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SYNTHESIS AND CHARACTERIZATION OF TRANSITION METAL COMPLEXES OF (1-CINNAMYL)- AND (1-BENZYL)-2,4-DIAZA-1,3-BUTANEDIONE.

Joshua A. Obaleye[1],*, Chike L. Orjiekwe[1] and Dennis A. Edwards[2]

[1]Department of Chemistry, University of Ilorin, Ilorin, Kwara State, Nigeria[2]; School of Chemistry, University of Bath, U. K.

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ABSTRACT. The Mn^{II}, Co^{II}, Ni^{II} and Zn^{II} complexes of the ligands (1-cinnamyl)- and (1-benzyl)-2,4-diaza-1,3-butanedione have been prepared and characterized by physicochemical properties, elemental analysis, i.r., UV-Vis and NMR spectroscopic techniques. Based on the magnetic and spectral data, a high spin octahedral structure has been proposed for the complexes with the exception of Zn^{II} complexes. A five coordinate square-pyramidal structure is also assigned to the Mn^{II} complex of 1-benzyl-2,4-diaza 1,3-butanedione.

INTRODUCTION

The application of urea and its compounds in agriculture, industry and pharmacy is versatile. A literature survey on its compounds reveals monodentate character in spite of the presence of the ligand having three potential coordination sites [1]. The infrared studies on urea related complexes show a marked difference in the absorption pattern of the C=O and C-N stretch bands after oxygen-to-metal or nitrogen-to-metal bonding [2-4] has occurred. The magnetic and electronic spectra studies on most urea complexes reveal octahedral geometry and oxygen-to-metal bonding [5-7] with a few exception [8, 9]. Crystal structure of some metal-urea complexes has been studied [10-12]. In all cases the urea ligand is bonded to the metal atom via the oxygen-metal bond. In view of the diverse structural aspects and physiological properties of these urea related complexes, interest in them continues to increase [13-18]. This paper describes the synthesis and structural features of transition metal complexes of (1-cinnamyl)- and (1-benzyl)-2,4-diaza 1,3-butanedione (CU/BU) with emphasis on their spectroscopic properties.

EXPERIMENTAL

All the chemical reagents of analytical grade were purchased from Aldrich and were used directly. All solvents used were purified and dried by vacuum distillation according to standard methods. Infrared spectra were recorded as nujol mulls in the 4000-200 cm^{-1} range using NaCl and CsI cells on Unicam 360 FT infrared spectrophotometer. The ^{1}H and ^{13}C NMR spectra were obtained from Joel JMN-GX 270 FT NMR spectrometer and were recorded in deuterated DMSO using SiMe$_4$ as internal standard. The magnetic measurements were conducted on a Johnson Matthey balance as described by Gerloch [19]. The C, H and N contents were determined with an elemental microanalyzer at the Inorganic Laboratory, School of Chemistry, University of Bath, U.K. Atomic absorption spectrophotometer was used for the metal analyses. All other physical measurements and analytical procedures were similar to those described previously in our earlier papers [20-22].

Preparation of ligands. The ligands (1-cinnamyl)-2,4-diaza-1,3-butadione and (1-benzyl)-2,4-diaza-1,3-butadione (CU and BU, respectively) were prepared by employing previously reported methods (23-24). The urea (0.02 mol) in MeOH (60 cm^3) was mixed and refluxed with cinnamoyl chloride (0.02 mol) or benzoyl chloride (0.02 mol) in a 1:1 mole ratio. The mixture was refluxed until the evolution of gas ceased. The volume of reaction mixture was reduced to one-half by slow evaporation and set aside to cool in an ice bath. The white solid crystals formed were recovered by filteration, purified by recrystallization from MeOH and stored in a desiccator over $CaCl_2$.

Preparation of metal complexes. A solution of the prepared ligand (0.02 mol) in dry EtOH (60 cm^3) was refluxed with a solution of the appropriate metal chloride salt in acetone (80 cm^3) for 8 h. Optimum yield was obtained at this time. A coloured solid products (green and pink, respectively) precipitated from solution on refluxing the Ni^{II} and Co^{II} complexes while white solid complexes of Mn^{II} and Zn^{II} were formed on storage overnight on refrigeration after concentration of the solution to one-half the volume by rotary evaporation. Using anhydrous metal chloride salts as starting materials was not encouraging due to low yield; especially in the case of Mn and Zn reactions. Hence, hydrated salts were used.

