Journal of the Serbian Chemical Society
JSCS@tmf.bg.ac.rs • www.shd.org.rs/JSCS

J. Serb. Chem. Soc. 75 (5) 639–648 (2010)
JSCS–3994

UDC 547.53'788+547.235:546.562'742'472
Original scientific paper

Benzothiazolylazo derivatives of some *β*-dicarbonyl compounds and their Cu(II), Ni(II) and Zn(II) complexes

KRISHNANNAIR KRISHNANKUTTY[1], MUHAMMED BASHEER UMMATHUR[2]* and DAMODARAN KAMALAKSHY BABU[3]

[1]Department of Chemistry, University of Calicut, Kerala-673635, [2]Department of Chemistry, Unity Women's College, Manjeri, Kerala-676122 and [3]Department of Chemistry, Zamorin's Guruvayurappan College, Calicut, Kerala-673014, India

(Received 16 August, revised 4 December 2009)

Abstract: The coupling of diazotized 2-aminobenzothiazole with 1,3-dicarbonyl compounds (benzoylacetone, methyl acetoacetate and acetoacetanilide) yielded a new series of tridentate ligand systems (HL). Analytical, IR, ^{1}H-NMR, ^{13}C-NMR and mass spectral data indicated that the compounds exist in the intramolecularly hydrogen bonded azo-enol tautomeric form in which one of the carbonyl groups of the dicarbonyl moiety had enolised and hydrogen bonded to one of the azo nitrogen atoms. The compounds formed stable complexes with Ni(II), Cu(II) and Zn(II) ions. The Cu(II) complexes conform to [CuL(OAc)] stoichiometry while the Ni(II) and Zn(II) complexes are in agreement with [ML$_2$] stoichiometry. Analytical, IR, ^{1}H-NMR, ^{13}C-NMR and mass spectral data of the complexes are consistent with the replacement of the chelated enol proton of the ligand with a metal ion, thus leading to a stable six-membered chelate ring involving a cyclic nitrogen, one of the azo nitrogens and the enolate oxygen. The Zn(II) chelates are diamagnetic while Cu(II) and Ni(II) complexes showed a normal paramagnetic moment.

Keywords: benzothiazolylazo-*β*-dicarbonyls; azo-enol form; Cu(II), Ni(II) and Zn(II) complexes; IR, mass and NMR spectral studies.

INTRODUCTION

The chemistry of 2-aminobenzothiazole has gained increasing interest in both synthetic organic chemistry and biological fields.[1] The substitution of an aryl diazonium group at the active methylenic carbon provides for the possibility of azo-hydrazone tautomerism.[2] In recent years, a significant number of tridentate azo compounds containing heteroaryl ring systems have been developed in order to improve the colouring properties and to achieve more specificity and selectivity in chemical analysis.[3] Metal dye complexes play a very important role in dye-

---

* Corresponding author. E-mail: mbummathur@gmail.com

doi: 10.2298/JSC090816040K

stuff technology[4] and find application in many other fields, especially in analytical chemistry.[5] However, structural aspect of many of these products and their metal derivatives have received only scanty attention. In continuation of studies on arylazo[6–11] derivatives of β-dicarbonyl compounds and their metal complexes, the synthesis and characterization of benzothiazolylazo derivatives of three β-dicarbonyl compounds: benzoylacetone, methyl acetoacetate and acetoacetanilide, are reported herein. Typical Cu(II), Ni(II) and Zn(II) complexes of these compounds were also synthesized and characterized.

EXPERIMENTAL

Methods, instruments and materials

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) 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 was determined in DMF ($\approx 10^{-3}$ mol/L) at room temperature (301 ± 1 K). The magnetic susceptibilities were determined at room temperature on a Guoy type magnetic balance, Sherwood Scientific Ltd., England, at room temperature using $Hg[Co(NCS)_4]$ as the standard.

Benzoylacetone, methyl acetoacetate, acetoacetanilide, 2-aminobenzothiazole, methanol, urea and the metal acetates were of AR grade, purchased from Merck, Germany.

