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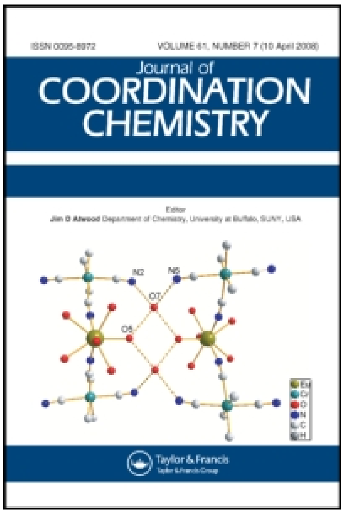

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ZINC(II), CADMIUM(II) AND MERCURY(II) COMPLEXES OF MACROCYCLIC LIGANDS DERIVED FROM 2,6-DIACETYLPYRIDINE

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ZINC(II), CADMIUM(II) AND MERCURY(II) COMPLEXES OF MACROCYCLIC LIGANDS DERIVED FROM 2,6-DIACETYLPYRIDINE

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A novel series of complexes, of the type [M(DAPCH)X_2] (M = Zn(II), Cd(II) or Hg(II); DAPCH = planar pentadentate ligand derived from 2,6-diacetylpyridine and carbohydrazide, X = Cl, Br, I, NO_3, CH_3COO) have been synthesized and characterized by elemental analyses, conductance measurements and infrared spectral data. The ligand DAPCH appears to behave as a pentadentate ligand, having coordination sites at one pyridine nitrogen, two azomethine nitrogen and two amide oxygen atoms. Possible structures are proposed for these complexes. All the complexes contain terminal hydrazinic nitrogen atoms with an unshared electron pair and may take part in nucleophilic condensations. Therefore, the reactions of these complexes (X = Cl, Br, NO_3) with 2,6-diacetylpyridine have also been studied *viz*., ring closure and formation of macrocyclic ligand complexes. Two types of cyclic products *viz*., mononuclear [M(L′)X_2] and binuclear [M_2(L′)X_4] (M = Zn(II), Cd(II) or Hg(II); L = macrocyclic ligand derived from DAPCH and 2,6-diacetylpyridine; X = Cl, Br, NO_3) have been isolated by carrying out the reactions by different methods. The infrared spectra of these cyclic products are reported.

INTRODUCTION

2,6-Diacetylpyridine is a versatile tridentate chelating agent, having two reactive carbonyl groups capable of undergoing Schiff base condensation with a variety of di- and polyamines. The use of metals as templates in such reactions has led to the synthesis of a large number of metal complexes of macrocyclic ligands.[1,2] However, few complexes of macrocyclic ligands having a denticity more than five are known.[3–5] The study of metal complexes of high denticity ligands appears to be useful and interesting in view of the possibility of obtaining coordination compounds of unusual structure and stability.[3–5] Such complexes are known to have relevance to biological systems, thus providing an opportunity to design and study the model biological systems to understand the subtle chemical changes taking place in such cases.[1,6–9]

With this view, a new high denticity ligand, 2,6-diacetylpyridinebis-(carbohydrazone) (DAPCH), capable of undergoing cyclization *via* the metal template effect has been designed. This paper reports the synthesis and characterization of zinc(II), cadmium(II) and mercury(II) complexes of DAPCH and their reactions with 2,6-diacetylpyridine.

EXPERIMENTAL

Carbohydrazide was prepared as reported in the literature.[10] 2,6-Diacetylpyridine-bis-(carbohydrazone) (DAPCH), was prepared by the following method.

Preparation of the ligand, DAPCH

2,6-Diacetylpyridine (1 mol) was added to an aqueous ethanolic solution of carbohydrazide

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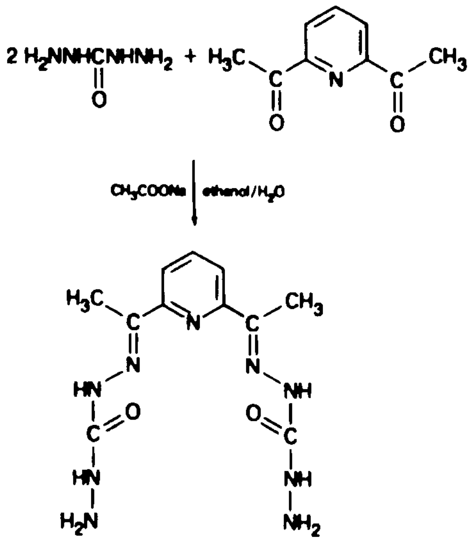
(2 mol) in the presence of sodium acetate. The reaction mixture was refluxed for 30 min., when a yellow product separated out which was filtered, washed with an ethanolic solution of sodium acetate and distilled water and dried *in vacuo*.



