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COBALT(II) AND NICKEL(II) COMPLEXES OF 1,5-DICINNAMYL-2,4-DIAZA-1,3,5-PENTANETRIONE

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ABSTRACT. The reactions of 1,5-dicinnamyl-2,4-diaza-1,3,5-pentanetrione, dcu, with $MCl_2.6H_2O$ led to the formation of $[(MCl_2(H_2O)_2)_2dcu]$ (where M = Co, Ni) complexes. These complexes have been characterized by vibrational, electronic and NMR spectroscopies, as well as magnetic studies, conductivity measurements and complete elemental analyses. A six coordinate octahedral geometry about metal ion is inferred. The magnetic data show that d^n states are retained.

INTRODUCTION

The chemistry of urea based ligands has been developed rapidly in recent years because of interest in their geometrical structures, complexing ability and relevance to man [1-5]. Urea has been used intravenously in the treatment of acute increases in intra-cranial pressure due to celebral oedema. It has been given to maintain the output of urine during surgical operations. Hypertonic solution of urea have been given by intra-amniotic injection for the induction of abortion. Urea creams which has 10% urea constitutent is used in the treatment of ichthyosis and hyperkeratotic skin disorders [2]. Urea compounds and its derivatives are commonly used as fertilizers due to its high nitrogen content [3]. Urea is used in the production of urea formaldehyde resins which is used as adhesives for surface coating, paper and textile finishes. It is used as a supplement in cattle feeds [3]. It is also used as diuret, in the treatment of ulcers and sickle cell anemia [4]. Other important applications for urea are in the manufacture of glues, solvents and some drugs such as barbiturates [3].

From the structural point of view, urea has three coordination sites; the carbonyl oxygen and the two nitrogen atoms. Inspite of its three coordination sites, urea acts as a monodentate ligand [6]. Urea uses either the carbonyl oxygen or the nitrogen for bonding. Exceptional cases were reported where urea acts as a bidentate ligand by using the carbonyl oxygen and one of the nitrogen atoms for bonding [1,5,7].

In view of the aforementioned, viz-a-viz, application and structural perspective of urea and its compounds; we reported in our previous paper, the synthesis and characterization of urea based type of ligands: (1-cinnamyl)- and (1-benzyl)-2,4-diaza-1,3-butanedione and their complexes [1]. We therefore extended the earlier investigation of the urea type based ligand, and tried to coordinate, 1,5-dicinnamyl-2,4-diaza-1,3,5-pentanetrione to cobalt(II) and nickel(II) ions, with the aim to obtain novel stable urea based complexes which would give better insight into the ligational effect of this type of compounds. This paper describes the synthesis and characterization of such compounds.

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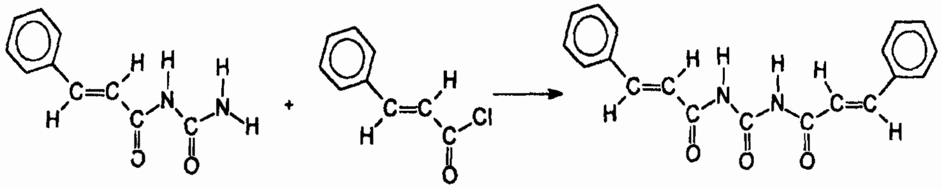
EXPERIMENTAL

All chemicals (Aldrich) were reagent grade and were used as such without purification. Solvents were purged with N_2 and tested for peroxides; and purified as reported elsewhere [1] before use. Elemental analyses were carried out on a C, H, N-microanalyzer (Inorganic Laboratory, School of Chemistry, University of Bath, U.K.). Cobalt and nickel were determined chelatometrically and with AAS. Chloride was estimated gravimetrically as silver chloride. The conductivities at 25 ± 0.1°C of 10^{-2} M alcohol solution of the complexes were measured using WTW bridge with a cell constant of 1.63. The electronic spectra were recorded on a Unicam 400/360 uv-vis spectrophotometer using ethanol as solvent. Spectra were measured for 10^{-2} M solutions of both forms of $[(MCl_2(H_2O)_2)_2dcu]$. The IR [8], ^1H and ^{13}C NMR spectra of the ligand [1], as well as the magnetic susceptibilities [9,10] were obtained as described in the cited papers. All other physical measurements and analytical procedures were as described elsewhere [11,12].

