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Complexes of a New Series of α-Diimine Macrocycles, I: Template Synthesis of Cadmium(II) Complexes of Tetraazamacrocycles Derived from 2,3-Butanedione or Benzil

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Summary. Cadmium(II) complexes of the type [Cd*L*] $(NO_3)_2$ (where *L* = tetraazamacrocycle with a 12 to 32-membered ring) have been synthesized by the reactions of 2,3-butanedione or benzil with different aliphatic diamines viz. ethylenediamine, 1,3-diaminopropane, 1,4-diaminobutane, 1,6-diaminohexane, 1,8-diaminooctane and 1,12-diaminododecane in the presence of Cd(II) as template. These complexes have been characterized by elemental analyses, conductivity measurements and IR and NMR spectral studies.

Keywords. Macrocyclic complexes; Conductances; IR spectra; NMR spectra.

Komplexe einer neuen Serie von α-Diimin-Macrocyclen, 1. Mitt.: Synthese von Cadmium(II)-Komplexen von Tetraazamacrocyclen aus 2,3-Butandion oder Benzil

Zusammenfassung. Es wurden Cadmium(II)-Komplexe des Typs [Cd*L*] $(NO_3)_2$ (wobei *L* einen 12- bis 32-gliedrigen Tetraazamacrocyclus darstellt) mittels der Reaktion von 2,3-Butandion oder Benzil mit verschiedenen aliphatischen Diaminen (Ethylendiamin, 1,3-Diaminopropan, 1,4-Diaminobutan, 1,6-Diaminohexan, 1,8-Diaminooctan und 1,12-Diaminododecan) hergestellt. Die Komplexe wurden mittels Elementaranalyse, Leitfähigkeitsmessungen und Infrarot- bzw. Kernresonanzspektroskopie charakterisiert.

Introduction

Macrocyclic complexes of cadmium with porphyrin and corrin type macrocycles have received much attention [1, 2]. A quinquedentate macrocyclic complex of cadmium bearing similarities to porphyrin has been prepared [3]. Cd(II), Hg(II), and Pb(II) complexes of nonporphyrin tetraazamacrocycles have also been studied but are generally confined to a macrocyclic ring size of up to 16 atoms [4]. 14-Membered tetraazamacrocyclic complexes of Zn(II), Cd(II), Hg(II), and Pb(II) have been synthesized by Alcock et al. [5]. Pyridine containing pentaazamacrocyclic complexes of Cd(II) and Hg(II) have also been reported [6].

The template condensation of α-diketones with 1,3-diaminopropane in the presence of Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) leads to 14-membered macrocyclic complexes containing two α-diimines. A number of complexes of such macrocycles derived from 2,3-butanedione [7–9], benzil [10, 11] or substituted benzils [12] have been reported. In the present paper the synthesis of Cd(II) complexes of tetraazamacrocycles derived from α-diketones such as 2,3-butanedione or benzil and α,ω-diaminoalkanes is described.

Experimental

$Cd(NO_3)_2 \cdot 4H_2O$ was of AR grade. Benzil (SISCO, India) was recrystallized and 2,3-butanedione (Fluka), 1,2-diaminoethane (BDH), 1,3-diaminopropane (E. Merck), 1,4-diaminobutane (Fluka), 1,6-diaminohexane (Fluka), 1,8-diaminooctane (Fulka), methanol and butanol were distilled before use. 1,12-Diaminododecane (Fluka) was used as such.

Cd(II) *Complexes of Tetraazamacrocycles Derived from 2,3-Butanedione and Alkyldiamines*

$Cd(NO_3)_2 \cdot 4H_2O$ (1 mmol in 20 ml) was dissolved in *n*-butanol with stirring and 2,3-butanedione (2 mmol in 10 ml *n*-butanol) was added. Alkyldiamine (2 mmol in 20 ml) was added dropwise with constant stirring. Precipitation occurred immediately. After stirring for 7–8 h it was kept over night. The resulting solid was filtered, washed with *n*-butanol and dried under vacuo.

Tetraazamacrocyclic Complexes of Cd(II) *Derived from Benzil and Alkyldiamines*

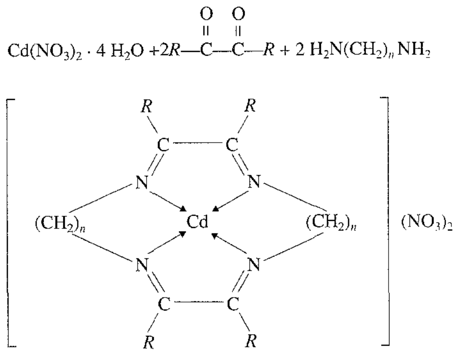
$Cd(NO_3)_2 \cdot 4H_2O$ (1 mmol in 25 ml) was dissolved in methanol and benzil (2 mmol in 15 ml) was added. The colour of the solution became yellow. It was refluxed for 24 h and then diamine (2 mmol in 25 ml methanol) was added. Precipitation occurred immediately. It was stirred for 16–20 h and the temperature was maintained at 60°C. The precipitate was allowed to settle over night and the resulting solid was filtered, washed and dried under vacuo.

