing for 1 h. The compound which precipitated during refluxing was filtered off and washed several times with water and hot ethanol, and dried in air at room temperature. Crystallisation of the crude products from ethanol/chloroform furnished a bis(azine) compound.

Synthesis of complexes $[Ni(L)(H_2O)]_2$ (IV), $[Cu(L)(H_2O)]_2$ (V), $[Ni_2(L)Cl_2(H_2O)_2] \cdot 3H_2O$ (VI), $[Cu_2(L)Cl_2(H_2O)_2] \cdot 2H_2O$ (VII)

A solution of $Ni(AcO)_2 \cdot 4H_2O$ (0.249 g, 1 mmol) (for *IV*) or $Cu(AcO)_2 \cdot H_2O$ (0.20 g, 1 mmol) (for *V*) or $NiCl_2 \cdot 6H_2O$ (0.475 g, 2 mmol) (for *VI*) or $CuCl_2 \cdot 2H_2O$ (0.341 g, 2 mmol) (for *VII*) in EtOH (10 mL) (for *IV* and *VI*) or MeOH (10 mL) (for *V* and *VII*) was added dropwise over 1 h to a hot solution containing bis(azine) (H_2L) (0.549 g, 1 mmol) and NaOH (0.80 g, 2 mmol) (for *IV* and *VI*) in EtOH (30 mL) (for *IV* and *VI*) or TEA (0.205 g, 2 mmol) (for *V* and *VII*) in acetone (30 mL) (for *V* and *VII*) under stirring. The reaction mixture was refluxed for 5 h (for *IV*, *V*, and *VII*) or 7 h (for *VI*). The precipitated complexes were filtered off, and washed with water and chloroform.

Results and discussion

Synthesis and spectral characterisation

Symmetric bis(azine) ligand (H_2L) was prepared by the condensation of (1*Z*,1′*Z*)-1,1′-{propane-1,3-diylbis[oxybenzene-4,1-diyl(1*Z*)eth-1-yl-1-ylidene]} dihydrazine (*III*) with salicylaldehyde at the mole ra-

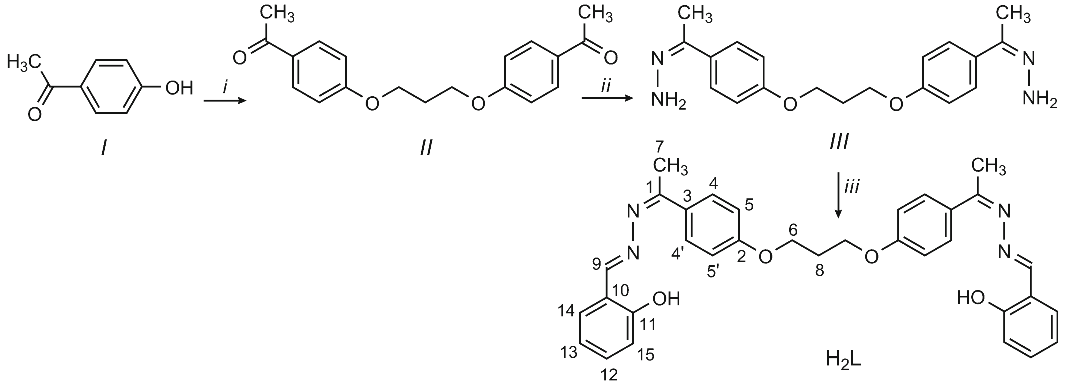

Fig. 1. Reaction conditions: *i*) 1,3-dibromopropane, K_2CO_3, acetone, reflux, 15 h; *ii*) hydrazine monohydrate, EtOH, reflux 4 h; *iii*) salicylaldehyde, EtOH, reflux, 4 h.

Table 1. Physical and analytical data of the newly synthesised compounds

Compound	Colour	μ_{eff} / B.M.	M.p. / °C	Yield / %	w_i(calc.)/% w_i(found)/% C	H	N	Metal
H_2L	yellow	–	160	73	72.24 71.88	5.88 5.56	10.22 10.63	–
IV	light green	2.87	296	74	63.53 63.97	5.13 5.26	8.98 8.77	9.42 9.65
V	brown	1.57	243	78	63.04 62.70	5.09 5.21	8.99 9.18	10.11 10.39
VI	light green	3.92	> 300	83	48.43 48.33	4.89 4.43	6.75 6.35	14.23 14.40
VII	light brown	1.66	241	87	48.49 48.33	4.65 4.43	6.61 6.35	15.55 15.20