General procedure for the preparation of benzothiazolylazo derivatives of β-dicarbonyl compounds

An aqueous solution of 2-benzothiazoldiazonium ion was prepared by a standard method.[12] To a solution of $NaNO_2$ (1.4 g) in H_2SO_4 (12 M, 20 mL), kept below 278 K, a cooled ($\approx$278 K) solution of 2-aminobenzothiazole (1.5 g, 0.010 mol) in 15 mL DMF was added slowly under stirring. The stirring was continued for $\approx$1 h, after which the reaction mixture was filtered to obtain a clear yellow diazonium salt solution. After destroying the excess nitrous acid with urea, the diazonium salt solution (0.010 mol) was added slowly under stirring to an ice-cold (< 278 K) solution of the required β-dicarbonyl compound (benzoylacetone, methyl acetoacetate or acetoacetanilide, 0.010 mol in 25 mL ethanol). Cooled (< 278 K) NaOH solution (1.0 M, 20 mL) was added dropwise to maintain the pH of the mixture at around 5. Stirring was continued for about 30 min and the precipitated compound was filtered, washed several times with deionised water and recrystallized twice from hot methanol to obtain chromatographically pure material: 2-(2-benzothiazolylazo)-1-phenyl-1,3-butanedione (Hbba), methyl 2-(2-benzothiazolyazo)-3-oxobutanoate (Hbma) and 2-(2-benzothiazolylazo)-3-oxo-*N*-phenylbutanamide (Hban) (TLC on silica gel, acetone as the solvent). All the compounds were crystalline in nature with a reddish pink colour and were soluble in common polar and non-polar organic solvents, such as benzene, methanol, ethanol, chloroform and carbon tetrachloride. The compounds formed stable complexes with Ni(II), Cu(II) and Zn(II) ions.

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

A concentrated aqueous solution of metal(II) acetate (0.010 mol) was added under stirring to a methanolic solution of one of the ligands (0.020 mol, 20 mL). Stirring was continued for the following ≈2 h. The precipitated complex was filtered, washed with water, recrystallized from hot chloroform and dried under vacuum. The Ni(II), Cu(II) and Zn(II) complexes had a greenish black, dark violet and dull white colour, respectively. The complexes were well soluble in CH_3CN, DMSO and DMF but insoluble in methanol, ethanol, carbon tetrachloride and water.

Determination of magnetic susceptibility

A thin cylindrical glass tube filled with the sample was vertically suspended from the beam of a balance in a draught-free enclosure in such a way that its lower end lied between the poles of an electromagnet. The weight of the sample was determined with the field off and with the field on. Corrections for diamagnetism of the constituents were made using Pascal constants.[13] The effective magnetic moments were calculated using the formula $\mu_{\rm eff} = 2.83(\chi_{\rm M}T)^{1/2}(9.274\times10^{-24})$ A m^2, where $\chi_{\rm M}$ is the corrected molar susceptibility and T is temperature. The Zn(II) chelates were diamagnetic while the Cu(II) and Ni(II) complexes showed a normal paramagnetic moment.

RESULTS AND DISCUSSION

The observed elemental analytical data of the benzothiazolylazo derivatives (Table I) indicate that the diazo-coupling reaction between the diazotized 2-aminobenzothiazole and the β-dicarbonyl compounds occurred in the 1:1 mole ratio. The analytical data (Table I) together with non-electrolytic nature in DMF (specific conductance < 10 S cm^{-1}; 10^{-3} M solution) suggested the formula [ML_2] for the complexes where M(II) = Zn and Ni, and [CuL(OAc)] for the Cu(II) complexes.

TABLE I. Physical and analytical data of the new benzothiazolylazo derivatives of β-dicarbonyl ligands and their metal complexes (Hbba: 2-(2-benzothiazolylazo)-1-phenyl-1,3-butanedione; Hbma: methyl 2-(2-benzothiazolylazo)-3-oxobutanoate; Hban: 2-(2-benzothiazolylazo)-3-oxo-*N*-phenylbutanamide; –OAc: acetate)

