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Heteroarylazo derivatives of cyclohexane-1,3-dione and their metal complexes

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Abstract: The coupling of diazotized 2-aminothiazole and 2-aminobenzothiazole with cyclohexane-1,3-dione yielded a new type of tridentate ligand system (HL). Analytical, IR, ^{1}H-NMR, ^{13}C-NMR and mass spectral data indicate the existence of the compounds in the intramolecularly hydrogen bonded azo–enol tautomeric form. Monobasic tridentate coordination of the compounds in their [CuL(OAc)] and [ML$_2$] complexes [M = Ni(II) and Zn(II)] was established based on the analytical and spectral data. The Zn(II) chelates are diamagnetic while the Cu(II) and Ni(II) complexes showed a normal paramagnetic moment.

Keywords: heteroarylazo derivatives; 2-aminothiazole; 2-aminobenzothiazole; cyclohexane-1,3-dione; metal complexes; spectral data.

INTRODUCTION

Metallizable azo dyes containing one heterocyclic donor atom suitably located for the formation of annulated chelate complex were the subject of numerous studies,[1–3] the most common being those containing a hetero nitrogen atom in a position adjacent to the azo group.[4,5] They have wide application in analytical chemistry, metallurgy, the textile industry, optical data storage, photo switching and nonlinear optical materials,[6–10] and are also involved in many biological reactions.[11] In recent years, a significant number of tridentate azo compounds have been developed to improve the colouring properties, and to achieve more specificity and selectivity in chemical analysis.[12] Metal complexation alters the properties of a dye, both qualitatively and quantitatively.[13] However, the structural aspects of many of these dyestuffs and their metal complexes have not received as much attention as they deserve. In continuation of studies on

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heteroarylazo derivatives of 1,3-diketones and their metal complexes,[14–19] the synthesis and characterization of two new heteroarylazo derivatives obtained by coupling the diazonium salts of 2-aminothiazole and 2-aminobenzothiazole with the active methylene group of cyclohexane-1,3-dione are reported herein. Typical metal complexes of these ligand systems were also synthesized and characterized.

EXPERIMENTAL

Methods, instruments and materials

The carbon, hydrogen and nitrogen contents were determined by microanalyses (Heraeus Elemental Analyzer from RSIC, Central Drug Research Institute, Lucknow, India, and Catalysis Division, Department of Chemistry, Indian Institute of Technology, Chennai, India) and the metal contents of the complexes by AAS (Perkin Elmer 2380 spectrometer). The electronic spectra of the compounds in methanol (10^{-4} mol L^{-1}) were recorded on a 1601 Shimadzu UV–Vis spectrophotometer, the IR spectra (KBr discs) on an 8101 Shimadzu FTIR spectrophotometer, the ^{1}H-NMR spectra ($CDCl_3$ or DMSO-d_6) on a Varian 300 NMR spectrometer and the mass spectra on a Jeol/SX-102 mass spectrometer (FAB using argon and *meta*-nitrobenzyl alcohol as the matrix). The molar conductance of the complexes were determined in DMF ($\approx 10^{-3}$ mol L^{-1}) at room temperature (301±1 K). The magnetic susceptibilities were determined at room temperature on a Guoy-type magnetic balance, Sherwood Scientific Ltd., UK, at room temperature (301±1 K) using $Hg[Co(NCS)_4]$ as the standard.

Cyclohexane-1,3-dione, 2-aminothiazole, 2-aminobenzothiazole, methanol, urea and the metal acetates were of AR grade, purchased from Merck, Germany.

General procedure for the preparation of the 2-(thiazol-2-ylazo)cyclohexane-1,3-dione (HL^1) and 2-(benzothiazol-2-ylazo)cyclohexane-1,3-dione (HL^2) ligands

2-Aminothiazole/2-aminobenzothiazole was diazotized as reported previously.[20] After quenching the excess nitrous acid with urea, the diazonium salt solution (0.01 mol) was added dropwise to a well stirred ethanolic solution of cyclohexane-1,3-dione (0.01 mol, 20 mL) kept in an ice–salt bath and stirred well for ≈1 h. Sodium acetate (≈3 g) was added to adjust the pH to around 6. The precipitated product was filtered, washed with cold water and recrystallized from hot methanol.