RESULTS AND DISCUSSION

An alcoholic solution of urea readily undergoes a condensation reaction with carboxylic acid chloride to form 1,3-dicarbonyl compounds of general formula:

$$NH\text{-}C(=O)NH\text{-}R\text{-}C(=O)NH\text{-}C(=O)\text{-}NH_2$$

where $R = C_6H_5CH{=}CH$ or C_6H_5

The metal chloride salt reacts with the synthesized ligand, L (BU or CU), according to the following proposed general equations:

$$MX_2.nH_2O + 2L \rightleftharpoons ML_2X_2 + nH_2O \quad (\text{where } M = Co^{II} \text{ or } Ni^{II},\ n = 6) \qquad (1)$$

$$MX_2.nH_2O + 2L \rightleftharpoons ML_2X_2.2H_2O + (n\text{-}2)H_2O \quad (\text{where } M = Mn^{II} \text{ or } Zn^{II},\ n = 6) \qquad (2)$$

Details of the physical properties and elemental analysis are presented in Table 1. The complexes are generally soluble in polar organic solvents but insoluble in non-polar organic solvents. The values of the magnetic moment, conductivity and elemental analyses support the compounds as neutral high spin octahedral complexes. The mode of formation and spectral studies for Co^{II} and Ni^{II} complexes support polymeric structures through chlorine bridges. The molecular weight data (Rast's camphor method) indicate polymeric nature of the complexes. Several attempts have been made to grow crystals of the complexes in solvents (such as acetonitrile, methanol, and dichloromethane) without any success of getting suitable samples for x-ray studies.

Table 1. Physical properties and elemental analyses of the ligands and their metal complexes[a].

Compound	Color	Yield (%)	m.p. (°C)	M (%)	N (%)	C (%)	H (%)	µeff (BM)	Λ $\Omega^{-1}cm^{-1} mol^{-1}$
CU	White	76	199		14.7 (14.7)	63.0 (63.1)	5.25 (5.26)	0	0.4
$Co(CU)_2Cl_2$	Pink	54	242	11.25 (11.55)	10.78 (10.98)	46.6 (47.0)	3.93 (3.93)	5.85	2.4
$Ni(CU)_2Cl_2$	Green	65	243	11.20 (11.51)	10.5 (10.9)	46.8 (47.1)	3.89 (3.95)	2.92	2.6
$Mn(CU)_2Cl_2.2H_2O$	White	61	234	10.0 (10.13)	10.1 (10.3)	43.30 (44.30)	4.40 (4.46)	6.28	6.2
$Zn(CU)_2Cl_2.3H_2O$	White	63	244	17.10 (17.20)	6.75 (7.36)	30.7 (31.57)	3.91 (4.20)	0.67	6.4
BU	White	63	166		16.9 (17.0)	57.9 (58.5)	4.84 (4.88)	0	0.3
$Ni(BU)_2Cl_2$	Green	64	232	12.60 (12.82)	12.15 (12.30)	41.70 (41.92)	3.40 (3.49)	2.93	2.5
$Co(BU)_2Cl_2$	Pink	57	233	12.65 (12.86)	12.20 (12.30)	41.7 (41.9)	3.50 (3.49)	6.30	2.6
$Mn(BU)_2Cl_2.2H_2O$	White	60	231	16.70 (16.84)	8.55 (8.59)	30.1 (30.0)	3.67 (3.68)	6.30	6.4
$Zn(BU)_2Cl_2.2H_2O$	White	64	235	13.0 (13.06)	11.27 (11.19)	38.86 (38.39)	3.95 (4.03)	0.6	7.2

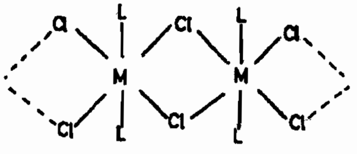
[a] Values in parentheses are calculated values.

The i.r. spectra of the complexes (Table 2) were similar to that of the ligands, consistent with coordination through the oxygen donor atom of the carbonyl group [3, 25-28]. Two carbonyl stretching bands were observed in the spectra of all the compounds within the region 1700 - 1600 cm^{-1} which have been assigned to the presence of 1,3-dicarbonyl system in all the compounds [29-33]. The decrease in the absorption frequency of the second carbonyl band for the complexes relative to the free ligand is strong evidence of bonding the carbonyl bond of the urea moiety [3]. A moderate and weak sharp bands observed around 890 cm^{-1} and 400-220 cm^{-1} in the spectra of the complexes which are completely absent in the spectra of the free ligands have been assigned to (M-O) and (M-Cl) bonds respectively (34-36). In Co^{II} and Ni^{II} complexes, stretching frequencies involving bridging chlorine [7] occur around 200 cm^{-1}.