(DAPCH)

Preparation of complexes of DAPCH, $[M(L)X_2]$ *(M = Zn, Cd or Hg; L = DAPCH; X = Cl, Br, I,* NO_3*, or* CH_3COO*)*

A general procedure was followed to synthesize these complexes. The procedure involves the addition of the ligand DAPCH (0.02 mol) to an aqueous ethanolic (60%) solution of the appropriate metal salt (0.02 mol). The mixture was refluxed for *ca.* 6–7 hrs on a water bath. Light yellow or light orange masses which appeared immediately in the case of the halo complexes or on keeping the solution overnight in the case of nitrate and acetate complexes, were filtered, washed with ethanol and hot water and dried *in vacuo* at room temperature.

Preparation of mononuclear complexes of macrocyclic ligand, $[M(L')X_2]$ *(M = Zn, Cd or Hg; X = Cl, Br,* NO_3*; L' = new macrocyclic ligand derived by condensation of DAPCH with 2,6-diacetylpyridine)*

A common procedure was adopted to synthesize these complexes. 2,6-Diacetylpyridine dissolved in aqueous ethanol (60%) (0.01 mol in 50 cm^3) was added to the appropriate DAPCH complex (0.01 mol) and refluxed for 16–18 hrs. The colour of the mixture was intensified and the precipitate obtained was filtered, washed with ethanol and hot water and dried *in vacuo* at room temperature.

Preparation of binuclear complexes of the macrocyclic ligand, $[M_2(L')X_4]$ *(M = Zn, Cd or Hg; X = Cl, Br,* NO_3*)*

A general procedure was adopted to synthesize these complexes involved the addition of an excess of appropriate metal salt to an aqueous ethanolic solution of 2,6-diacetylpyridine (0.01 mol) and carbohydrazide (0.01 mol). The solution was refluxed for *ca.* 18–20 hrs. when dark yellow or orange coloured precipitates appeared which were filtered, washed thoroughly with ethanol and dried *in vacuo* at room temperature.