Compound Empirical formula	Yield %	M.p. °C	$\mu_{\rm eff}\times10^{24}$ A m^2	Found (Calcd.), %			
				C	H	N	M
Hbba	60	180	–	63.10	3.98	12.98	–
$C_{17}H_{13}N_3SO_2$				(63.16)	(4.02)	(13.00)	
Hbma	70	98	–	51.88	3.99	15.05	–
$C_{12}H_{11}N_3SO_3$				(51.99)	(3.97)	(15.16)	
Hban	70	182	–	60.23	4.14	16.64	–
$C_{17}H_{14}N_4SO_2$				(60.36)	(4.14)	(16.57)	
[Ni(bba)$_2$]	60	170	25.8	58.20	3.48	11.98	8.50
$C_{34}H_{24}N_6NiS_2O_4$				(58.06)	(3.42)	(11.95)	(8.35)
[Ni(bma)$_2$]	65	>300	25.9	47.30	3.30	13.65	9.54
$C_{24}H_{20}N_6NiS_2O_6$				(47.16)	(3.27)	(13.75)	(9.61)
[Ni(ban)$_2$]	70	270	26.1	55.53	3.54	15.24	8.02
$C_{34}H_{26}N_8NiS_2O_4$				(55.68)	(3.55)	(15.29)	(8.01)

TABLE I. Continued

Compound Empirical formula	Yield %	M.p. °C	$\mu_{eff}\times10^{24}$ A m^2	Found (Calcd.)/ % C	 H	 N	 M
[Cu(bba)(OAc)]	65	220	16.2	51.40	3.34	9.36	14.19
$C_{19}H_{15}CuN_3SO_4$				(51.29)	(3.37)	(9.45)	(14.29)
[Cu(bma)(OAc)]	65	>300	16.5	42.26	3.23	10.70	15.85
$C_{14}H_{13}CuN_3SO_5$				(42.15)	(3.26)	(10.54)	(15.94)
[Cu(ban)(OAc)]	72	>300	16.8	49.55	3.45	12.28	13.75
$C_{19}H_{16}CuN_4SO_4$				(49.61)	(3.48)	(12.19)	(13.83)
[Zn(bba)$_2$]	68	208	–	57.58	3.38	11.80	9.35
$C_{34}H_{24}N_6S_2O_4Zn$				(57.52)	(3.38)	(11.84)	(9.22)
[Zn(bma)$_2$]	72	>300	–	46.56	3.23	13.63	10.72
$C_{24}H_{20}N_6S_2O_6Zn$				(46.65)	(3.24)	(13.61)	(10.59)
[Zn(ban)$_2$]	68	225	–	55.28	3.53	15.03	8.75
$C_{34}H_{26}N_8S_2O_4Zn$				(55.18)	(3.52)	(15.15)	(8.84)

IR Spectra

The IR spectra of the benzothiazolylazo derivatives show a strong band at ≈1640 cm^{-1}, assignable to the stretching of the enolised acetyl carbonyl group[8] (Fig. 1). The free benzoyl, ester and anilide carbonyl bands of Hbba, Hbma and Hban were observed at 1650, 1738 and 1670 cm^{-1}, respectively.[14,15] In the spectra of all the compounds, two medium intensity bands were observed at ≈1280 and 1470 cm^{-1}, assignable to C–O–H in-plane bending and ν(N=N), respectively.[14,15] The aromatic ν(C=C) vibrations appeared at ≈1580 cm^{-1} and benzothiazole ring ν(C=N) was observed at ≈1620 cm^{-1}. The broad band in the range 2500–3300 cm^{-1} indicates the existence of strong intramolecular hydrogen bonding in these compounds. Thus, the IR spectra strongly support the existence of the compounds in the intramolecularly hydrogen-bonded azo-enol tautomeric form.

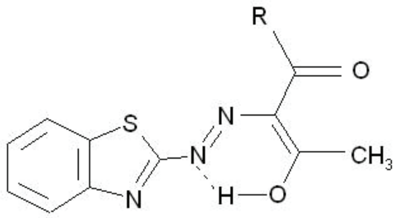

Fig. 1. Schematic view representing the geometry of the prepared benzothiazolylazo derivatives, where R = C_6H_5 (Hbba); OCH_3 (Hbma); NHC_6H_5 (Hban).

