Asian Journal of Chemistry Vol. 19, No. 4 (2007), 2831-2838

Synthesis and Characterization of the Complexes of Cobalt(II), Nickel(II), Copper(II) and Zinc(II) with 2-(2-carboxyphenylazo)-1,3-diketones

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Cobalt(II), nickel(II), copper(II) and zinc(II) complexes with three potentially tridentate ligands formed by coupling of diazotised anthranilic acid with 1,3-diketones (acetylacetone, benzoylacetone, dibenzoylmethane) have been synthesized and characterized on the basis of elemental analysis, molar conductance, magnetic susceptibility, UV-Visible, IR and NMR spectral data. The spectral studies reveal that the ligands exist in the hydrazone form rather than the azo-enol form and coordinated to the metal ion through one of the carbonyl groups of the 1,3-diketone moiety, carboxylate oxygen and deprotonated hydrazeno nitrogen. All the complexes exhibit 1:1 metal ligand ratio. On the basis of UV-Visible spectral data and magnetic susceptibility, suitable geometry has been proposed for each metal complex. The EPR spectral data reveal that the metal-ligand bond has considerable covalent character. The copper(II) complexes have been screened for their antibacterial properties. It has been observed that the metal complexes are more potent bactericides than the ligands.

Key Words: Metal(II) complexes, 2-(2-Carboxyphenylazo) -1,3-diketones, Antibacterial activity.

INTRODUCTION

Structural diversities exhibited by the arylazo derivatives of compounds containing active methylene group such as 1,3-diketones have evoked considerable interest during the past few decades[1,2]. Among such coupling products, those derived from diazotised anthranilic acid with acetylacetone, benzoylacetone or dibenzoylmethane are capable of exhibiting some interesting structural properties and uses. There are recent reports that substitution at 2-position of anthranilic acid by different substituted aryl or heteroaryl

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moieties markedly modulate the biological properties of anthranilic acid[3]. In present studies, we have prepared some anthranilic acid derivatives of acetylacetone, benzoylacetone and dibenzoylmethane by coupling of diazotised anthranilic acid with the above mentioned β-diketones. The products formed *viz*. 3-(2-carboxyphenylazo)penta-2,4-dione (H_2AAA), 2-(2-carboxyphenylazo)-1-phenylbuta-1,3-dione (H_2BAA) and 2-(2-carboxyphenylazo)-1,3-diphenylpropa-1,3-dione (H_2DBA) have been used as prospective chelating agents for some selected *d*-block metal ions in their common oxidation states and the resulting complexes have been examined with particular reference to the structural aspects of the ligand moieties in the metal complexes. The copper(II) complexes have been also screened for their antibacterial activity.

EXPERIMENTAL

All the chemicals used were analytical grade. Commercial solvents were distilled and used for synthesis. For physico-chemical measurements they were purified by standard methods. Carbon, hydrogen, nitrogen and sulphur analyses were performed using EL III CHN Analyzer. Infrared spectral studies were carried out using KBr discs on a Shimadzu 8201 PC FT Infrared Spectrophotometer and electronic spectra were recorded on a Hitachi 320 UV-Visible Spectrophotometer. The proton NMR spectra of the ligands and the zinc complex were recorded on a Jeol GSX 400NB 400 MHz FTNMR Spectrometer. The EPR spectra of the complexes were recorded in the solid state and also in DMSO at liquid nitrogen temperature using a Varion E-112 EPR Spectrometer and DPPH as reference material. The magnetic moment measurements at room temperature were made by using a Gouy magnetic balance. Antibacterial screening of the ligands and the metal complexes were carried out by agar diffusion method[4].

Synthesis of ligands: The ligands were prepared from diazotised anthranilic acid according to the following general procedure. 1,3-Diketone (1 mmol) dissolved in methanol (40 mL) was added dropwise with constant stirring to a solution containing diazotised anthranilic acid (1 mmol). The system was kept at a low temperature (below 3°C) and the pH was adjusted to be around 7.0 using sodium acetate trihydrate. The excess nitrous acid was removed by adding urea. The precipitated compound was filtered, washed with water, dried and recrystallized from glacial acetic acid. Yield: 55-60 %.