Synthesis of the Ni(II), Cu(II) and Zn(II) complexes

A concentrated aqueous solution of metal(II) acetate, [$Ni(CH_3COO)_2 \cdot 4H_2O$, $Cu(CH_3COO)_2 \cdot H_2O$ and $Zn(CH_3COO)_2 \cdot 2H_2O$] (0.01 mol, 15 mL) was added to a hot methanolic solution of the required ligand (0.02 mol, 20 mL). The mixture was refluxed on a water bath for ≈2 h. The precipitated complex after cooling to room temperature was filtered, washed with water, recrystallized from hot benzene and dried under vacuum over anhydrous $CaCl_2$.

RESULTS AND DISCUSSION

The yields, melting points and analytical data for the prepared ligands and complexes and the magnetic moments for the Ni and Cu complexes are given below.

HL^1. Yield: 60 %; m.p.: 151 °C; Anal. Calcd. for $C_9H_9N_3SO_2$: C, 48.43; H, 4.04; N, 18.83 %. Found: C, 48.20; H, 4.15; N, 18.68 %.

HL^2. Yield: 50 %; m.p.: 148 °C; Anal. Calcd. for $C_{13}H_{11}N_3SO_2$: C, 57.14; H, 4.03; N, 15.38 %. Found: C, 56.90; H, 4.10; N, 15.20 %.

$Ni(L^1)_2$. Yield: 60 %; m.p.: 250 °C; Anal. Calcd. for $C_{18}H_{16}N_6NiO_4S_2$: C, 42.97; H, 3.18; N, 16.71; Ni, 11.68 %. Found: C, 42.86; H, 3.12; N, 16.54; Ni, 11.70 %; Magnetic moment, $\mu_{\rm eff}$: 2.78 $\mu_{\rm B}$.

$Ni(L^2)_2$. Yield: 65 %; m.p.: >300 °C; Anal. Calcd. for $C_{26}H_{20}N_6NiO_4S_2$: C, 51.77; H, 3.32; N, 13.94; Ni, 9.74 %. Found: C, 51.56; H, 3.32; N, 14.01; Ni, 9.71 %; Magnetic moment, $\mu_{\rm eff}$: 2.74 $\mu_{\rm B}$.

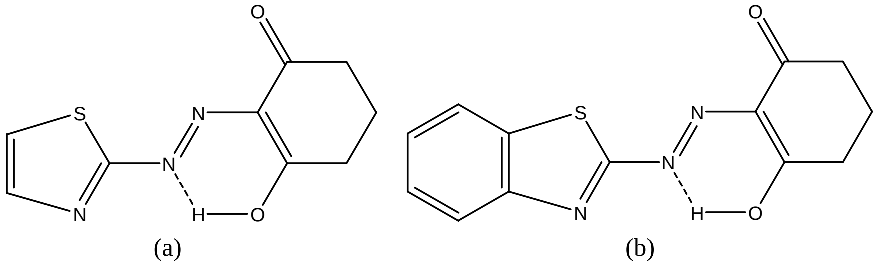
$Cu(L^1)(OAc)$. Yield: 70 %; m.p.: 260 °C; Anal. Calcd. for $C_{12}H_{13}CuN_3O_4S$: C, 40.16; H, 3.63; N, 11.71; Cu, 17.72 %. Found: C, 40.08; H, 3.53; N, 11.65; Cu 17.50 %; Magnetic moment, $\mu_{\rm eff}$: 1.75 $\mu_{\rm B}$.