In the IR spectra of all the complexes, the broad free ligand band in the region 2500–3300 cm^{-1} had disappeared, indicating the replacement of the enol proton by a metal ion during complexation.[7,8] Several medium intensity bands were present in this region of the spectra due to various ν(C–H) vibrations. The absence of the free ligand band at ≈1270 cm^{-1} due to C–O–H bending also supports the replacement of the enol proton by a metal ion. The free carbonyl band of the compounds was only marginally shifted indicating that this carbonyl is not involved in the coordination. However, the band due to the hydrogen bonded acetyl carbonyl group disappeared and instead a new band appeared at ≈1570 cm^{-1} in the spectra of all the complexes, supporting the involvement of the enolised carbonyl in the bonding with the metal ion.[16] In the spectra of all the complexes, the band at ≈1470 cm^{-1} due to ν(N=N) and the band due to benzothiazole ν(C=N) at ≈1620 cm^{-1} of the ligands were appreciably shifted (20–30 cm^{-1}) to lower wave numbers, indicating the involvement of these groups in the bonding with the metal ion, as shown in Figs. 2 and 3.

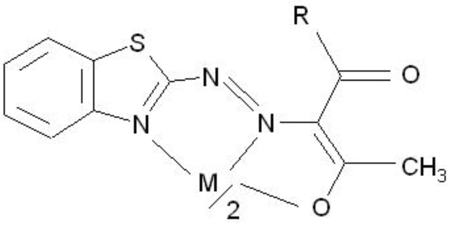

Fig. 2. Schematic view representing the proposed geometry of the metal complexes of the benzothiazolylazo derivatives within 1/2 molecules.

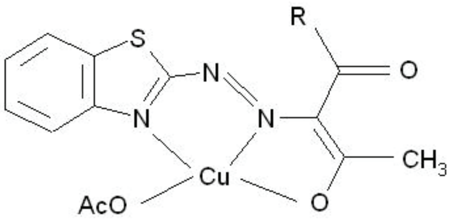

Fig. 3. Schematic view representing the proposed coordination in the Cu(II) complexes of the benzothiazolylazo derivatives.

As in the spectrum of the ligand, the complexes of Hban showed a band at ≈3400 cm^{-1} due to the NH group of anilide. In the spectra of the Cu(II) complexes, a comparatively strong band at ≈1625 cm^{-1} and a medium intensity band at ≈1310 cm^{-1} appeared due to the antisymmetric and symmetric stretching of the monodentate acetate group, respectively,[16,17] as in Fig. 3. The presence of new medium intensity bands in the 420–490 and 530–560 cm^{-1} regions, assignable to ν(M–O) and ν(M–N) in the spectra of all the complexes[16] also support Figs. 2 and 3. Important bands that appeared in the spectra are given in Table II.

NMR Spectra

The ^{1}H-NMR spectra of the benzothiazolylazo derivatives are characterized by the presence of a low field, one proton signal at δ 13 ppm, which is considerably lower than that reported for arylazo derivatives of *β*-diketones that exist in the hydrazone form.[9–11] Since azo-enol protons show a signal in the δ range 10–14 ppm, the signal at δ 13 ppm can be assigned to the intramolecularly hydrogen bonded enol proton of Fig. 1.[8,9,18] The integrated intensities of all other protons 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 chelated hydrogen disappeared, indicating its replacement by the metal ion during complexation.[8,19] The non-involvement of the ester carbonyl and the anilide NH groups in the coordination is evident from the observed position of the

OCH_3 and anilide NH resonance signals, which remain unaltered. The position of the signal of the methyl proton in the chelates is downfield shifted, indicating the involvement of the acetyl carbonyl in the coordination. The integrated intensities of all other protons agree well with the structure of the complexes presented in Fig. 2. The assignments of the various proton signals observed are assembled in Table III.

TABLE II. Characteristic IR stretching bands (cm^{-1}) of the ligands and their metal complexes (abbreviations as in Table I)