Table 2. Spectral data of the newly synthesised compounds

Compound	Spectral data[a]
H_2L	IR, $\tilde{\nu}$/cm^{-1}: 3158–2600 (b) (HO···H), 1610 (s) (C=N—N=C), 1253 (s) and 1175 (m) (C—O—C) ^{1}H NMR (DMSO-d_6), δ: 12.00 (s, 2H, OH), 8.69 (s, 2H, CH=N), 7.92 and 6.95 (dd, 8H, ArH, J = 7 Hz), 7.38–6.98 (m, 8H, ArH), 4.26 (t, 4H, OCH$_2$, J = 6 Hz), 2.32 (q, 2H, CH$_2$, J = 6 Hz), 2.55 (s, 6H, CH$_3$) ^{13}C NMR (DMSO-d_6), δ: 166.4 (C1), 163.2 (C9), 160.6 (C2), 160.1 (C11), 133.1 (C3), 132.4 (C10), 131.3 (C15), 129.7 (C14), 120.3 (C5), 119.7 (C4), 117.6 (C12), 114.3 (C14), 65.0 (C6), 29.5 (C7), 16.8 (C8) UV-VIS (CHCl$_3$), λ/nm: 348, 317
IV	IR, $\tilde{\nu}$/cm^{-1}: 3463 (b) (OH), 1601 (s) (C=N—N=C), 1245 (s) and 1174 (m) (C—O—C)
V	IR, $\tilde{\nu}$/cm^{-1}: 3452 (b) (OH), 1598 s (C=N—N=C), 1245 (s) and 1173 (m) (C—O—C)
VI	IR, $\tilde{\nu}$/cm^{-1}: 3452 (b) (OH), 1598 s (C=N—N=C), 1245 (s) and 1173 (m) (C—O—C)
VII	IR, $\tilde{\nu}$/cm^{-1}: 3397 (b) (OH), 1599 (s) (C=N—N=C), 1242 (s) and 1174 (m) (C—O—C)

a) Absorption bands in IR: b – broad, s – strong, m – medium; signals in NMR: s – singlet, dd – doublet of doublets, t – triplet, m – multiplet, q – quintet; Ar – aryl.

tio of 1 : 2 (Fig. 1). The reaction proceeded smoothly affording H_2L in good yield. The ligand is soluble in common organic solvents but insoluble in water. The structure of the ligand was determined on basis of elemental analysis and FTIR, UV-VIS, and NMR spectral data. The complexes were synthesised by reacting the ligand with metal(II) salt at the mole ratio of 1 : 1 and 1 : 2, respectively. Attempts to isolate crystals suitable for single crystal X-ray diffraction were unsuccessful. Therefore, the overall geometry of the complexes was inferred from the powder X-ray diffraction data, thermal and elemental analysis, IR and electronic spectra. Some physical and analytical data of the newly synthesised compounds are given in Table 1.

In the ^{1}H NMR spectra (Table 2) of H_2L, the singlet at δ = 8.69 was assigned to the proton of the

CH=N group. The signals of OH were observed as a singlet at $\delta = 12.00$ (Creaven et al., 2005; Mahon et al., 2008). The appearance of the signal of phenolic OH protons at lower frequency can be explained by strong intermolecular hydrogen bonding C11—O—H···N=C9. The protons of 1,4-disubstituted aryl moiety gave doublet-doublet peaks at $\delta = 6.95$ and $\delta = 7.92$, resembling an AB pattern of two distorted doublets, while the aromatic protons of the salicylaldehyde part of the ligand appeared as multiplets at $\delta = 6.98$–7.38. Singlet at $\delta = 2.55$ (CH_3 protons), triplet at $\delta = 4.26$ (O—CH_2—C protons) and quintet at $\delta = 2.32$ (C—CH_2—C protons) are in agreement with the previously reported data for similar compounds (Zhang et al., 2004; West & Marnet, 2006; Pogozelski & Tullius, 1998; Burrows & Muller, 1998; Chen et al., 1994, 1995). Characteristic chemical shifts of the azine C1=N—N=C9 carbon atoms observed at $\delta = 166.4$ and $\delta = 163.2$ and the signal at $\delta = 160.1$ attributed to C(15)—OH carbon atom of the salicylaldehyde moiety are in good agreement with those reported previously (Nour et al., 1988; Chen et al., 1994, 1995; Picón-Ferrer et al., 2009; Moreno-Mañas et al., 2001; Glaser et al., 2004). Due to the insolubility of the complexes, their NMR spectra could not be obtained.

The IR spectrum of H_2L did not display bands of the NH_2 group but a medium band at 1610 cm^{-1} was observed characteristic of the stretching vibration of the azine group (C=N—N=C). A broad band observed in the region of 2600–3158 cm^{-1} was assigned to the intermolecular H-bonding vibration (O—H···O) (El-Sayed et al., 2002; Chi et al., 2009; Davidson et al., 2006; Gup et al., 2006; Krishna et al., 2004). The other characteristic IR peaks (Table 2) are in accord with those previously reported for similar compounds (Zhang et al., 2004; West & Marnet, 2006; Pogozelski & Tullius, 1998; Burrows & Muller, 1998; Dede et al., 2009; Wang et al., 2006).