Preparation of metal complexes: The complexes were prepared by adding an aqueous solution of metal(II) salt to a stirred methanolic (100 mL) solution of the ligand (1 mmol) maintained at about 60°C. After refluxing the mixture for 4 to 6 h, the volume of the resulting solution was reduced to half the initial volume by evaporation. It was then allowed to cool and the complex separated was filtered and dried. The complexes were further purified by recrystallization from hot ethanol.

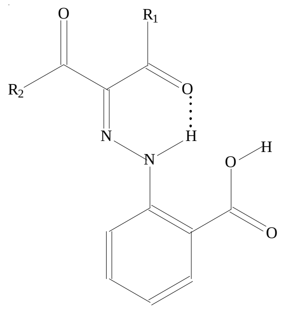
RESULTS AND DISCUSSION

Analytical data of the ligands indicate that the coupling reaction has occurred in 1:1 ratio. This type of coupling products give rise to azo-hydrazo tautomerism. Bands have been assigned to individual tautomers, *i.e.* the monophenyl azo and the monophenyl hydrazone derivatives. The former type of compounds give a strong band in the range 270-284 nm while the monophenyl hydrazone exhibit a strong band above 320 nm in ethanol medium[5,6]. The ultraviolet spectrum of H_2AAA recorded in ethanol showed a strong band at 325 nm characteristic of the hydrazone form. The ultraviolet spectra of H_2BAA and H_2DBA gave the characteristic band for the hydrazone form at 330 and 335 nm, respectively.

Infrared spectrum of H_2AAA recorded in KBr pellets exhibited two strong bands at 1670 and 1625 cm^{-1}. From their high intensity, these bands can be easily recognized as carbonyl bands. It is evident that one of the bands is due to conjugated free carbonyl and the other due to hydrogen bonded carbonyl[7]. Apart from this a strong band centered at 1710 cm^{-1} has also been observed in the free ligand. This can be attributed to the carbonyl stretching frequency of the carboxyl group of anthranilic acid moiety. The observed high carbonyl stretching frequency indicates that the carboxylate group is not involved in any sort of hydrogen bonding.

These spectral data clearly indicate that it is the acetyl carbon of the *ortho* substituted phenylazoacetylacetone is hydrogen bonded with the hydrazone NH. In conformity with this internally hydrogen bonded hydrazone structure, (Fig. 1) the spectrum of the ligand exhibited a very broad band ranging from 3300 to 2900 cm^{-1} region. The spectral features of H_2BAA and H_2DBA are almost similar except that the free carbonyl stretching frequencies are observed at 1672 and 1675 cm^{-1} respectively; the hydrogen bonded carbonyls showed the characteristic peaks at 1620 and 1618 cm^{-1}, respectively.

In agreement with the UV and IR spectral data, proton NMR spectrum of *o*-carboxyphenylazoacetylacetone (H_2AAA) recorded in $CDCl_3$, displayed two methyl proton signals of equal intensity each around 2.58 δ and 2.69 δ which show that the methyl protons are not equivalent. Apart from multiplets around 7.80 δ, for aromatic protons, it also showed a low field signal for the chelated hydrazone NH at 13.71δ. Absence of =CH-proton signal of the β-diketone moiety and the presence of a low field broad signal at 13.71 δ in the NMR spectrum confirms that the ligand exists in the internally hydrogen bonded hydrazone form[5]. These observations are in good agreement with the data reported for similar types of compounds which existed in the hydrogen bonded hydrazone form[5,8]. The carboxylic acid proton could not be detected, presumably due to fast isotopic exchange.



$R_1 = R_2 = CH_3$; $R_1 = R_2 = C_6H_5$; $R_1 = CH_3$, $R_2 = C_6H_5$

Fig. 1.

The analytical data of the complexes obtained are given in Table-1. All the complexes are stable at room temperature and the molar conductance values are in the range expected for a non-electrolyte species[9].