Compound	Free ν(C=O)	Chelated ν(C=O)	Acetate ν(C=O) and ν(C–O)	ν(C=N)	ν(N=N)	ν(M–N)	ν(M–O)
Hbba	1650	1640	–	1615	1468	–	–
$[Ni(bba)_2]$	1648	1572	–	1590	1440	548	420, 470
[Cu(bba)(OAc)]	1645	1566	1622, 1305	1593	1444	540	428, 490
$[Zn(bba)_2]$	1652	1570	–	1588	1446	548	420, 478
Hbma	1738	1644	–	1618	1460	–	–
$[Ni(bma)_2]$	1737	1574	–	1589	1435	555	430, 468
[Cu(bma)(OAc)]	1735	1566	1622, 1300	1590	1436	540	420, 485
$[Zn(bma)_2]$	1734	1568	–	1594	1438	540	420, 466
Hban	1670	1638	–	1615	1460	–	–
$[Ni(ban)_2]$	1665	1565	–	1590	1438	538	435, 488
[Cu(ban)(OAc)]	1666	1562	1620, 1305	1588	1440	545	422, 480
$[Zn(ban)_2]$	1668	1574	–	1592	1435	550	428, 477

TABLE III. ^{1}H-NMR spectral data (δ / ppm) of the ligands and their Zn(II) complexes (abbreviations as in Table I)

Compound	OH	CH_3	R	Benzothiazolyl
Hbba	12.80 (1H, *s*, *br*)	2.61 (3H, *s*)		6.80–8.07 (9H, *m*)
$[Zn(bba)_2]$	–	2.88 (6H, *s*)		6.98–8.02 (18H, *m*)
Hbma	12.52 (1H, *s*, *br*)	2.45 (3H, *s*)	3.82 (3H, *s*)	6.90–7.50 (4H, *m*)
$[Zn(bma)_2]$	–	2.82 (6H, *s*)	3.85 (6H, *s*)	7.10–7.60 (8H, *m*)
Hban	12.99 (1H, *s*, *br*)	2.59 (3H, *s*)	11.20 (1H, *s*, anilide NH)	7.15–7.81 (9H, *m*)
$[Zn(ban)_2]$	–	2.85 (6H, *s*)	11.16 (2H, *s*, anilide NH)	7.20–8.01 (18H, *m*)

The ^{13}C-NMR spectrum of Hbma clearly indicates its existence in the azo-enol form. That the two carbonyl groups are in different electronic environments is evident from the large separation of the carbonyl carbon signals. The comparatively large chemical shift of the methyl carbon signal in the spectrum indicates the enolised nature of the acetyl group and its involvement in hydrogen bonding.[8] The involvement of the enolate oxygen and hetero nitrogen atoms in the bonding with the metal ion is evident from the position of the various signals in the ^{13}C-NMR spectrum of its Zn(II) complex (Table IV).

TABLE IV. ^{13}C-NMR spectral data (δ / ppm) of Hbma and its Zn(II) complex (abbreviations as in Table I)

Compound	C=O	CH_3	C–N	Benzothiazolyl
Hbma	196.7, 198.3	26.5, 30.8	165.3	121.7, 122.4, 124.9, 126.9, 132.1, 135.5, 141.7
$[Zn(bma)_2]$	195.7, 196.6	28.2, 33.1	147.2	118.9, 122.0, 124.0, 125.8, 126.6, 127.5, 131.5

Mass spectra

The formulation of the benzothiazolylazo derivatives as shown 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 ArN_2 from molecular ion, characteristic of tautomers,[9,20,21] in the spectra support the azo structure of the compounds. Fragments due to the elimination of RCO and CH_3CO are also present in the spectra of all the ligands. The origin of the peak at *m/z* 175 in the mass spectra of the compounds can be explained by the formation of the ion radical $BT–N_2CH]^+$ (BT = benzothiazole ring) through the elimination of CH_3CO and RCO from P^+. If the compounds existed in the hydrazone form, the most facile reaction would be the cleavage of the N–N bond[21] and an ion of *m/z* 175 could not be formed. Thus, all available evidences support the existence of the compounds in the azo-enol form rather than the keto-hydrazone form. The FAB mass spectra of the Cu(II) complexes showed molecular ion peaks corresponding to [CuL(OAc)] stoichiometry. Peaks corresponding to $[P–RCO]^+$, $[P–CH_3CO]^+$, $[RCO]^+$, $[CH_3CO]^+$, $[CuL]^+$, L^+ and fragments of L^+ were also present in the spectra. The spectra also showed peaks due to $[P–CH_3COO]^+$. The spectra of all the chelates contained a number of fragments containing copper in the 3:1 natural abundance of ^{63}Cu and ^{65}Cu isotopes (Table V).