Preparation of ligand. The preparative technique for the ligand, 1,5-dicinnamyl-2,4-diaza-1,3,5-pentanetrione, dcu, was the same as in the previous studies [1,13]. The ligand, dcu, was prepared by further acylation of the already prepared 1-cinnamyl-2,4-diaza-1,3-butanedione (cdb) [1] with cinnamoyl chloride in toluene in 1:1 molar ratio. The solid product was checked for purity by elemental analysis, melting point, TLC test and spectroscopically characterised. The cdb was pure white while the dcu ligand was reddish brown.



cdb dcu

Preparation of metal complexes. The metal complexes were prepared in the same fashion as reported in our previous studies [1], with the use of dcu (0.050 mol) in place of cdb. The cobalt(II) and nickel (II) complexes of the urea based ligand, 1,5-dicinnamyl-2,4-diaza-1,3,5-pentanetrione, dcu, were prepared by refluxing 0.025 mole each of metal chloride salt with 0.050 mole of dcu in 25 mL of acetone until precipitates of the complexes appeared. The coloured crystals were filtered, washed and recrystallized from methanol and stored in a desiccator over $CaCl_2$.

RESULTS AND DISCUSSION

Reaction of dcu with hydrated MCl_2 in acetone gave complexes of stoichiometry $[(M(H_2O)_2Cl_2)_2dcu]$ (M = Co or Ni)

$$2MCl_2.6H_2O + dcu \rightarrow [(M(H_2O)_2Cl_2)_2dcu] + 8H_2O$$

The details of physical properties and analytical data are given in Table 1. There is not much difference in the colors of these substances when compared with the cdb analogues [1]. All the complexes are found to be soluble in polar organic solvents such as acetone, ethanol, acetonitrile and dimethyl acetamide and insoluble in solvents of low polarity such as chloroform, dichloromethane, petroleum ether and toluene. They are stable and do not melt at temperature less than 262°C. The results of conductivity measurements in methanol are listed in Table 1. In complete analogy with cdb complexes [1], it may be seen that the values of Λ_m for these compounds in methanol are close for a non-electrolyte. The results of effective magnetic moment are shown in Table 1. The magnetic moments presented are the average values of four independent measurements. The values of the effective magnetic moment for the two chelates are characteristic for $^4T_{1g}$ and $^3A_{2g}$ ground state of the central Co(II) and Ni(II) ion, respectively. The magnetism of these compounds and the reported values of the cdb complexes [1] were reasonably in good agreement. The susceptibilities shown are the average values of three independent measurements within the temperature range 77-295 K, the susceptibilities values were gradually reduced. This may be due to antiferromagnetic interactions (Table 1). This suggests high spin octahedral or possibly pseudooctahedral geometry. The complexes are all paramagnetic. The mode of formation, the molecular weight data (Rast's camphor method) and spectral data for these compounds support the proposed structures (Figure 1) through -C=O bridge of the dcu ligand.

Table 1. Physical properties and analytical data of the ligand and its metal complexes.*

Compound	Colour	Yield (%)	m.p. °C	M(%)	N(%)	C(%)	H(%)	μ_{eff} (BM) (T)	Λ_m Ω^{-1} cm^2 mol^{-1}	M W (g/mol)
dcu	reddish brown	71	221	-	8.81 (8.74)	70.70 (71.24)	4.94 (5.03)	-	0	317.20 (320.35)
$[(CoCl_2(H_2O)_2)_2dcu]$	pink	58	262	17.80 (18.08)	4.20 (4.30)	34.90 (35.00)	3.33 (3.71)	6.2 (295K) 5.9 (273K) 5.7 (77 K)	2.3	655.18 (652.09)
$[(NiCl_2(H_2O)_2)_2dcu]$	green	62	264	17.70 (18.01)	4.29 (4.30)	34.70 (35.02)	3.31 (3.71)	3.1 (295K) 2.8 (273K) 2.5 (77 K)	2.5	654.14 (651.60)

*Values in parenthesis are calculated values.