TABLE I
Analytical data of the complexes

Complex	Colour	Found (Calcd.) %				
		C	H	N	M	X
[Zn(DAPCH)Cl$_2$]	light yellow	29.5	3.7	28.2	14.5	16.0
		(29.7)	(3.8)	(28.4)	(14.7)	(16.0)
[Zn(DAPCH)Br$_2$]	light yellow	24.6	3.0	23.2	12.0	29.9
		(24.7)	(3.1)	(23.6)	(12.2)	(30.0)
[Zn(DAPCH)I$_2$]	light yellow	21.0	2.5	20.0	10.0	40.4
		(21.0)	(2.7)	(20.1)	(10.4)	(40.5)
[Zn(DAPCH)(NO$_3$)$_2$]	light orange	26.2	3.2	30.8	13.0	24.8
		(26.5)	(3.4)	(31.0)	(13.1)	(24.9)
[Zn(DAPCH)(CH$_3$COO)$_2$]	reddish yellow	36.6	4.3	25.6	13.0	—
		(36.7)	(4.6)	(25.6)	(13.3)	
[Zn(mac)Cl$_2$]	dark yellow	42.0	3.5	24.4	11.3	12.0
		(42.0)	(3.8)	(24.5)	(11.4)	(12.4)
[Zn(mac)(NO$_3$)$_2$]	dark yellow	38.2	3.3	26.5	10.1	19.5
		(38.5)	(3.5)	(26.9)	(10.4)	(19.8)
[Zn$_2$(mac)Cl$_4$]	dark yellow	33.6	3.0	19.6	18.2	20.0
		(33.9)	(3.1)	(19.8)	(18.4)	(20.0)
[Zn$_2$(mac)Br$_4$]	dark yellow	27.0	2.1	15.6	14.2	36.0
		(27.1)	(2.4)	(15.8)	(14.7)	(36.1)
[Zn$_2$(mac)(NO$_3$)$_4$]	dark yellow	29.5	2.6	24.0	15.8	30.4
		(29.5)	(2.7)	(24.1)	(16.0)	(30.5)
[Cd(DAPCH)Cl$_2$]	light yellow	26.7	3.0	25.6	22.7	14.1
		(26.9)	(3.4)	(25.6)	(22.9)	(14.4)
[Cd(DAPCH)Br$_2$]	light yellow	22.6	2.9	21.5	19.1	27.4
		(22.7)	(2.9)	(21.7)	(19.3)	(27.6)
[Cd(DAPCH)I$_2$]	light yellow	19.4	2.3	18.2	16.2	37.7
		(19.6)	(2.5)	(18.7)	(16.6)	(37.7)
[Cd(DAPCH)(NO$_3$)$_2$]	light orange	24.0	2.8	28.1	20.4	22.6
		(24.2)	(3.1)	(28.3)	(20.6)	(22.8)
[Cd(DAPCH)(CH$_3$COO)$_2$]	light orange	33.2	4.0	23.2	20.8	—
		(33.4)	(4.2)	(23.4)	(20.9)	
[Cd(mac)Cl$_2$]	dark yellow	38.6	3.1	22.3	18.1	11.0
		(38.8)	(3.5)	(22.6)	(18.2)	(11.4)
[Cd(mac)Br$_2$]	dark yellow	33.6	3.0	19.6	15.5	22.3
		(33.9)	(3.1)	(19.8)	(15.9)	(22.6)
[Cd(mac)(NO$_3$)$_2$]	orange	35.4	3.0	25.0	16.4	18.2
		(35.7)	(3.2)	(25.0)	(16.7)	(18.4)
[Cd$_2$(mac)Cl$_4$]	dark yellow	29.6	2.5	17.2	27.8	17.7
		(29.9)	(2.7)	(17.4)	(28.0)	(17.7)
[Cd$_2$(mac)Br$_4$]	dark yellow	24.2	2.0	14.3	22.9	32.2
		(24.5)	(2.2)	(14.3)	(22.9)	(32.6)
[Cd$_2$(mac)(NO$_3$)$_4$]	dark orange	26.2	2.3	21.4	24.3	27.0
		(26.4)	(2.4)	(21.6)	(24.7)	(27.3)
[Hg(DAPCH)Cl$_2$]	light yellow	22.6	2.9	21.5	34.2	12.0
		(22.8)	(2.9)	(21.7)	(34.6)	(12.2)
[Hg(DAPCH)Br$_2$]	light yellow	19.2	2.4	18.8	29.7	33.0
		(19.7)	(2.5)	(18.8)	(30.0)	(33.3)
[Hg(DAPCH)I$_2$]	light yellow	17.2	2.0	16.2	26.1	33.0
		(17.3)	(2.2)	(16.5)	(26.3)	(33.3)
[Hg(DAPCH)(NO$_3$)$_2$]	yellowish orange	20.5	2.2	19.7	31.2	19.4
		(20.8)	(2.6)	(19.9)	(31.7)	(19.6)
[Hg(DAPCH)(CH$_3$COO)$_2$]	pink	28.6	3.4	20.0	32.0	—
		(28.7)	(3.6)	(20.1)	(32.0)	
[Hg(mac)Cl$_2$]	dark yellow	33.5	3.0	19.4	28.2	10.0
		(34.0)	(3.1)	(19.8)	(28.4)	(10.0)
[Hg(mac)Br$_2$]	dark yellow	30.1	2.4	17.2	25.0	20.0
		(30.2)	(2.7)	(17.6)	(25.2)	(20.1)

TABLE I (*cont.*)
Analytical data of the complexes

Complex	Colour	Found (Calcd.) % C	H	N	M	X
$[Hg(mac)(NO_3)_2]$	dark orange	31.2 (31.6)	2.4 (2.9)	22.0 (22.1)	26.2 (26.4)	16.2 (16.3)
$[Hg_2(mac)Cl_4]$	dark yellow	24.2 (24.5)	2.0 (2.2)	14.0 (14.3)	41.0 (41.0)	14.2 (14.5)
$[Hg_2(mac)Br_4]$	dark yellow	20.4 (20.7)	1.7 (1.9)	12.0 (12.1)	34.2 (34.7)	27.9 (27.7)
$[Hg_2(mac)(NO_3)_4]$	red	22.0 (22.1)	1.9 (2.0)	18.0 (18.0)	37.1 (37.0)	22.6 (22.8)

where, DAPCH = 2,6-diacetylpyridine-bis-(carbohydrazone);
mac = macrocyclic ligand derived from DAPCH and 2,6-diacetylpyridine.