Analytical Methods

Carbon and hydrogen were determined on a Coleman C, H analyser model 33. Nitrogen was estimated by Kjeldahl's method. Some of the complexes were analyzed at the Microanalytical Laboratory of James Cook University of North Queensland, Australia. Cadmium was estimated volumetrically using *EDTA*. Conductance was measured using a Systronics Digital Conductivity Meter 304 with a cell having a cell constant of $1.0 \cdot 10^{-3} M$ solutions in *DMSO* were used. Infrared spectra in the region 4000–200 cm^{-1} were recorded on a Perkin Elmer 577 IR spectrophotometer using KBr pellets. ^1H NMR spectra were recorded at 90 MHz in *DMSO-*d_6 on a Jeol FX90Q FT NMR spectrometer using *TMS* as an internal reference.

Results and Discussion

The reactions of $Cd(NO_3)_2 \cdot 4H_2O$ with 2,3-butanedione or benzil and different aliphatic diamines viz. 1,2-diaminoethane, 1,3-diaminopropane, 1,4-diaminobutane, 1,6-diaminohexane, 1,8-diaminooctane and 1,12-diaminododecane in 1:2:2 molar ratios result in the formation of macrocyclic complexes (**1**) according to the formula scheme.



$Cd(NO_3)_2 \cdot 4\,H_2O + 2R{-}\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}R + 2\,H_2N(CH_2)_nNH_2$

(1)

$n = 2, 3, 4, 6, 8, 12$

$R = CH_3, C_6H_5$

The resulting complexes are white or yellow solids. Most of them are soluble in dimethyl sulphoxide and insoluble in most organic solvents such as methanol, chloroform, carbon tetrachloride, acetonitrile, nitromethane, acetone, tetrahydrofuran and dimethyl formamide. The analysis and the characteristics of the complexes are given in Table 1.

Infrared Spectra

Characteristic IR bands of Cd(II) complexes are recoded in Table 2. No absorption band was observed at 1 700 cm^{-1} and 3 200 – 3 300 cm^{-1} indicating the absence of unreacted $>C=O$ and $-NH_2$ groups. In Pb(II) complexes of N_6O_4 macrocycles, Drew et al. [13] have reported the absence of any absorption at 1 700 cm^{-1} and 3 200 – 3 400 cm^{-1} which could occur if residual carbonyl of primary diamine groups were present. Cabral et al. [14] have shown the absence of absorption bands at 1 700 cm^{-1} or 3 200 – 3 400 cm^{-1} attributable to unreacted $>C=O$ or $-NH_2$ groups in hexaimine macrocyclic complexes of alkaline earth metals. Macrocyclic complexes of Cd(II) exhibit a strong absorption band at 1 600 – 1 640 cm^{-1} assignable to coordinated $>C=N$ group. Jackels et al. [15] have reported the $\nu C=N$ at 1 640 – 1 660 cm^{-1} for Zn(II) complexes of tetraazamacrocycles derived from 1-phenyl-1,2-propanedione and 1,3-diaminopropane. Macrocyclic complexes of alkaline earth metals have been reported to exhibit a sharp band at 1 640 cm^{-1} due to $>C=N$-linkage [16]. IR spectra of Cd(II) macrocyclic complexes show bands at 1 385, 829, and 720 cm^{-1} due to free nitrate and at 1 460, 1 280, 1 029, 805, and 740 cm^{-1} due to unidentate nitrate coordination. Thus the complexes appear to be pentacoordinated. For the complexes of Cd(II) with saturated tetraazamacrocyles Alcock at al. [17] have also observed bands at 1 460, 1 285, 1 030 and 805 cm^{-1} for unidentate coordination of nitrate and at 1 385, 829, and 720 cm^{-1} for free nitrate and have reported trigonal bipyramidal geometry. Strong bands at 430 – 490 cm^{-1} are assigned to νM-N [18, 19]. In case of Cd(II) complexes of macrocycles derived from benzil, bands at 1 570 – 1 600 cm^{-1} are observed due to phenyl groups similar to those reported for benzil [12].