$Cu(L^2)(OAc)$. Yield: 75 %; m.p.: >300 °C; Anal. Calcd. for $C_{16}H_{15}CuN_3O_4S$: C, 47.00; H, 3.67; N, 10.28; Cu, 15.55 %. Found: C, 46.88; H, 3.61; N, 10.44; Cu 15.35 %; Magnetic moment, $\mu_{\rm eff}$: 1.74 $\mu_{\rm B}$.

$Zn(L^1)_2$. Yield: 70 %; m.p.: 270 °C; Anal. Calcd. for $C_{18}H_{16}N_6O_4S_2Zn$: C, 42.40; H, 3.14; N, 16.49; Zn, 12.84 %; Found: C, 42.32; H, 3.20; N, 16.40; Zn, 13.05 %.

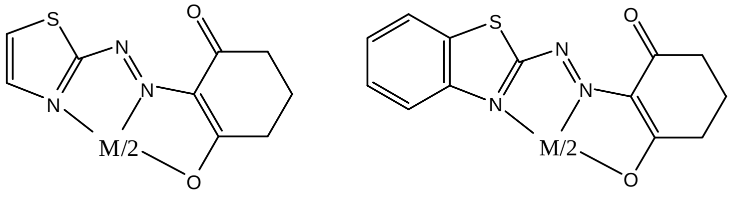
$Zn(L^2)_2$. Yield: 60 %; m.p.: >300 °C; Anal. Calcd. for $C_{26}H_{20}N_6O_4S_2Zn$: C, 51.20; H, 3.28; N, 13.78; Zn, 10.73 %. Found: C, 51.14; H, 3.22; N, 13.72; Zn 10.78 %.

The observed analytical data of the hetero-arylazo derivatives (HL^1 and HL^2) indicate that the diazo-coupling reaction had occurred in a 1:1 ratio. The compounds are crystalline in nature and soluble in common organic solvents. They formed stable complexes with Ni(II), Cu(II) and Zn(II) ions. The analytical data together with the non-electrolytic nature in DMF (specific conductance <10 S cm^{-1} in 10^{-3} M solution) suggest [ML_2] stoichiometry of the complexes, except for the Cu(II) complexes that have [CuL(OAc)] stoichiometry. The Zn(II) chelates are diamagnetic while the Ni(II) and Cu(II) complexes showed a normal paramagnetic moment. The observed IR, ^{1}H-NMR, ^{13}C-NMR and mass spectral data are in conformity with Fig. 1 of the hetero-arylazo derivatives and Fig. 2 of the complexes. The Cu(II) complexes conform to Fig. 3.



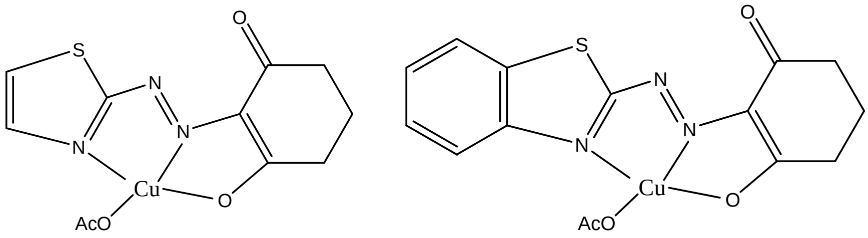
(a) (b)

Fig. 1. Structural formulae of the a) HL^1 and b) HL^2 ligands.



(a) (b)

Fig. 2. Structural formulae of the Ni(II) and Zn(II) complexes; a) $[M(L^1)_2]$ and b) $[M(L^2)_2]$; M = Ni(II) or Zn(II).



(a) (b)

Fig. 3. Structural formulae of the a) $[Cu(L^1)(OAc)]$ and b) $[Cu(L^2)(OAc)]$ complexes.