TABLE-1
ANALYTICAL DATA AND OTHER DETAILS OF THE METAL COMPLEXES OF H_2AAA, H_2BAA, AND H_2DBA

Complex	Yield (%)	Analysis (%) Found (Calcd.)				μ_{eff} B.M.	Molar# conductance ohm^{-1} cm^2 mol^{-1}
		M	C	H	N		
[Co(AAA)(H_2O)]	76	18.14	44.88	3.64	8.61	4.49	9.3
		(18.25)	(44.59)	(3.72)	(8.67)		
[Ni(AAA)(H_2O)]	73	18.33	44.92	3.80	8.60	3.18	8.4
		(18.19)	(44.62)	(3.72)	(8.68)		
[Cu(AAA)(H_2O)]	77	19.46	44.12	3.87	8.42	1.89	8.0
		(19.33)	(43.83)	(3.95)	(8.50)		
[Zn(AAA)(H_2O)]	74	20.01	43.40	3.57	8.61	diamag.	9.1
		(19.85)	(43.72)	(3.64)	(8.50)		
[Co(BAA)(H_2O)]	75	15.21	53.39	3.57	7.17	4.37	9.1
		(15.31)	(53.00)	(3.64)	(7.27)		
[Ni(BAA)(H_2O)]	76	15.39	52.65	3.56	7.36	3.21	8.3
		(15.26)	(53.03)	(3.64)	(7.28)		
[Cu(BAA)(H_2O)]	74	16.37	51.88	3.94	7.1	1.88	8.3
		(16.27)	(52.23)	(4.01)	(7.17)		
[Zn(BAA)(H_2O)]	70	16.56	52.48	3.51	7.06	diamag.	9.7
		(16.70)	(52.12)	(3.58)	(7.15)		
[Co(DBA)(H_2O)]	79	13.29	58.74	3.67	6.18	4.37	9.1
		(13.19)	(59.07)	(3.58)	(6.26)		
[Ni(DBA)(H_2O)]	78	13.23	58.79	3.49	6.19	3.14	7.3
		(13.14)	(59.10)	(3.58)	(6.27)		
[Cu(DBA)(H_2O)]	76	13.92	58.09	3.66	6.28	1.89	8.6
		(14.04)	(58.33)	(3.75)	(6.18)		
[Zn(DBA)(H_2O)]	75	14.30	57.94	3.45	6.10	diamag.	8.8
		(14.42)	(58.23)	(3.53)	(6.18)		

Measured in DMF

Ultraviolet spectral bands of the ligands were only marginally red shifted indicating that no structural alterations of the ligands occur on metal chelation.

The key infrared spectral bands of the metal chelates are presented in Table-2. The position of the free carbonyl band of the ligand is only marginally shifted in the spectra of the metal chelates. In H_2AAA complexes, instead of the band at 1620 cm^{-1} due to hydrogen bonded carbonyl, the spectra exhibited a strong band around 1560 cm^{-1}, assignable to the metal bonded carbonyl group[10]. A weak band appearing around 1610 cm^{-1} in the spectra of the metal chelates as a shoulder on $\nu_{asy}(COO)$ band can be attributed to conjugated $\nu(C=N)$. In the spectra of the ligand, this band is presumably masked by the strong absorption occurring in the same region of hydrogen bonded carbonyl. In the metal chelates, this band appears as a shoulder on the $\nu_{asy}(COO)$ band. The broad band appearing in the region 3300-2900 cm^{-1} clears from this region and instead a broad band of medium intensity appears in the higher wave number region ranging from 3500-3220 cm^{-1}. This clearly indicates the presence of coordinated water molecule[11]. The other band for coordinated water is observed at *ca.* 845 cm^{-1}. In the metal complexes, the carboxylate stretching frequency in the free ligand disappears and two intense bands at *ca.* 1600 cm^{-1} and 1395 cm^{-1} appeared and this can be assigned to asymmetric and symmetric stretching vibrations of the carboxylate group, respectively. In the present complexes $\Delta\nu(COO)$ observed is consistently > 200 cm^{-1}. This observation adequately confirms that the carboxylate ion acts as unidentate in all the complexes[12].