The electronic absorption bands (Table 3) show that the ligands and the metal complexes gave three absorption bands within the range ~ 294 and 186 nm. These bands are therefore tentatively assigned to charge transfer and intra-ligand transitions based on their relative intensities and positions [30-36]. The slight bathochromic shift of the bands in the complexes relative to the ligand have been attributed to complexation. As expected, no extra bands were observed for Mn^{II}CU and Zn complexes with ^6S and ^1S spectroscopic terms respectively whereas extra bands have been observed for Ni^{II} and Co^{II} complexes which have been attributed to d- d transitions. Mn^{II}BU gave three weak absorption bands at 502, 470, and 380 nm which are characteristic of Mn^{II} complexes [37]. Co^{II} and Ni^{II} complexes of CU ligands gave d- d bands at 528 and 534, respectively. They have been assigned to their lowest transitions $^4T_{1g}$ $^4T_{2g}$ and $^3A_{2g}$ $^3T_{2g}$, respectively. Similar bands were obtained for the BU complexes at 530 nm, and at 750 and 407 nm respectively for the same metal complexes. However, other expected higher transitions for the complexes appear to have been submerged by the more intense transitions because of their relatively low intensity.

The chemical shifts observed in the assigned NMR spectra (Table 4 and 5) of the ligands and their diamagnetic Zn^{II} complexes corroborate that coordination occurred through the urea carbonyl oxygen since only the carbon-1 atom and the adjacent protons b and c gave an appreciable upfield chemical shift [38].

The $N_{eff.}$ values for Ni^{II} complexes in the range 2.92 - 2.93 BM and that of Co^{II} complexes (~ 5.85 - 6.30 BM) suggesting octahedral or pseudooctahedral geometry [13, 39] around Ni^{II} and Co^{II} ion respectively. This is supported in terms of the polymeric nature of the complexes as shown by molecular weight determination. The Ni^{II} and Co^{II} complexes can be tentatively represented by the structure.



L =CU or BU

This trans-isomer is being proposed on account of steric hindrance and based on available experimental data and assignment of similar structure elsewhere [39, 40].

Considering the fact that Zn^{II} and Mn^{II} can assume a number of configurations with the ligands having oxygen donors and both H_2O and Cl^- ion, it is difficult to assign an unequivocal structure to these complexes from the available experimental data.

Steric hindrance and spectroscopic data provide ample evidence in favour of the existence of the structure I. Halides were estimated as the corresponding silver salts with absolutely no free ions outside the coordination sphere.

The presence of coordinated water molecules in the isolated complexes is confirmed by both the elemental analysis and the presence of a broad band due to the antisymmetric and symmetric O-H stretching modes at 3520-3200 cm^{-1} in the ir spectra [40, 41]. It is difficult to distinguish the

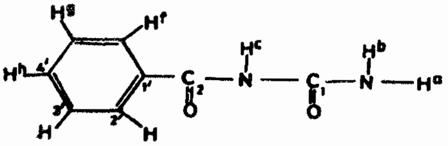
Table 2. Selected infrared spectra for characterization of the metal complexes.

Compound	Infrared bands (cm^{-1})							
	ν(N-H)		ν(CH=CH)		ν(C=O)	ν(NH)$_2$	ν(N-C=O)	ν(M-Cl)
CU	3333 s	3200 s		1711 s	1668 s	1620 s	1099 vs	
Co(CU)$_2$ Cl$_2$	3414 vs	3298 s	3198 vs	1707 s	1576 m	1815 s	1095 vw	218 w,sh
Ni(CU)$_2$ Cl$_2$	3420 vs	3310 s	3204 s	1709 s	1576 m	1814 s	1094 vw	225 w,sh
Mn(CU)$_2$Cl$_2$.2H$_2$O	3383 s	3277 s	3200 s	1696 s	1576 s	1632 s	1099 vw	225 w,sh
Zn(CU)Cl$_2$.3H$_2$O	3520 s	3287 s	3200 s	1698 s	1576 m	1611 s	1095 vw	220 w,sh
BU	3344 s	3219 s		1709 s	1660 m	1612 s	1097 vs	
Ni(BU)$_2$ Cl$_2$	3373 s	3267		1705 s	1576 m	1612 s	1099 vw	219 w,sh
Co (BU)$_2$ Cl$_2$	3374 s	3268		1706 s	1575 m	1612 s	1099 vw	224 w,sh
Mn(BU)Cl$_2$.2H$_2$O	3406 s	3277 s		1705 s	1585 m	1603 s	1101 vw	225 w,sh
Zn(BU)$_2$Cl$_2$.2H$_2$O	3408 s	3276		1703 s	1579 m	1612 s	1099 vw	222 w,sh

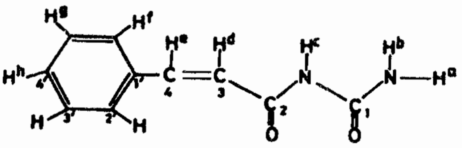
Table 3. Selected electronic absorption spectra for characterization of the metal complexes [a].