The band at 3158–2600 cm^{-1} corresponding to the stretching vibration of phenolic OH involved in hydrogen bonding disappeared upon the formation of the complexes, indicating the deprotonation and participation of phenolate in the complexation (Sreeja et al., 2003; Gup, 2006; Dömer et al., 2009). On the other hand, a new band at 3450 cm^{-1} which can be assigned to the stretching vibration of the water molecules present in all metal complexes was registered. It is well known that the coordination of the ligand to metal ions through an imine nitrogen atom reduces the electron density of this bond lowering the C=N symmetric stretching frequency (Nakamoto, 1978). Therefore, this band of the free ligand was moved to lower frequency after the complexation, indicating that the bis(azine) ligand is coordinated through its imine group. Comparing the IR spectrum of the free ligand and its complexes, it can be concluded that ligand acts as a dianionic tetradentate ligand coordinating to azine and salicylaldehyde moiety (El-Sayed et al., 2002; Chi et al., 2009; Davidson et al., 2006; Picón-Ferrer et al., 2009; Tang et al., 2009; Abd El-halim et al., 2011).

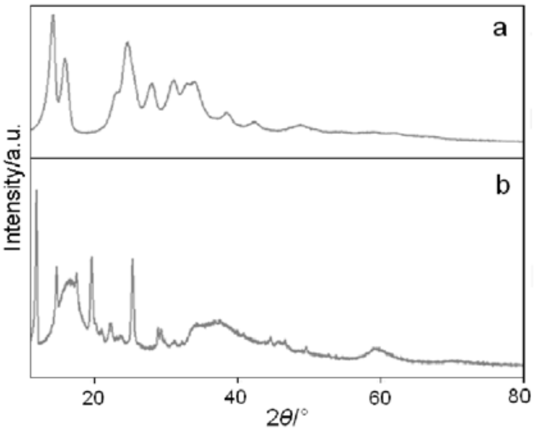

Fig. 2. Powder X-ray diffraction patterns of complexes *V* (a) and *VI* (b).

The electronic spectra of H_2L exhibited maxima at 348 nm and 317 nm corresponding, probably, to the $n \rightarrow \pi^*$ electronic transitions of the nonbonding electron pairs (Gup & Giziroğlu, 2006; Usluer & Gup, 2007). Due to the insolubility of the binuclear complexes, the electronic spectra could not be measured.

Powder X-ray diffractograms of the bis(azine) metal complexes $[Cu(L)(H_2O)_2]_2$ (*V*) and $[Ni_2(L)Cl_2(H_2O)_2] \cdot 3H_2O$ (*VI*) are shown in Fig. 2. Both complexs showed sharp peaks indicating that the binuclear complexes are crystalline in nature and probably have different crystal structure. The sharp peaks are indicative of complex *VI* having higher crystallinity than complex *V*.

Thermogravimetry studies

Data obtained from thermogravimetry (TG) of the complexes are given in Table 3. TGA curves of all the complexes exhibit stepwise mass losses. TGA curves of the double-stranded binuclear complexes $[M_2(L)_2]$ are different from those of the dinuclear complexes $[M_2(L)Cl_2(H_2O)_2]$.

According to TGA curves, thermal degradation of the double-stranded binuclear complexes *IV* and *V* occurred in five steps. In the first step, the loss of two molecules of water and some part of ligand occurred below approximately 280 °C. This high temperature loss confirms that the water molecules participate in coordination. Decomposition in the second to the fourth step can be attributed to the loss of functional groups of the double-stranded binuclear bis(azine) complexes. The last step is the breakage of the binuclear complexes leaving metallic ash as a residue. The dinuclear complexes *VI* and *VII* undergo a four step thermal degradation. The first step within

Table 3. Thermal decomposition of the bis(azine) metal complexes

Complex	T/℃	Mass loss^a/%	Assignment
IV	25–280	10.40	loss of coordinated H_2O and functional groups
	280–380	9.30	loss of functional groups
	380–590	29.95	loss of functional groups
	590–950		decomposition of remaining organic part leaving ash
V	25–300	19.32	loss of coordinated H_2O and functional groups
	300–580	31.68	loss of functional groups
	580–900		decomposition of remaining organic part leaving ash
VI	25–285	13.36 (13.88)^b	loss of $2H_2O$ and 2Cl
	285–410	12.10	loss of functional groups
	410–530	26.35	loss of functional groups
	530–950		decomposition of remaining organic part leaving ash
VII	25–280	13.10 (13.71)^b	loss of $2H_2O$ and 2Cl
	280–400	11.29	loss of functional groups
	400–535	26.00	loss of functional groups
	535–950		decomposition of remaining organic part leaving ash

a) Estimated values; *b*) calculated values in parentheses.