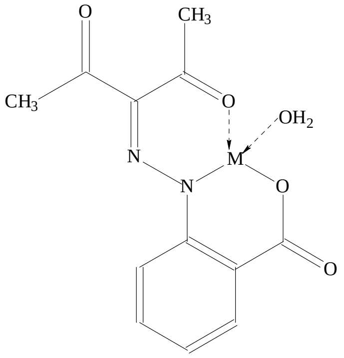
TABLE-2

INFRARED (cm^{-1}) AND ULTRAVIOLET SPECTRAL DATA OF THE METAL COMPLEXES OF H_2AAA, H_2BAA, AND H_2DBA

Complex	Conjugated Free $\nu(C = O)$	$\nu(C=N)$	ν_a (COO)	ν_S (COO)	$\Delta\nu$ (COO)	Metal bonded $\nu(C=O)$	$\nu(M-O)$	$\nu(M-N)$	λ_{max} (nm)
$[Co(AAA)(H_2O)]$	1665	1610	1600	1395	205	1560	514	420	328
$[Ni(AAA)(H_2O)]$	1668	1612	1603	1390	213	1555	512	425	330
$[Cu(AAA)(H_2O)]$	1668	1614	1597	1392	205	1558	514	420	335
$[Zn(AAA)(H_2O)]$	1668	1613	1595	1385	210	1554	525	424	338
$[Co(BAA)(H_2O)]$	1664	1604	1600	1394	206	1558	510	425	336
$[Ni(BAA)(H_2O)]$	1664	1605	1597	1393	204	1555	507	420	338
$[Cu(BAA)(H_2O)]$	1676	1608	1600	1395	205	1559	514	422	335
$[Zn(BAA)(H_2O)]$	1676	1603	1598	1390	208	1556	512	424	334
$[Co(DBA)(H_2O)]$	1674	1608	1597	1380	217	1542	512	420	338
$[Ni(DBA)(H_2O)]$	1672	1607	1600	1383	217	1538	510	420	337
$[Cu(DBA)(H_2O)]$	1675	1604	1598	1388	210	1532	520	422	335
$[Zn(DBA)(H_2O)]$	1672	1609	1598	1392	206	1534	515	424	336

The complexes showed medium intense broad non-ligand bands in the ranges 530-510 cm^{-1} and 430-420 cm^{-1} assignable to ν(M-O) and ν(M-N) vibrations, respectively[13].

The proton magnetic resonance spectrum of the zinc(II) complex with H_2AAA was recorded in DMSO-d_6 and the NH proton signal of the ligand has been absent in the zinc(II) complex. Signals of methyl group, methylene protons and aromatic protons did not show any significant changes when compared to the free ligand. This is a clear indication that the nitrogen atom of the NH moiety is coordinated to the metal ion after deprotonation. Thus the ligands exist entirely as intramolecularly hydrogen bonded 2-arylhydrazones and this form of the ligand persists in metal chelates also in which the hydrogen bonded carbonyl group and deprotonated hydrazeno nitrogen atom and one of the carboxylate oxygen atoms bond with the metal ion, leaving one of the carbonyl groups free (Fig. 2).



M = Co(II), Ni(II), Cu(II or Zn(II)

Fig. 2.

The electronic spectra of cobalt(II) complexes exhibited a broad band in the region 18500-16500 cm^{-1}. For a tetrahedral cobalt(II) complex, three electronic transitions are expected;

$$^4A_2 \rightarrow {}^4T_2(F), \quad ^4A_2 \rightarrow {}^4T_1(F), \quad ^4A_2 \rightarrow {}^4T_1(P)$$

The first two transitions occur in the IR and near IR region and hence these bands are not recorded in the electronic spectra. The band corresponding to the third transition is only recorded. These observations are consistant with a tetrahedral geometry for the cobalt (II) complexes[14].