IR spectra

The IR spectra of HL^1 and HL^2 show a strong band at ≈1720 cm^{-1} and a medium intensity band at ≈1610 cm^{-1}, assignable to the stretching of free carbonyl and ring C=N functions, respectively.[19,21] The two medium intensity bands observed at ≈1280 and 1480 cm^{-1} are due to C–O–H in-plane bending and N=N stretching, respectively.[16,21]. The medium intensity band present at ≈1460 cm^{-1} is assignable to CH_2 scissoring vibrations.[22] The broad band ranging from 3200 to 3500 cm^{-1} is due to strong O–H···N hydrogen bonding.[21] Thus, the IR spectra support the intramolecularly hydrogen bonded azo–enol tautomeric form of the compounds as in Fig. 1.

In the IR spectra of all the metal complexes, the free ligand bands at 1280 and 3200–3500 cm^{-1} were absent, indicating the replacement of enol protons by metal ions during complexation.[23,24] The free carbonyl band of the ligands is only marginally shifted in the spectra of the complexes, indicating the non-involvement of the carbonyl groups in the coordination. In the spectra, The band at ≈1480 cm^{-1} due to ν(N=N) and the band due to ring ν(C=N) at 1610 cm^{-1} of the free ligands were shifted appreciably to lower wave numbers,[15] indicating the involvement of these groups in complexation, as shown in Figs. 2 and 3. The IR spectra of the Cu(II) complexes showed a comparatively strong band at ≈1625 cm^{-1} and a medium intensity band at ≈1310 cm^{-1}. The energy separation between $\nu_{asym(COO-)}$ and $\nu_{sym(COO-)}$ was >144 cm^{-1}, which confirms the monodentate nature of the acetate ion,[25,26] since in the event of bidentate coordination, the energy separation was reported[27] to be <144 cm$^{–1}$. The presence of new medium intensity bands at ≈420 and 540 cm$^{–1}$, assignable to ν(M–O) and ν(M–N) in the spectra of all the complexes[24,28,29] also support the structures shown in Figs. 2 and 3. Important bands that appeared in the spectra are given in Table I.

TABLE I. Characteristic IR stretching bands (cm^{-1}) of HL^1, HL^2 and their metal complexes; in the case of the copper complexes, the two additional bands given under C=O are due to the acetate groups

Compound	Free C=O	Cyclic C=N	N=N	M–N	M–O
HL^1	1715 *s*	1612 *m*	1472 *m*	–	–
[Ni(L^1)$_2$]	1712 *s*	1580 *m*	1442 *m*	538 *m*	426 *m*
[Cu(L^1)(OAc)]	1718 *s*, 1625 *s*, 1312 *m*	1582 *m*	1435 *m*	522 *m*	418 *m*
[Zn(L^1)$_2$]	1710 *s*	1593 *m*	1438 *m*	525 *m*	430 *m*
HL^2	1722 *s*	1612 *m*	1478 *m*	–	–
[Ni(L^2)$_2$]	1718 *s*	1588 *m*	1438 *m*	532 *m*	432 *m*
[Cu(L^2)(OAc)]	1720 *s*, 1622 *s*, 1310 *m*	1590 *m*	1445 *m*	528 *m*	422 *m*
[Zn(L^2)$_2$]	1720 *s*	1592 *m*	1448 *m*	530 *m*	420 *m*

NMR spectra

The ^{1}H-NMR spectra of HL^1 and HL^2 are characterized by the presence of a low-field, one-proton signal at δ ≈13.50 ppm, which is considerably lower than that reported for arylazo derivatives of 1,3-diketones existing in the hydrazone form.[15,30] Since azo–enol protons show a signal in the range δ 10–14 ppm, the signal at δ 13.5 ppm could be assigned to the intramolecularly hydrogen bonded enol proton.[31,32] The high resolution spectra show three types of alicyclic protons in the range δ 1.30–2.90 ppm, indicating the existence of three methylene groups in different electronic environments.[22,33] The hetero-aryl protons are observed in the range δ 7.30–8.40 ppm. The integrated intensities of the various signals agree well with the structure of the compounds presented in Fig. 1.