Physical Measurements

The details of physical measurements are the same as described earlier.[11]

Analytical Procedures

Microanalyses for carbon and hydrogen were performed by the C.D.R.I., Lucknow and by the Department of Chemistry, B.H.U., Varanasi. Nitrogen was estimated by Kjeldahl's method. Metals were estimated by standard literature procedures.[12]

Analytical data of the complexes prepared are given in Table I.

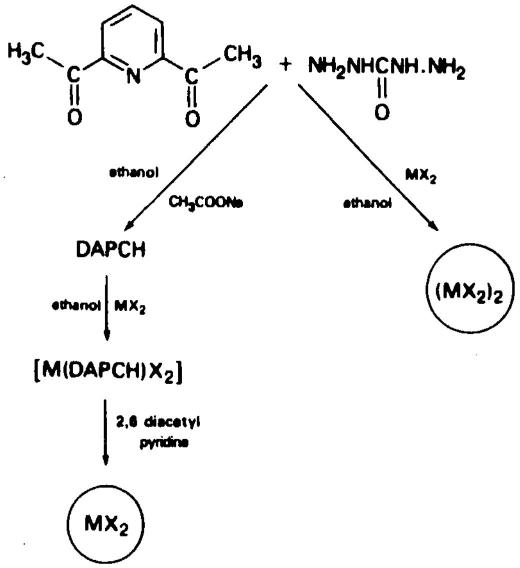
RESULTS AND DISCUSSION

The zinc(II), cadmium(II) and mercury(II) complexes of the planar pentadentate ligand 2,6-diacetylpyridine-bis-(carbohydrazone) (DAPCH), have been synthesized by refluxing the equimolar solutions of the appropriate metal salt with DAPCH both dissolved in aqueous ethanol.

The elemental analyses of the complexes show 1 : 1 metal-to-ligand stoichiometry. These complexes are soluble in dimethylformamide, dimethylsulphoxide and partially soluble in nitrobenzene. The electrical conductances in dimethylformamide indicate their non-electrolytic nature. All the complexes have high melting points and do not decompose up to 200°C. Accordingly, they can be formulated as, $[M(L)X_2]$, (where M = Zn, Cd or Hg; L = DAPCH; X = Cl, Br, I, NO_3, CH_3COO).

On treating one mol of the zinc(II), cadmium(II) or mercury(II) complexes of DAPCH with one mole of 2,6-diacetylpyridine, intensely coloured products have been isolated. It appears that in the zinc(II), cadmium(II) and mercury(II) complexes of DAPCH, the two terminal hydrazinic groups remain uncoordinated and can take part in nucleophilic condensation with 2,6-diacetylpyridine, giving rise to metal complexes of macrocyclic ligands.

However, if the reactions are carried out *in situ*, i.e., the metal salt, carbohydrazide and 2,6-diacetylpyridine are mixed together in ethanol and refluxed, an entirely different binuclear product is obtained. The reaction is proposed to proceed as follows:



The metal to ligand stoichiometry of all these macrocyclic products has been established on the basis of elemental analyses (Table). These complexes have high melting points (>200°) and are soluble in dimethylformamide and dimethylsulphoxide. The complexes behave as non-electrolytes in dimethylformamide. Since these cyclic products could not be isolated in the absence of metal ion, Zn(II), Cd(II) and Hg(II) appear to act as a kinetic 'template'.