The tetrahedral geometry of nickel(II) complexes have been supplemented by electronic spectral studies[15]. In a tetrahedral environment, nickel(II) complexes should give three *d-d* transitions. In the present case, only two transitions are recorded since the band due to the first transition occur in the IR region. The band occurring around 16500 cm^{-1} is assigned to $^3T_1(F) \rightarrow {}^3T_1(P)$ and the other at 9550 cm^{-1} is assignable to $^3T_1(F) \rightarrow {}^3A_2(F)$ transitions, respectively. This observation together with the magnetic moment values adequately support a tetrahedral geometry for nickel(II) complexes[15].

Copper(II) complexes exhibited two bands; a low energy less intense band around 10500 cm^{-1} and a relatively strong band around 14000 cm^{-1}. The electronic spectral data and the magnetic moment value are compatible with those values reported for copper(II) complexes with distorted tetrahedral geometry[16].

Zinc(II) ion is flexible with respect to the number of ligands it can adopt in the coordination sphere. Analytical data and molar conductance values of the zinc(II) complexes adequately support their formulation as in Table-1. A tetrahedral geometry has been presumed for the zinc(II) complexes. It has been reported that tetrahedral geometry is the most preferred structure for such a four coordinated zinc(II) complex[17].

The EPR spectra of the copper(II) complexes were recorded in the powder form at room temperature as well as in DMSO at liquid nitrogen temperature. The various spin Hamilton parameters computed are presented in Table-3. The trend $g_{II} > g_{\perp} > g_e$ indicates that the unpaired electron lies predominantly in the d_{x2-y2} orbital. In addition to this, the covalency parameter α^2 has been calculated using Kivelson and Neiman equation[18]. The α^2 values obtained also support the fairly covalent nature of the metal-ligand bond[19].

TABLE-3
EPR SPECTRAL PARAMETERS OF THE COPPER(II) COMPLEXES

Complex	g_{II}	$g_{\perp}$	A_{II}	$A_{\perp}$	α^2
$[Cu(AAA)(H_2O)]$	2.201	2.044	170	40	0.73
$[Cu(BAA)(H_2O)]$	2.223	2.041	165	42	0.74
$[Cu(DBA)(H_2O)]$	2.226	2.068	150	44	0.72

Antibacterial activity: Antibacterial activity of the ligands and the copper(II) complexes are presented in Table-4. It is observed that the metal complexes show more activity than the ligands. This can be explained on the basis of chelation theory[20]. Chelation reduces the polarity of the metal ion considerably, mainly because of the partial sharing of it's positive charge with donor groups and possible electron π delocalization on the whole chelate rings. The lipids and polysaccharides are some important constituents of cell wall and membranes, which are preferred for metal ion interaction. In addition to this, cell wall also contains many amino phosphates, carbonyl and cysteinyl ligands which maintain the integrity of the membrane by acting as a diffusion barrier and also provides suitable sites for binding. Chelation can considerably reduce the polarity of the metal ion, which in turn increases the lipophilic character of the chelate, and the interaction between metal ion and the lipid is favoured. This may lead to the breakdown of the permeability barrier of the cell, resulting in interference with the normal cell process. If the geometry and charge distribution around the molecule are incompatible with the geometry and charge distribution around the pores of the bacterial cell wall, penetration through the wall by the toxic agent cannot take place and this will prevent the toxic reaction within the pores.

TABLE-4
ANTIBACTERIAL ACTIVITY OF THE LIGAND AND THE METAL(II) COMPLEXES

Compound	Zone of inhibition (mm)		
	E. coli	*S. aureus*	*S. caure*
H_2AAA	10	11	11
[Cu(AAA)(H_2O)]	18	17	16
H_2BAA	11	12	13
[Cu(BAA)(H_2O)]	20	18	18
H_2DBA	12	12	13
[Cu(DBA)(H_2O)]	19	20	21

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(*Received*: 15 April 2006; *Accepted*: 23 January 2007) AJC-5329