TABLE V. Mass spectral data of the new ligands and their Cu(II) complexes (abbreviations as in Table I)

Compound	Mass spectral data (*m/z*)
Hbba	323, 280, 218, 175, 162, 161, 134, 105, 43
Hbma	277, 234, 218, 175, 162, 134, 115, 59, 43
Hban	338, 295, 218, 176, 175, 162, 134, 120, 43
[Cu(bba)(OAc)]	446, 444, 403, 401, 387, 385, 344, 342, 341, 339, 323, 280, 239, 237, 175, 162, 105
[Cu(bma)(OAc)]	400, 398, 341, 339, 357, 355, 282, 280, 277, 239, 237, 175, 162, 134, 115
[Cu(ban)(OAc)]	461, 459, 402, 400, 341, 339, 418, 416, 282, 280, 239, 237, 338, 295, 176, 175, 162, 120

Electronic spectral and magnetic measurements data

The UV spectra of the benzothiazolyl azo derivatives show two broad bands with maxima at ≈380 nm and ≈270 nm due to various n → π* and π → π* transitions. The absorption maxima of the metal chelates bore close resemblance with those of the free ligands, which indicates that no structural alteration to the ligand had occurred during complexation. However, the values were shifted to slightly longer wavelength in the spectra of the metal complexes,[22] indicating the involvement of the carbonyl and azo groups in metal complexation. In the Cu(II) complexes, the presence of a broad visible band at ≈15,000 cm^{-1} (log ε ≈ ≈ 0.73) and the measured $\boldsymbol{\mu}_{\text{eff}}$ values (Table I) support a square-planar structure.[23] The Ni(II) chelates showed three well-separated absorption bands in the spectra at $\lambda_{\max}$ ≈ 8100 (log ε = 0.67–0.72), ≈13200 (log ε = 0.69–0.84) and ≈24200 cm^{-1} (log ε = 0.77–0.82), corresponding to the transitions: $^3A_{2g} \rightarrow {}^3T_{2g}$; $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$, respectively.[24] These, together with their measured $\boldsymbol{\mu}_{\text{eff}}$ values (Table I), support the octahedral structure.

Thus, the observed analytical, IR, ^{1}H-NMR, ^{13}C-NMR and mass spectral data are in conformity with the structures given in Fig. 1 for the benzothiazolylazo derivatives and in Fig. 2 for their Ni(II) and Zn(II) complexes. The analytical and spectral data of the Cu(II) complexes are in agreement with Fig. 3.

CONCLUSIONS

Three new arylazo derivatives were prepared by coupling 2-benzothiazolediazonium ion with the active methylene group of the β-dicarbonyl compounds benzoylacetone, methyl acetoacetate and acetoacetanilide (HL). The analytical and spectral data of the compounds confirmed their existence in the azo-enol form in which one of the carbonyl groups of the dicarbonyl moiety was enolised and hydrogen bonded to one of the azo nitrogens. For the Cu(II) complexes, the formulas [CuL(OAc)] are assumed, while the Ni(II) and Zn(II) complexes are represented with [ML$_2$]. The analytical and spectral data clearly indicated the monobasic tridentate nature of the compounds and the involvement of the cyclic nitrogen, one of the azo nitrogens and the enolate oxygen in the bonding with the metal ion.

ИЗВОД

БЕНЗОТИОАЗОЛИЛАЗО ДЕРИВАТИ НЕКИХ β-ДИКАРБОНИЛ ЈЕДИЊЕЊА И ЊИХОВИХ Cu(II), Ni(II) И Zn(II) КОМПЛЕКСА

KRISHNANNAIR KRISHNANKUTTY[1], MUHAMMED BASHEER UMMATHUR[2]
и DAMODARAN KAMALAKSHY BABU[3]

[1]*Department of Chemistry, University of Calicut, Kerala-673635,* [2]*Department of Chemistry, Unity Women's College, Manjeri, Kerala-676122 и* [3]*Department of Chemistry, Zamorin's Guruvayurappan College, Calicut, Kerala-673014, India*