Infrared Spectra

The pentadenate DAPCH shows bands due to pyridine rings, amide groups, amino groups and hydrazine or azomethine groups. The infrared spectrum of the ligand DAPCH shows bands at 1675, 1500, 1260, 660 and 530 cm^{-1} which may be assigned to amide-I (νC=O) amide-II (νCN + δNH), amide-III (δNH), amide-IV (ϕC=O) and amide VI (πC=O) vibrations[13,14] respectively. In the complexes, all these bands except amide-I show upward shifts (~60–20 cm^{-1}), whereas the amide-I band shows a downward shift (~35–25 cm^{-1}). These changes in amide group vibrations indicate that the amide oxygen (ketonic) takes part in coordination to the metal atom.[15,16] This has further been confirmed by the appearance of new bands at *ca*. 490–60 cm^{-1} assignable[17] to ν(M—O).

The ligand shows a weak band at *ca*. 1640 cm^{-1}, which can be assigned[18] to the ν(C=N) vibration of azomethine linkage. The appearance of a weak (νC=N) band is in accord with the observations of several other workers.[18,19] The band due to ν(C=N) appears at slightly lower wavenumbers (~1625–1620 cm^{-1}) in its complexes suggesting that nitrogen atom of the azomethine is coordinated to the metal atom.[18] The bands appearing in the region 400–360 cm^{-1} may be assigned to ν(M—N) vibrations.[17] The pyridine ring vibrations most affected by pyridine nitrogen coordination to the metal atom are 8a (pyridine ring deformation), 6a (in-plane ring deformation) and 16b (out-of-plane deformation).[20,21] These vibrations appear at 1580, 620 and 410 cm^{-1}, respectively, in the free ligand. In all the complexes, these bands show upward shifts (~30–10 cm^{-1}) indicating pyridine nitrogen coordination to the metal atom.[20,21] The ν(M—Py) vibrations are located at *ca.* 275–250 cm^{-1}. The ligand DAPCH also shows a broad band at 3250 cm^{-1} along with two shoulders at 3300 and 3230 cm^{-1} which may be due[22] to ν_{sym}(NH) and ν_{asym}(NH) vibrations. In the complexes these bands persist indicate the non-coordination of the terminal amino group to the metal atom.

On the basis of above spectral features, a seven-coordinated structure may be suggested for the Zn(II), Cd(II), and Hg(II) complexes of DAPCH, in which the ligand coordinates *via* one pyridine nitrogen, two azomethine nitrogen and two amide oxygen atoms and the two axial positions are occupied by different anions.

The infrared spectra of the macrocyclic complexes do not show any significant changes. However the ν(NH$_2$) bands disappear. Only one band is observed in the ν(NH) region at 3200 cm^{-1} which may be due to a secondary amino group, establishing the condensation of the primary amino group with the carbonyl group of 2,6-diacetylpyridine. This is further supported by the appearance of a very weak band at 1638 cm^{-1}, in the [M(L′)X$_2$] complexes, establishing the formation of an azomethine linkage. In the binuclear complexes, this band disappears which may be taken as evidence of coordination of the azomethine nitrogen to another metal atom. Further, the medium or weak bands appearing at *ca.* 1570, 620 and 420 cm^{-1} in [M(L′)X$_2$] type complexes, may be due to 8a, 6a, 16b vibrations of the non-coordinated pyridine group.[20] In the binuclear complexes, these bands shift to higher frequency and overlap with the coordinated pyridine ring vibrations of the first metal as a result of which broad bands appear at *ca.* 1595, 630 and 425 cm^{-1}. This confirms the coordination of the second pyridine nitrogen to another metal atom. The spectral features in conjunction with the intense colour of the complexes support the formation of macrocyclic ligand complexes. The intense colour originates from the high degree of conjugation present in the macrocyclic systems.

In addition to the above bands, the nitrato complexes of zinc, cadmium and mercury show bands at *ca.* 1550–1530, 1270–1260, 1040–1025 cm^{-1} due to ν_{asym}NO$_2$, ν_{sym}NO$_2$ and νNO indicating the presence of coordinated nitrate groups in the complexes. In the chloro, bromo and iodo complexes, the bands appearing at *ca.* 360–340, 310–300 and 280–275 cm^{-1} may be assigned to ν(M—Cl), ν(M—Br) and ν(M—I) vibrations,[17] respectively. The infrared spectra of the acetato complexes show bands at *ca.* 1540–1530 and 1270–1260 cm^{-1} due[22] to asymmetric and symmetric COO stretching vibrations and confirming the presence of coordinated acetate groups in the complexes.

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