In the ^{1}H-NMR spectra of the diamagnetic Zn(II) complexes, the low field signal due to the intramolecularly hydrogen bonded OH protons disappeared, indicating their replacement by metal cations during complexation.[34] The integrated intensities of various signals agree well with the [ML$_2$] stoichiometry of the complexes as presented in Fig. 2.

The ^{13}C-NMR spectra of HL^1 and HL^2 clearly indicate their existence in the azo–enol form. The carbonyl (C$_1$) and enolic (C$_3$) sp^2 carbon atoms appear as separate signals in the low field region, at δ ≈ 200 ppm. Separation of the C$_4$ and C$_6$ signals confirms the different electronic environment for these methylene carbons,[31] as shown in Fig. 1. The involvement of the enolate oxygen and the hetero nitrogen atom in bonding with the metal ion, as shown in Fig. 2, is evident from the positions of the various signals in the ^{13}C-NMR spectra of their Zn(II) complexes.

The assignments of the various observed signals are assembled in Table II.

TABLE II. ^{1}H-NMR and ^{13}C-NMR spectral data (δ / ppm) of HL^1, HL^2 and their Zn(II) complexes; *s* = singlet, *d* = doublet ($J \approx 3.7$ Hz), *t* = triplet ($J \approx 6.9$ Hz), *m* = multiplet

Compound	^{1}H-NMR			^{13}C-NMR				
	OH	Heteroaryl	Methylenic	C=O	C–O	CH$_2$	C–N	Heteroaryl
HL^1	13.52 (1H, *s*)	7.50 (1H, *d*) 7.90 (1H, *d*)	1.30 (2H, *m*) 1.90 (2H, *t*) 2.80 (2H, *t*)	192.94	198.24	18.21 39.24 39.39	166.31	140.87 132.34 116.12
[Zn(L^1)$_2$]	–	7.30 (2H, *d*) 7.80 (2H, *d*)	1.40 (4H, *m*) 1.80 (4H, *t*) 2.90 (4H, *t*)	192.63	188.93	19.43 36.55 39.75	142.32	137.09 129.37 119.33
HL^2	13.46 (1H, *s*)	7.50–8.30 (4H, *m*)	1.50 (2H, *m*) 1.90 (2H, *t*) 2.90 (2H, *t*)	192.59	197.34	17.92 39.17 39.37	151.21	133.07 132.51 126.67 125.04 122.31 121.70
[Zn(L^2)$_2$]	–	7.60–8.40 (8H, *m*)	1.40 (4H, *m*) 1.90 (4H, *t*) 2.90 (4H, *t*)	192.47	184.34	17.73 38.12 39.68	129.23	134.17 132.34 126.22 124.14 122.00, 121.61

Mass spectra

The formulation of the compounds as in Fig. 1 is clearly supported from the presence of an intense molecular ion peak in the mass spectra. The presence of peaks due to the elimination of N_2 from the molecular ion, characteristic of tautomers,[31,35,36] in the spectra support the azo structure of the compounds. Fragments due to the elimination of CH_2=CHCHO, heteroaryl groups, *etc*. are typical of the spectra.

The FAB mass spectra of the Cu(II) and Ni(II) complexes showed molecular ion peaks corresponding to [CuL(OAc)] and [NiL$_2$] stoichiometry. Peaks correspond to [ML]$^+$, L$^+$ and fragments of L$^+$ are also present in the spectra. The spectra of the Cu(II) complexes also showed peaks due to [P – CH_3COO]$^+$ and a number of fragments containing copper in the 3:1 natural abundance of ^{63}Cu and ^{65}Cu isotopes. The important mass spectral fragments and their assignments are assembled in Table III.