Куповањем диазотованог 2-аминобензотиазола са 1,3-дикарбонилним једињењима (бензоилацетоном, метил-ацетоацетатом и ацетоацетанилидом) добијена је нова серија тридентатних лигандних система (HL). Аналитички, IR, ^{1}H-NMR, ^{13}C-NMR и масени спектрални подаци указују да једињења постоје у интрамолекулско водонично везаном азо-енол таутомерном облику у коме је једна од карболилних група у дикарбонилној околини енолизована и водонично везана за један од азо азота. Једињења су градила стабилне комплексе са Ni(II), Cu(II) и Zn(II) јонима. Cu(II) комплексима одговара [CuL(OAc)] стехиометрија, док су Ni(II) и Zn(II) комплекси у складу са [ML$_2$] стехиометријом. Аналитички, IR, ^{1}H-NMR, ^{13}C-NMR и масени спектрални подаци су у складу са заменом хелатног енолног протона лиганда металним јоном, што доводи до стабилног шесточланог хелатног прстена укључујући циклични азот, један од азо азота и енолатни кисеоник. Zn(II) хелати су дијамагнетични, док су Cu(II) и Ni(II) комплекси имали нормални парамагнетични момент.

(Примљено 16. августа, ревидирано 4. децембра 2009)

REFERENCES

1. a) S. Bondock, W. Fadaly, M. A. Metwally, *J. Sulfur Chem.* **30** (2009) 74; b) Q. Ding, X. He, J. Wu, *J. Comb. Chem.* **11** (2009) 587; c) A. E. Berns, P. Conte, H. Philipp, E. G. Witte, H. Lewandowski, *Vadose Zone J.* **8** (2009) 670; d) M. M. El-ajaily, F. I. El-moshaty, R. S. El-zweay, A. A. Maihub, *Int. J. Chem. Tech. Res.* **1** (2009) 80; e) C. Chorao, F. Charmantray, P. B. Hoggan, M. Sancelme, A. Cincilei, M. Traikia, G. Mailhot, A. M. Delort, *Chemosphere* **75** (2009) 121; f) S. D. Srivastava, J. P. Sen, *Indian J. Chem.* **47B** (2008) 1583
2. a) D. R. Matazo, R. A. Ando, A. C. Borin, P. S. Santos, *J. Phys. Chem. A.* **112** (2008) 4437; b) T. Hihara, Y. Okada, Z. Morita, *Dyes Pigments* **61** (2004) 199; c) T. Hihara, Y. Okada, Z. Morita, *Dyes Pigments* **59** (2003) 25; d) K. H. Saunders, R. L. M. Allen, *Aromatic Diazo compounds,* 3rd ed., Edward Arnold, London, 1985
3. a) T. Yasui, N. Komatsu, K. Egami, H. Yamada, A. Yuchi, *Anal. Sci.* **23** (2007) 1011; b) P. Manashi, D. Chayan, H. Chen-Hsiung, G. Sreebrata, *J. Chem. Sci.* **119** (2007) 3; c) C. Sudipta, S. Anasuya, H. Chen-Hsiung, G. Sreebrata, *Z. Anorg. Allg. Chem.* **663** (2007) 1775; d) C. P. Morley, S. Ford, M. D. Vaira, *Polyhedron* **23** (2004) 2967; e) M. G. B. Drew, B. Vickery, G. R. Willey, *J. Chem. Soc., Perkin Trans. 2.* **10** (1982) 1297
4. a) F. Zaubitzer, T. Riis-Johannessen, K. Severin, *Org. Biomol. Chem.* **7** (2009) 4598; b) X. Wang, L. Feng, *Spectrochim. Acta Part A. Mol. Biomol. Spectrosc.* **71** (2008) 1433; c) K. Venkataraman, *Chemistry of Synthetic Dyes,* Vol. 5, Academic Press, New York, 1977
5. a) M. A. Fox, J. K. Whitesell, D. Magde, L. Zhu, *Molecules* **14** (2009) 3851; b) R. Gup, E. Giziroglu, B. Kirkan, *Dyes Pigments* **73** (2007) 40; c) B. Salih, R. Zenobi, *Anal. Chem.* **70** (1998) 1536; d) R. R. Myers, J. L. Long, *Pigments, Part I,* Marcel Dekker, New York, 1975
6. K. Krishnankutty, M. B. Ummathur, D. K. Babu, *Indian J. Inorg. Chem.* **4** (2009) 83
7. a) K. Krishnankutty, M. B. Ummathur, P. Ummer, *J. Serb. Chem. Soc.***74** (2009) 1273; b) K. Krishnankutty, P. Sayudevi, M. B. Ummathur, *J. Serb. Chem. Soc.* **72** (2007) 1075; c) K. Krishnankutty, M. B. Ummathur, P. Sayudevi, *J. Indian Chem. Soc.* **86** (2009) 325; d) K. Krishnankutty, M. B. Ummathur, P. Sayudevi, *J. Indian Chem. Soc.* **85** (2008) 48; e) K. Krishnankutty, M. B. Ummathur, P. Sayudevi, *J. Indian Chem. Soc.* **84** (2007) 518; f) K. Krishnankutty, M. B. Ummathur, P. Sayudevi, *J. Indian Chem. Soc.* **84** (2007) 337
8. K. Krishnankutty, D. K. Babu, *J. Indian Chem. Soc.* **73** (1996) 379
9. K. Krishnankutty, V. T. Rema, *Synth. React. Inorg. Met.-Org. Chem.* **25** (1995) 243