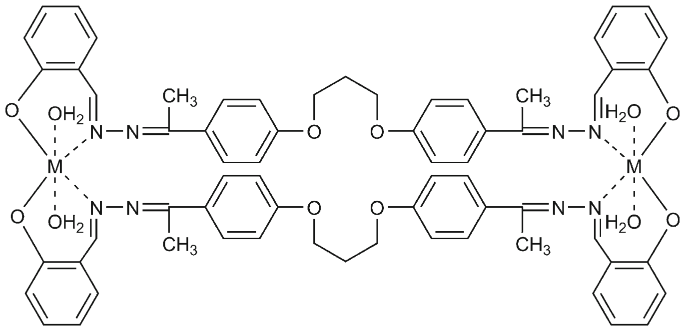

Fig. 3. Proposed structure of double-stranded binuclear complexes of bis(azine). M = Ni(II) or Cu(II).

the temperature range of 25–285 ℃ is the elimination of coordinated molecules of water and the chloride anion attached to the metal ion which is connected with the mass loss of 13.36 % and 13.10 % in the expected Ni(II) and Cu(II) complex stoichiometries, respectively. The final decomposition step in the temperature range of 535–950 ℃ involves the loss of the organic part of ligand leaving metallic ash as a residue.

Magnetic susceptibility studies

Data of magnetic susceptibilities (Table 1) showed that all complexes are paramagnetic at ambient temperature. Magnetic moment (μ_{eff}) values of the binuclear Cu(II) complexes are in the range of 1.57–1.66 B.M., while those of the Ni(II) complexes are in the range of 2.87–3.92 B.M. at 303 K. In case of binuclear copper(II) complexes, μ_{B} values are slightly lower than the theoretical value of 1.73 B.M. for one d^9 copper ion, while the observed μ_{B} values for binuclear nickel(II) complexes are slightly higher than the theoretical value of 2.82 B.M. for one d^8 nickel ion. However, these μ_{B} values are lower than that expected for binuclear copper(II) and nickel(II) complexes. These abnormal values can be explained by weak antiferromagnetic intramolecular interactions within the dinuclear M(II) subunits, resulting in a decrease in the magnetic moments (West & Marnett, 2006; Usluer & Gup, 2007; Serin et al., 2007). On the other hand, the dinuclear complexes *IV* and *V* showed slightly higher antiferromagnetic exchange interactions than those of complexes *VI* and *VII,* probably due to their double-stranded structures. Magnetic data showed that the nickel(II) complex *IV*, which is in the octahedral environment created by additional axial coordination of the water molecules, adopts a high-spin configuration in the double-stranded binuclear complexes (Fig. 3). However, taking into account the above data, the coordination spheres of Ni(II) ions in the dinuclear complex *VI* seem to prefer the distorted tetrahedral geometries whose third and fourth positions were occupied by one molecule of water and a chloride ion (Fig. 4) (Gup, 2006; Tiwari et al., 2011).

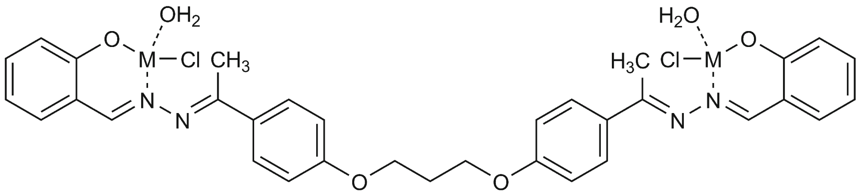

Fig. 4. Proposed structure of dinuclear complexes of bis(azine). M = Ni(II) or Cu(II).

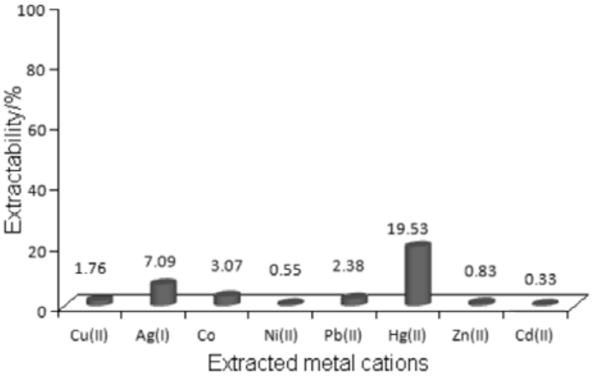

Fig. 5. Extraction percentages of metal cations with bis(azine) ligand. Aqueous phase: metal nitrate (10^{-2} M), picric acid (2.5×10^{-5} M); organic phase: dichloromethane; ligand (10^{-3} M); 25 °C, 1 h.

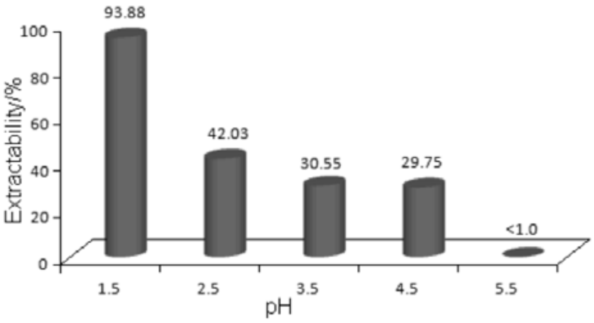

Fig. 6. Extraction percentages of dichromate anion with bis (azine) ligand at pH 1.5–4.5. Aqueous phase: $Na_2Cr_2O_7$ (10^{-4} M); organic phase: dichloromethane; ligand (10^{-3} M); 25 °C, 1 h.