Electronic spectral and magnetic measurements data

The UV spectra of HL^1 and HL^2 showed two broad bands with maxima at ≈380 and ≈260 nm due to various $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ transitions. These absorption maxima shifted appreciably to low wave numbers in the spectra of the complexes. The Cu(II) complexes showed a broad band centred at ≈660 nm. This, together with the measured μ_{eff} value (≈1.75 μ_{B}) suggests their square-planar geometry.[15,37] The Ni(II) chelates are paramagnetic (μ_{eff} value ≈2.80 μ_{B}) and show three well-separated absorption bands in the spectra at λ_{max} ≈925, ≈750 and ≈420 nm corresponding to the transitions $^3A_{2g}\rightarrow{}^3T_{2g}$, $^3A_{2g}\rightarrow{}^3T_{1g}(F)$ and $^3A_{2g}\rightarrow{}^3T_{1g}(P)$, respectively. Thus, the metal ion is in an octahedral environment.

TABLE III. Mass spectral data of HL^1, HL^2 and their Ni(II) and Cu(II) complexes

Ligands			Ni(II) complexes			Cu(II) complexes		
Fragment	*m/z*		Fragment	*m/z*		Fragment	*m/z*	
	HL^1	HL^2		$Ni(L^1)_2$	$Ni(L^2)_2$		$[Cu(L^1)(OAc)]$	$[Cu(L^2)(OAc)]$
P^+	223	273	P^+	503	603	P^+	346, 344	396, 394
$[P–N_2]^+$	195	245	$[P–Ar]^+$	419	469	$[P–OAc]^+$	287, 285	337, 335
$[P–CH_2=CH––CHO]^+$	167	217	$[P–C_6H_6O_2]^+$	393	493	$[P–Ar]^+$	262, 260	262, 260
$[P–Ar]^+$	139	139	$[P – 2Ar]^+$	335	335	$[P––C_6H_6O_2]^+$	236, 234	286, 284
$[P–ArN_2]^+$	111	111	$[P––2C_6H_6O_2]^+$	283	383	Ligand fragments	223, 168, 139	273, 245, 134
Ar^+	84	134	$[NiL]^+$	281	331	–	–	–
$CH_2=CH–CHO$	56	56	Ligand fragments	223, 195, 84, 56	273, 245, 139, 111, 56	–	–	–

CONCLUSIONS

Two heteroarylazo derivatives were prepared by the coupling of diazotized 2-aminothiazole and 2-aminobenzothiazole with cyclohexane-1,3-dione. Analytical, IR, ^{1}H-NMR, ^{13}C-NMR and mass spectral data revealed 1:1 products in which one of the carbonyl groups of the diketone is enolized and involved in intramolecular hydrogen bonding with one of the azo nitrogens. Analytical, physical and spectral data of the $[ML_2]$ complexes of Ni(II) and Zn(II) showed monobasic tridentate N_2O coordination involving one of the azo nitrogens, the ring nitrogen and the enolized carbonyl oxygen. The Cu(II) complexes conform to [CuL(OAc)] stoichiometry. The Zn(II) chelates are diamagnetic, while the Ni(II) and Cu(II) complexes showed normal paramagnetic moments.

ИЗВОД

ХЕТЕРОАРИЛАЗО ДЕРИВАТИ ЦИКЛОХЕКСАН-1,3-ДИОНА И ЊИХОВИ МЕТАЛНИ КОМПЛЕКСИ

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У реакцији диазотизованог-2-аминотиазола и 2-аминобензотиазола са циклохексан-1,3-дионом добијени су нови тридентатни лиганди типа HL. Резултати елементалне микроанализе, IR, ^{1}H-NMR и ^{13}C-NMR спектроскопских испитивања, као и резултати добијени на основу масених спектара, указују да добијени лиганди постоје као азо-енолне таутомерне форме у којима су присутне интрамолекулске водоничне интеракције. На бази аналитичких и спектроскопских испитивања нађено је да су добијени лиганди тридентатно координовани у одговарајућим [CuL(OAc)] и [ML_2] комплексима [M = Ni(II) и Zn(II)]. Резултати магнетних испитивања су показали да је хелатни Zn(II) комплекс дијамагнетичан, док комплекси Cu(II) и Ni(II) показују очекиване парамагнетичне моменте.

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