The important infrared frequencies of the ligand and the complexes are compiled in Table 2. Chelation of the ligand is established by examination of IR spectra of the compounds. In analogy to cdb, which showed strong and broad bands at 3376-3200 cm^{-1} due to ν(N-H)[1]; the ligands, dcu, underwent a red shift to 3247-3166 cm^{-1}, for ν(N-H) as a result of substitution on the nitrogen [16,17]. The bands at 1754 cm^{-1} and 1615 cm^{-1} for dcu are due to ν(C=O) [8,18,19]. On the other hand, the very strong bands near 1700 cm^{-1} for the complexes apparently belong [1,7,8] to the stretch of the C=O link, for which a practically single bond may be expected from the oxygen towards the metal. There is possibility of overlapping of ν(CH=CH) on this band [1]. In these dcu-metal complexes, the greater shift in the ν(C=O) bands coupled with slight changes in associated ν(C-N-H), ν(N-C-N) and ν(N-H) bands are strong evidence of complexation through the oxygen atom(s) of the carbonyl bonds [20,21]. This is supported by the observed weak ν(N-C=O) bands due to decrease in double bond character of the carbonyl bond on complexation [7,20]. It is assumed that if coordination is through the nitrogen and oxygen donor atoms, a four membered cyclic ring through the nitrogen atoms will give unstable structure because of ring strain. However, the formation of a six membered bicyclic ring through the oxygen atoms is expected to give a very stable chelate structure. Assignment of a few other relevant bands in the vibrational spectra of dcu complexes (Table 2) was done by comparison with the spectra of the uncoordinated dcu ligand and the spectra of metal-cdb complexes [1]. In the spectra of the metal-cdb complexes, only the ν(C=O) band at 1668 cm^{-1} (in cdb, monodentate ligand) undergoes appreciable red shift to 1576 cm^{-1} whereas the two ν(C=O) bands in the dcu complexes undergo red shift (Table 2). These observations are strongly indicative of a bidentate character (with respect to a metal ion) of dcu in each of the two complexes. The low frequency bands of the dcu complexes observed around 721 cm^{-1} may be due to ν(M-O) while a weak band observed around ~ 400 cm^{-1} may be attributed to the M-Cl mode of vibration [1,22,23]. In the dcu complexes, a band of strong intensity at around 3424 cm^{-1}, a band at 679 cm^{-1} not present in the spectra of cdb complexes, and a weak band at 769 cm^{-1} are assigned to ν(O-H), ρ(H_2O) and ν(M-OH_2), respectively. Similar bands have been reported at similar energies to confirm the presence of water as an aquo ligand [24,25]. There is no loss of water observed when the complexes are strongly heated. This also supports the coordinating properties of H_2O.

Table 2. Selected infrared spectra of dcu ligand and its metal complexes.

Compound	Infrared bands (cm^{-1})									
	ν(O-H)	ν(N-H)	ν(C=O)	ν(N-C-N)	ν(C-N-H)	ν(N-C=O)	ν(M-O=C-N)	ν(M-OH_2)	ν(M-Cl)	ϱH_2O
dcu	-	3247 s 3166 m	1754 s, 1651 vs	1510 s	1463 m	1097 m	-	-		
[($CoCl_2(H_2O)_2)_2$ dcu]	3424 s	3240 m 3186 m	1701 vs 1599 vs	1498 m	1464 s	1101 w	721 w	769 w	410 w	679 w
[($NiCl_2(H_2O)_2)_2$ dcu]	3424 s	3240 m 3186 m	1699 vs 1599 vs	1499 m	1464 m	1102 w	721 w	769 w	412 w	679 w

Table 3. Electronic absorption spectra of dcu ligand and its complexes.*

Compound	Electronic bands (nm)				
dcu			220	210	195
[($CoCl_2(H_2O)_2)_2$dcu]		531	297	221	212
[($NiCl_2(H_2O)_2)_2$dcu]	750	405	298	220	213

*1 kK = 1,000 cm^{-1}.

The electronic spectrum of 1,5-dicinnamyl-2,4-diaza-1,3,5-pentanetrione, dcu, in ethanol is characterized by three strong absorptions at 51.3 kK, 47.6 kK, and 45.5 kK. These absorptions are tentatively assigned to the intramolecular transitions [1,8]. The lower band around 51.3 kK which is found to vary with solvent polarity; is assigned to $\pi \rightarrow \pi^*$ of the isolated urea moiety while the band around 47.6 kK may be due to $\pi \rightarrow \pi^*$ of the benzenoid ring and ethylenic bond. The higher band around 45.5 kK may be due to the conjugated system. The electronic spectra of the metal complexes dispay weak ligand field bands due to d-d transitions

at 18.8 kK ($^4T_{1g} \xrightarrow{\nu_1} {}^4T_{2g}$), and 33.7 kK ($^4T_{1g} \xrightarrow{\nu_3} {}^4T_{1g}(P)$) for the Co(II) complex (d^7); and