Extraction ability of the ligand

Schiff bases are used as highly selective reagents for the separation and determination of a number of metal ions. Therefore, the metal binding property of bis(azine) ligand was examined by solvent extraction of some heavy metal picrates (Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II), Pb(II), and Ag(I)) from the aqueous to the organic phase under neutral conditions. Data on the equilibrium concentration of picrate in the aqueous phase are shown in Fig. 5.

These data indicate that all the metal ions are not significantly extracted by the azine ligand. On the other hand, the ligand extracts Hg(II) ions poorly compared to the other metal ions. Probably, due to the presence of the azine group, this ligand acts as a soft base and binds selectively to soft and borderline acids (Hatay et al., 2008; Gup & Giziroğlu, 2006; Tabakci et al., 2003, 2007; Gup et al., 2002, 2006; Kulaksızoğlu, 2011).

Binding efficiency of the bis(azine) ligand towards aqueous solution of $Na_2Cr_2O_7$ was also studied by solvent extraction at different pH values. The results are summarised in Fig. 6. $Na_2Cr_2O_7$ is not extracted from the aqueous to the organic phase without any extractant. The bis(azine) ligand effectively extracts dichromate anions at low pH but the extraction efficiency of the azine increases with the decreasing pH of the aqueous phase. The best result was obtained with the pH of 1.5. Moreover, bis(azine) is also effective for the extraction of dichromate anions at pH 2.5. It can be concluded that the bis(azine) ligand is a selective extractant for dichromate anions at pH 1.5.

It is known that in more acidic aqueous solutions, dichromate anions exist in the $HCr_2O_7^-/Cr_2O_7^{2-}$ pair form. At higher acidic conditions $HCr_2O_7^-$ and $Cr_2O_7^{2-}$ dimers become the dominant Cr(VI) form. It seems that the bis(azine) ligand forms complexes with both $HCr_2O_7^-$ and $Cr_2O_7^{2-}$ ions. Dichromate anions are principally in their protonated form, $HCr_2O_7^-$, in the aqueous solutions having a lower pH.

The bis(azine) ligand forms hydrogen bonds with the dichromate anion through azine moieties. Therefore, dichromate anions can be transferred as a hydrogen-bonded ion pair interaction from the aqueous to the organic phase by the bis(azine) ligand. Following the proton transfer to the nitrogen atom of azine group in the ligand $Cr_2O_7^{2-}/HCr_2O_7^-$, an ion pair complex is formed in the two-phase extraction system (Kulaksızoğlu, 2011; Tabakci et al., 2003; Bozkurt et al., 2009; Memon et al., 2004). Furthermore, a hydrogen bonded complex can be also formed in the two-phase extraction system between the dichromate anion and the oxygen atom of salicylaldehyde units. As a consequence, based on the above results it has been concluded that both salicylaldehyde and azine units play an important role in the dichromate anions transfer from the aqueous to the organic phase (Fig. 7).

Conclusions

Two kinds of binuclear Cu(II) and Ni(II) com-

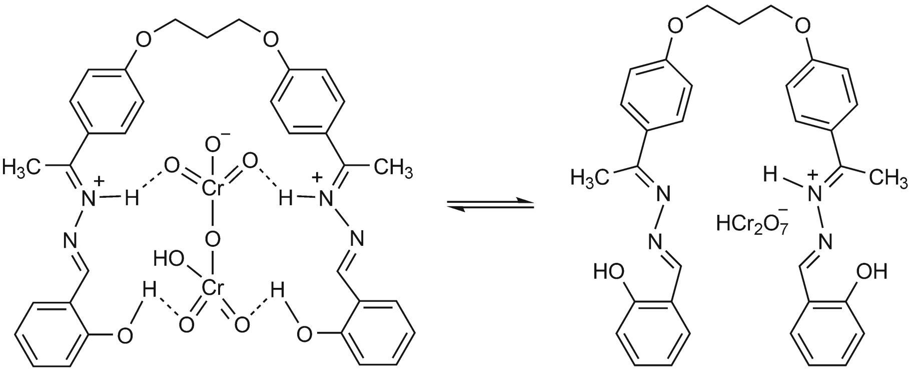

Fig. 7. Proposed interactions of bis(azine) with dichromate anions.