10. a) K. Krishnankutty, J. Michael, *J. Indian Chem. Soc.* **70** (1993) 238; b) K. Krishnankutty, J. Michael, *J. Coord. Chem.* **28** (1993) 259; c) *ibidum.* **22** (1990) 327
11. K. Krishnankutty, P. Ummer, *J. Indian Chem. Soc.* **66** (1989) 194; b) K. Krishnankutty, P. Ummer, *J. Indian Chem. Soc.* **65** (1988) 213
12. R. C. Elderfield, *Heterocyclic Compounds*, Vol. 1, Wiley, New York, 1950, p. 555
13. E. König, *Magnetic Properties of Coordination and Organometallic Transition Metal Compounds*, Springer-Verlag, Berlin, 1966
14. L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Chapman and Hall, London, 1980
15. C. N. R. Rao, *Chemical Applications of Infrared Spectroscopy*, Academic Press, London, 1963
16. N. Nakamoto, *Infrared Spectra and Raman Spectra of Inorganic and Coordination Compounds*, 5th ed., Wiley, New York, 1997
17. K. Krishnankutty, M. B. Ummathur, *J. Indian Chem. Soc.* **83 (**2006) 639
18. A. Lycka, J. Jirman, A. Cee, *Magn. Reson. Chem.* **28** (1990) 408
19. a) N. Raman, V. Muthuraj , S. Ravichandran, A. Kulandaisamy, *Proc. Indian Acad. Sci. (Chem. Sci.)* **115** (2003) 161; b) S. Vineeta, G. Rekha, *J. Fluorine Chem.* **76** (1996) 149; c) D. C. Nonhebel, *Tetrahedron* **24** (1968) 1869
20. a) A. Farghaly, Z. A. Abdallah, *Arkivoc* **17** (2008) 295; b) H. Budzikiewicz, C. Djerassi, D. H. Williams, *Mass Spectrometry of Organic Compounds*, Holden Day, San Francisco, CA, 1967
21. a) C. Zhimin, W. Yiqun, G. Donghong, G. Fuxi, *Dyes Pigments* **76** (2008) 624; b) K. Kobayashi, K. Kurishara, K. Hirose, *Bull. Chem. Soc. Jpn.* **45** (1972) 3551
22. a) R. Bahari, M. N. Garif, M. Shamsudheen, *Malaysian J. Anal. Sci.* **12** (2008) 272; b) J. P. Fackler Jr., F. A. Cotton, D. W. Barnum, *Inorg. Chem.* **2** (1963) 97
23. a) K. Ray, T. Weyhermüller, F. Neese, K. Wieghardt, *Inorg. Chem.* **44** (2005) 5345; b) K. C. Joshi, V. N. Pathak, *Coord. Chem. Rev.* **22** (1977) 37
24. a) M. B. Ummathur, K. Krishnankutty, S. Balagopal, *J. Serb. Chem. Soc.* **74** (2009) 259; b) K. Krishnankutty, V. D. John, *Synth. React. Inorg. Met.-Org. Chem.* **33** (2003) 343.