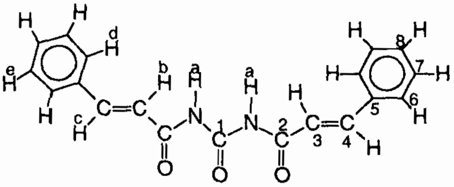
at 13.3 kK($^3A_{1g} \xrightarrow{\nu_1'} {}^3T_{2g}$), 24.7 kK ($^3A_{2g} \xrightarrow{\nu_2'} {}^3T_{1g}$) and 33.6 kK($^3A_{2g} \xrightarrow{\nu_3'} {}^3T_{1g}(P)$)

for the Ni(II) complex (d^8), typical of octahedral or pseudooctahedral Co(II) and Ni(II) complexes, respectively [1, 8, 26]. In the case of cobalt(II) complex, the absorption at 18.8 kK is also rather broad and unsymmetrical and may have contributions from both the two lower d-d transitions ($\nu_1 + \nu_2$). The highest energy band (~33.6 kK) for these complexes overlaps with the strong charge transfer absorption occurring in this region. The Dq values for the Co(II) and Ni(II) complexes are 1.48 kK and 1.33 kK, respectively.

In Table 4, as a result of the paramagnetic nature of the two complexes only the qualitative data of both the ^1H and ^{13}C NMR of the dcu ligand are shown. The individual ^1H and ^{13}C resonances of the ligand have been assigned in analogous to the reported cdb ligand and the relevant published chemical shift data [1,8,27]. All of the two studied M(II) complexes are found to be in the high spin configuration.

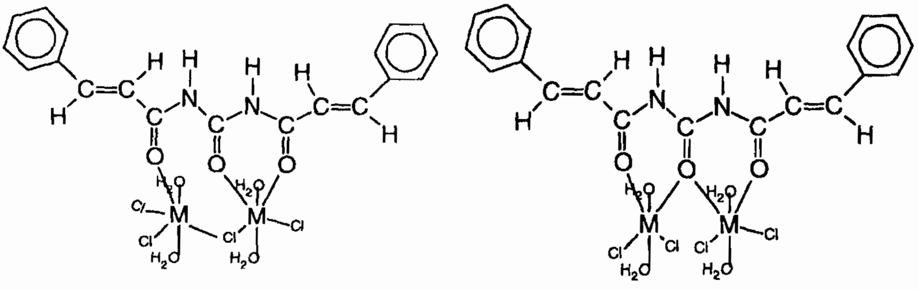
Table 4. ^1H and ^{13}C NMR spectral data of dcu ligand.*

^1H NMR signal (δ)		^{13}C NMR signal (δ)	
dcu	Assignment	dcu	Assignment
11.25 s (1)	a	166.2(1)	C(2)
7.7-7.8 d(1)	c	150.1(2)	C(1)
7.7 t(3)	d & f	144.5(2)	C(3)
7.5 t(2)	e	134.1(2)	C(4)
7.1-7.2 d(1)	b	130.8(2)	C(5)
		129.2(4)	C(6)
		128.4(4)	C(7)
		120.0(2)	C(8)



*s = singlet, d = doublet, t = triplet; values in parenthesis are integral values.

Considering all the above analytical data, elemental analysis, physicochemical properties, spectroscopic data and in the absence of X-ray crystallographic data, we tentatively propose the following structures for the complexes:



I

II

Figure 1. Proposed structures for the complexes.

There are many possible structures for these complexes. It is possible to have two free chloride ions which will increase the polarity of the complexes, i.e. $[((\mu\text{-Cl})M(H_2O)_2)_2]Cl_2$. This is not in support of the conductivity data. It is also possible to have a chloro bridge between the two metal ion in which all the chloro groups are coordinating (i.e. structure **I**). Alternatively, we may have a bridging carbonyl group as shown in structure **II**.

Attempts are in progress to get a suitable single crystal each for the X-ray studies of these compounds. It must be noted that the sum of electronic aspects and steric bulk limitations which accounts to the stabilization of hexa-coordinate species with respect to a metal(II) ion (in this studies) involves a chelate contribution. Consequently, bidentate character of dcu per metal ion plays a major role in the stabilization.

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