plexes of a new tetradentate bis(azine) derived from the condensation of $(1E,1'E)$-1,1′-{propane-1,3-diylbis [oxybenzene-4,1-diyl(1E)eth-1-yl-1-ylidene]}dihydrazine with salicylaldehyde were synthesised and characterised using different spectroscopic techniques. The ligand-to-metal ratio of 1 : 2 gave the dinuclear complexes $[M_2(L)Cl_2(H_2O)_2]$, whereas the ratio of 2 : 2 favoured the formation of the double-stranded binuclear complexes $[M(II)(N\text{-}O)(N'\text{-}O')]_2$. Ni(II) ions in the double-stranded binuclear complex have octahedral geometries while Ni(II) ions in the dinuclear complex have slightly distorted tetrahedral geometries. As a result, a new type of N—O/N—O ligand reacting in different stoichiometries with Ni(II) and Cu(II) ions to give different types of binuclear metal complexes was synthesised and characterised. Solvent extraction of selected transition metal cations (Cu(II), Ag(I), Co(II), Ni(II), Pb(II), Hg(II), Zn(II), Cd(II)) and dichromate anions from the aqueous to the organic phase was performed using the bis(azine) ligand. It was found that the ligand has no affinity towards cations. On the other hand, the azine ligand is an effective extractant for dichromate anions at low pH values.

Acknowledgements. The authors thank the Scientific Research Projects Foundation of the Mugla University for financial support of this work.

References

Abd El-halim, H. F., Omar, M. M., & Mohamed, G. G. (2011). Synthesis, structural, thermal studies and biological activity of a tridentate Schiff base ligand and their transition metal complexes. *Spectrochimica Acta Part A*, *78*, 36–44. DOI: 10.1016/j.saa.2010.06.003.

Abu-El-Wafa, S. M., Issa, R. M., & McAuliffe, C. A. (1985). Unusual Cu(III)—Schiff's base complexes. *Inorganica Chimica Acta*, *99*, 103–106. DOI: 10.1016/s0020-1693(00)86056-9.

Bozkurt, S., Kocabas, E., Durmaz, M., Yilaz, M., & Sirit, A. (2009). Synthesis and dichromate anion sorption of silica gel-immobilized calix[4]arenes. *Journal of Hazardous Materials*, *165*, 974–979. DOI: 10.1016/j.jhazmat.2008.10.096.

Burrows, C. J., & Muller, J. G. (1998). Oxidative nucleobase modifications leading to strand scission. *Chemical Reviews*, *98*, 1109–1152. DOI: 10.1021/cr960421s.

Chen, G. S., Anthamatten, M., Barnes, C. L., & Glaser, R. (1994). Stereochemistry and stereoelectronics of azines. A solid-state study of symmetrical, (*E*,*E*)-configured, *para*-substituted (H, F, Cl, Br, CN) acetophenone azines. *The Journal of Organic Chemistry*, *59*, 4336–4340. DOI: 10.1021/jo00094a059.

Chen, G. S., Wilbur, J. K., Barnes, C. L., & Glaser, R. (1995). Push-pull substitution *versus* intrinsic or packing related N–N *gauche* preferences in azines. Synthesis, crystal-structures and packing of asymmetrical acetophenone azines. *Journal of the Chemical Society, Perkin Transactions 2*, *1995*, 2311–2317. DOI: 10.1039/p29950002311.

Chi, S. M., Wang, Y. F., Gan, X., Wang, D. H., & Fu, W. F. (2009). Synthesis, structures, and spectroscopic properties of copper(I) complexes bearing 7-acetamido-4-methyl-1,8-naphthyridin-2-carbaldehyde azine and 1,2-bis(diphenylphosphino)ethane ligands. *Central European Journal of Chemistry*, *7*, 923–928. DOI: 10.2478/s11532-009-0087-y.

Creaven, B. S., Gernon, T. L., McCormac, T., McGinley, J., Moore, A. M., & Toftlund, H. (2005). Unusual reactivity of copper(I) complexes of functionalised calix[4]arenes. *Inorganica Chimica Acta*, *358*, 2661–2670. DOI: 10.1016/j.ica.2005.03.003.

Davidson, M. G., Johnson, A. L., Jones, M. D., Lunn, M. D., & Mahon, M. F. (2006). Titanium(IV) complexes of hydrazones and azines. *European Journal of Inorganic Chemistry*, *2006*, 4449–4454. DOI: 10.1002/ejic.200600501.

Dede, B., Karipcin, F., Arabalı, F., & Cengiz, M. (2010). Synthesis, structure, and solvent-extraction properties of tridentate oxime ligands and their cobalt(II), nickel(II), copper(II), zinc(II) complexes. *Chemical Papers*, *64*, 25–33. DOI: 10.2478/s11696-009-0095-6.

Dede, B., Özme, I., Karipcin, F., & Cengiz, M. (2009). Homo- and heteropolynuclear copper(II) complexes containing a new diimine–dioxime ligand and 1,10-phenanthroline: synthesis, characterization, solvent-extraction studies, catalase-like functions and DNA cleavage abilities. *Applied Organometallic Chemistry*, *23*, 512–519. DOI: 10.1002/aoc.1557.