Compound	Electronic bands (nm)					
CU		283 (3.97)	220 (3.5)		207 (3.10)	
Co(CU)$_2$ Cl$_2$	528 (1.82)	286 (3.86)	220 (3.85)		207 (3.0)	
Ni(CU)$_2$ Cl$_2$	534 (1.70)	285 (3.85)	220 (3.82)		207 (2.98)	
Mn(CU)$_2$Cl$_2$.2H$_2$O		285 (3.97)	220 (3.39)		201 (2.96)	
Zn(CU)Cl$_2$.3H$_2$O		286 (3.97)	220 (3.40)		190 (3.00)	
BU			220 (3.40)		190 (3.00)	
Ni(BU)$_2$ Cl$_2$	750 (1.18)	407 (01.42)	234 (3.87)	202 (3.40)	193 (2.88)	
Co (BU)$_2$ Cl$_2$		530 (1.54)	226 (3.90)	202 (3.50)	193 (2.85)	
Mn(BU)Cl$_2$.2H$_2$O	502 (0.35	470 (0.26)	380 (0.11)	233 (3.90)	210 (3.51)	193 (2.88)
Zn(BU)$_2$Cl$_2$.2H$_2$O				234 (3.77)	206 (3.51)	192 (2.91)

*Values in parentheses are the absorptivity maxima(ϵ_{max}) in $\log_{10}$.



1-Benzyl 2,4-diaza 1,3 butanedione (BU)



1-Cinnamyl 2,4-diaza 1,3 butanedione (CU)

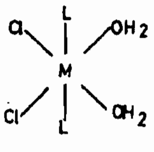
Table 4. Proton NMR spectral data of the ligands and Zn^{II} complexes.

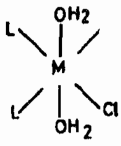
^1H NMR signal positions δ				
CU	$Zn(CU)Cl_2.3H_2O$	BU	$Zn(BU)_2Cl_2.2H_2O$	Assignment
6.79,6.85 d (1)	6.77-6.83 d (1)	-	-	e
7.36 s (1)	7.33 s (1)	7.44 s (1)	7.36 s (1)	a
7.42-7.45 q (2)	7.42-7.44 q (2)	7.46-7.52 t (2)	7.45-7.52 t (2)	g
7.57-7.59 t (2)	7.57-7.59 t (2)	7.56-7.63 t (2)	7.55-7.62 t (2)	f
7.61 s (1)	7.60 s (1)	7.94-7.97 d (1)	7.93-7.94 d (1)	h
7.64-7.69 d (1)	7.62-7.68 d (1)	-	-	d
7.94 s (1)	7.73 s (1)	8.28 s (1)	8.03 s (1)	b
10.7 s (1)	10.3 s (1)	10.77 s (1)	10.52 s (1)	c

Table 5. ^{13}C NMR spectral data for the ligands and Zn^{II} complexes.

^{13}C NMR siganl positions δ				
CU	$Zn(CU)Cl_2.3H_2O$	BU	$Zn(BU)_2Cl_2.2H_2O$	Assignment
166.6 (1)	166.4 (1)	168.3 (1)	167.2 (1)	C (1)
154.4 (1)	154.3 (1)	154.4 (1)	154.4 (1)	C (2)
143.5 (1)	143.1 (1)	-	-	C (3)
134.4 (1)	134.3 (1)	-	-	C (4)
130.8 (1)	130.6 (1)	132.8 (1)	132.5 (1)	C (1')
129.4 (2)	129.2 (1)	128.6 (2)	128.4 (2)	C (3')
128.4 (2)	128.2 (1)	128.3 (3)	128.3 (3)	C (2')
120.5 (1)	120.5 (1)			C (4')

However, four structures are likely for complexes 3 and 8 (Table 1) as follows:


I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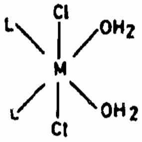
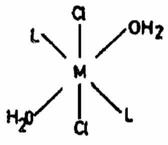
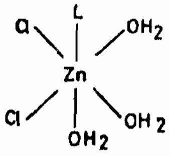

III

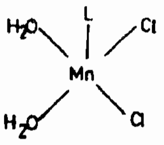

IV

stretching and deformation bands of O-H from N-H since both absorb within the same range. The assigned bands (3520-3200 cm^{-1}) were quite distinct.

The spectral data (i.r., UV-Vis) and stoichiometry led us to propose the following structures for complexes 4 and 7:


L=CU

Complex 4


L = BU

Complex 7

In the absence of x-ray crystallographic data, the proposed structures shown above are only tentative. Complex 7 shows a tentative square pyramidal structure. Complex 4 and 8 have different compositions. This may be due to steric effect and inertness of the hydrated compound formed by complex 4. The strength of the two ligands (CU and BU) are not identical. These might have contributed to the different products.

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