Dömer, J., Hupka, F., Hahn, F. E., & Fröhlich, R. (2009). Mono- and dinuclear coordination compounds with directional bis(bidentate) ligands. *European Journal of Inorganic Chemistry*, *2009*, 3600–3606. DOI: 10.1002/ejic.200900505.

El-Sayed, B. A., Abo Aly, M. M., Emara, A. A. A., & Khalil, S. M. E. (2002). Synthesis and structural study of the ligand *o*-OH acetophenone azine and its Cu(II), Ni(II), Co(II) and Zn(II) complexes. *Vibrational Spectroscopy*, *30*, 93–100. DOI: 10.1016/s0924-2031(02)00043-7.

Glaser, R., Chen, N., Wu, H., Knotts, N., & Kaupp, M. (2004). ^{13}C NMR study of halogen bonding of haloarenes: Measurements of solvent effects and theoretical analysis. *Jour-*

nal of the American Chemical Society, *126*, 4412–4419. DOI: 10.1021/ja0383672.

Gup, R. (2006). A new unsymmetrical *vic*-dioxime bearing salicylaldehyde 4-aminobenzoylhydrazone and its homo- and heterotrinuclear complexes with copper(II) and nickel(II) ions. *Russian Journal of Coordination Chemistry*, *32*, 99–108. DOI: 10.1134/s1070328406020047.

Gup, R., Alpoguz, H. K., & Beduk, A. D. (2002). Synthesis and extraction properties of 1,2-bis(amidoxime) derivatives. *Collection of Czechoslovak Chemical Communications*, *67*, 209–218. DOI: 10.1135/cccc20020209.

Gup, R., & Giziroğlu, E. (2006). Metal complexes and solvent extraction properties of isonitrosoacetophenone 2-aminobenzoylhydrazone. *Spectrochimica Acta Part A*, *65*, 719–726. DOI: 10.1016/j.saa.2006.01.004.

Gup, R., Kirkan, B., & Giziroğlu, E. (2006). Synthesis and characterization of complexes of copper(II), nickel(II) and cobalt(II) with vic-dioximes bearing *N′*-*p*-aminobenzoyl benzaldehyde hydrazone. *Chinese Journal of Chemistry*, *24*, 199–204. DOI: 10.1002/cjoc.200690038.

Hatay, I., Gup, R., & Ersöz, M. (2008). Silica gel functionalized with 4-phenylacetophynone 4-aminobenzoylhydrazone: Synthesis of a new chelating matrix and its application as metal ion collector. *Journal of Hazardous Materials*, *150*, 546–553 DOI: 10.1016/j.jhazmat.2007.05.002.

Krishna, P. G., Gladis, J. M., Rambabu, U., Rao, T. P., & Naidu, G. R. K. (2004). Preconcentrative separation of chromium(VI) species from chromium(III) by coprecipitation of its ethyl xanthate complex onto naphthalene. *Talanta*, *63*, 541–546. DOI: 10.1016/j.talanta.2003.11.032.

Kulaksızoğlu, S. (2011). *Synthesis of transition metal complexes of p-hydroxyacetophenone azines and investigation of liquid-liquid extraction properties*. M.Sc. thesis, Mugla University, Mugla, Turkey.

Mahon, M. F., McGinley, J., Rooney, A. D., & Walsh, J. M. D. (2008). Calix[4]arene Schiff bases—potential ligands for fluorescent studies. *Tetrahedron*, *64*, 11058–11066. DOI: 10.1016/j.tet.2008.09.091.

Memon, S., Roundhill, D. M., & Yilmaz, M. (2004). Remediation and liquid-liquid phase transfer extraction of chromium(VI). A review. *Collection of Czechoslovak Chemical Communications*, *69*, 1231–1250. DOI: 10.1135/cccc200 41231.

Moreno-Mañas, M., Pleixats, R., Andreu, R., Garín, J., Orduna, J., Villacampa, B., Levillain, E., & Sallé, M. (2001). The first 1,3-dithiol-2-ylidene donor-π-acceptor chromophores containing an azine spacer: synthesis, electrochemical and nonlinear optical properties. *Journal of Materials Chemistry*, *11*, 374–380. DOI: 10.1039/b007629p.

McLoughlin, C., Clyburne, J. A. C., & Weinberg, N. (2007). Azines: conjugation stoppers or conjugation switches. *Journal of Materials Chemistry*, *17*, 4304–4308. DOI: 10.1039/ b706964b.

Nakamoto, K. (1978). *Infrared and Raman spectra of inorganic and coordination compounds* (3rd ed.). New York, NY, USA: Wiley.

Nour, E. M., Taha, A. A., & Alnaimi, I. S. (1988). Infrared and Raman studies of [UO_2(salen)(L)] (L = H_2O and CH_3OH). *Inorganica Chimica Acta*, *141*, 139–144. DOI: 10.1016/s0020-1693(00)86387-2.

Pedersen, C. J. (1968). Ionic complexes of macrocyclic polyethers. *Federation Proceedings*, *27*, 1305–1309.

Picón-Ferrer, I., Hueso-Ureña, F., Illán-Cabeza, N. A., Jiménez-Pulido, S. B., Martínez-Martos, J. M., Ramírez-Expósito, M. J., & Moreno-Carretero, M. N. (2009). Chloro-*fac*-tricarbonylrhenium(I) complexes of asymmetric azines derived from 6-acetyl-1,3,7-trimethylpteridine-2,4(1*H*,3*H*)-dione with hydrazine and aromatic aldehydes: Preparation, structural characterization and biological activity against several human tumor cell lines. *Journal of Inorganic Biochemistry*, *103*, 94–100. DOI: 10.1016/j.jinorgbio.2008.09.014.

Pogozelski, W. K., & Tullius, T. D. (1998). Oxidative strand scission of nucleic acids: Routes initiated by hydrogen abstraction from the sugar moiety. *Chemical Reviews*, *98*, 1089–1108. DOI: 10.1021/cr960437i.

Raji, C., & Anirudhan, T. S. (1998). Batch Cr(VI) removal by polyacrylamide-grafted sawdust: Kinetics and thermodynamics. *Water Research*, *32*, 3772–3780. DOI: 10.1016/s0043-1354(98)00150-x.

Serin, M., Karayel, G., & Gup, R. (2007). Homo- and heteronuclear complexes of a new, vicinal dioxime ligand. *Chemical Papers*, *61*, 286–291. DOI: 10.2478/s11696-007-0035-2.

Sreeja, P. B, Sreekanth, A., Nayar, C. R., Kurup, M. R. P., Usman, A., Razak, I. A., Chantrapromma, S., & Fun, H. K. (2003). Synthesis, spectral studies and structure of 2-hydroxyacetophenone nicotinic acid hydrazine. *Journal of Molecular Structure*, *645*, 221–226. DOI: 10.1016/s0022-2860(02)00563-x.

Tabakci, M., Memon, S., & Yilmaz, M. (2007). Synthesis and extraction properties of new ‘proton-switchable’ tri- and tetra-substituted calix[4]arene derivatives bearing pyridinium units. *Tetrahedron*, *63*, 6861–6865. DOI: 10.1016/j.tet.2007.04.060.

Tabakci, M., Memon, S., Yilmaz, M., & Roundhill, D. M. (2003). Synthesis and extraction studies of a versatile calix[4]arene-based “proton-switchable extractant” for toxic metals and dichromate anions. *Journal of Inclusion Phenomena and Macrocyclic Chemistry*, *45*, 265–270. DOI: 10.1023/a:1024503708830.

Tang, X. D., Ding, Z. J., & Zhang, Z. M. (2009). High pressure study of acetophenone azine. *Solid State Communications*, *149*, 301–306. DOI: 10.1016/j.ssc.2008.11.034.

Tiwari, A. D., Mishra, A. K., Mishra, S. B., Mamba, B. B., Maji, B., & Bhattacharya, S. (2011). Synthesis and DNA binding studies of Ni(II), Co(II), Cu(II) and Zn(II) metal complexes of N^1,N^5-bis[pyridine-2-methylene]-thiocarbohydrazone Schiff-base ligand. *Spectrochimica Acta Part A*, *79*, 1050–1056. DOI: 10.1016/j.saa.2011.04.018.

Usluer, Ö., & Gup, R. (2007). Synthesis and characterization of copper(II) and nickel(II) complexes of isonitrosoacetophenone 4-aminobenzoylhydrazone. *Polish Journal of Chemistry*, *81*, 1257–1265.

Viñuelas-Zahínos, E., Luna-Giles, F., Torres-García P., & Bernalte-García, A. (2009). Chloride-bridged Ni(II) complexes with ferromagnetic exchange interaction from thiazoline hydrazone derivative ligands. *Polyhedron*, *28*, 1362–1368. DOI: 10.1016/j.poly.2009.02.030.

Wang, B. D., Yang, Z. Y, Wang, Q., Cai, T. K., & Crewdson, P. (2006). Synthesis, characterization, cytotoxic activities, and DNA-binding properties of the La(III) complex with naringenin Schiff-base. *Bioorganic & Medicinal Chemistry*, *14*, 1880–1888. DOI: 10.1016/j.bmc.2005.10.031.

West, J. D., & Marnett, L. J. (2006). Endogenous reactive intermediates as modulators of cell signaling and cell death. *Chemical Research in Toxicology*, *19*, 173–194. DOI: 10.1021/tx050321u.

Zhang, G., Shuang, S., Dong, C., Liu, D., & Choi, M. M. F. (2004). Investigation on DNA assembly to neutral red-cyclodextrin complex by molecular spectroscopy. *Journal of Photochemistry and Photobiology B: Biology*, *74*, 127–134. DOI: 10.1016/j.jphotobiol.2004.03.006.