Table 1. Analyses and characteristics of macrocyclic complexes of Cd(II)

Complex	Colour Decomposition point	Yield (%)	Analysis (%)			
			C found (calc.)	H found (calc.)	N found (calc.)	Cd found (calc.)
[Cd(*Me*$_4$) [12] tetraeneN$_4$] (NO$_3$)$_2$	Yellow 135°C	70	31.39 (31.55)	4.32 (4.40)	18.12 (18.40)	24.39 (24.60)
[Cd(*Me*$_4$) [14] tetraeneN$_4$] (NO$_3$)$_2$	Yellow 130°C	65	34.64 (34.68)	4.95 (4.98)	16.93 (17.33)	23.50 (23.18)
[Cd(*Me*$_4$) [16] tetraeneN$_4$] (NO$_3$)$_2$	Yellow 120°C	62	37.43 (37.47)	5.49 (5.50)	16.34 (16.39)	21.78 (21.91)
[Cd(*Me*$_4$) [20] tetraeneN$_4$] (NO$_3$)$_2$	Yellow 110°C	73	42.18 (42.22)	6.45 (6.37)	14.84 (14.77)	19.53 (19.75)
[Cd(*Me*$_4$) [24] tetraeneN$_4$] (NO$_3$)$_2$	Yellow 125°C	70	46.07 (46.11)	7.19 (7.09)	13.49 (13.44)	17.65 (17.98)
[Cd(*Me*$_4$) [32] tetraeneN$_4$] (NO$_3$)$_2$	Yellow 166°C	71	52.18 (52.13)	8.27 (8.20)	11.44 (11.39)	15.40 (15.24)
[Cd(*Ph*$_4$) [12] tetraeneN$_4$] (NO$_3$)$_2$	Colourless 135°C	61	54.48 (54.32)	3.98 (4.00)	11.78 (11.92)	15.73 (15.94)
[Cd(*Ph*$_4$) [14] tetraeneN$_4$] (NO$_3$)$_2$	Brownish 140°C	60	55.72 (55.70)	4.38 (4.40)	11.32 (11.46)	15.24 (15.33)
[Cd(*Ph*$_4$) [16] tetraeneN$_4$] (NO$_3$)$_2$	White 170°C	68	56.77 (56.80)	4.19 (4.24)	10.94 (11.04)	14.62 (14.76)
[Cd(*Ph*$_4$) [20] tetraeneN$_4$] (NO$_3$)$_2$	White 150°C	67	58.63 (58.79)	5.47 (5.43)	10.19 (10.28)	13.56 (13.75)
[Cd(*Ph*$_4$) [24] tetraeneN$_4$] (NO$_3$)$_2$	White 144°C	58	60.47 (60.51)	5.96 (6.00)	9.52 (9.62)	13.51 (12.87)
[Cd(*Ph*$_4$) [32] tetraeneN$_4$] (NO$_3$)$_2$	White 130°C	69	63.33 (63.37)	6.90 (6.95)	8.41 (8.52)	11.51 (11.40)

Conductance Measurements

Molar conductances of Cd(II) macrocyclic complexes are given in Table 2. The values fall in the range $50-90\,\mathrm{ohm^{-1}cm^2mol^{-1}}$ indicating them to be 2:1 electrolytes. Thus in solution both the nitrate groups are ionized whereas in solid one of the nitrate groups behaves as unidentate as evidenced by the IR spectra. For the transition metal macrocyclic complexes Lewis et al. [20] have reported conductances in the region $50-80\ \mathrm{ohm^{-1}cm^2mol^{-1}}$, suggesting them to be 2:1 electrolytes.

Nuclear Magnetic Resonance Spectra

δ (ppm) values of the protons in the ^{1}H-NMR spectra of the macrocyclic complexes of Cd(II) are given in Table 3. The spectra confirm the proposed structures of the

Table 2. Molar conductances and important IR bands (cm^{-1}) of Cd(II) macrocyclic complexes

Complex	Molar cond. ($ohm^{-1}cm^2mol^{-1}$)	νC=N	νC=C (aromatic)	νCd-N	νNO_3
$[Cd(Me_4)\ [12]\ tetraeneN_4]\ (NO_3)_2$	88	1631	–	450	1460, 1385, 1026, 829, 720
$[Cd(Me_4)\ [14]\ tetraeneN_4]\ (NO_3)_2$	89	1635	–	450	1385, 1029, 829, 740, 720
$[Cd(Me_4)\ [16]\ tetraeneN_4]\ (NO_3)_2$	87	1634	–	455	1385, 829, 865, 740, 720
$[Cd(Me_4)\ [20]\ tetraeneN_4]\ (NO_3)_2$	81	1636	–	458	1465, 1385, 830, 720
$[Cd(Me_4)\ [24]\ tetraeneN_4]\ (NO_3)_2$	[a]	1636	–	458	1385, 830, 740, 720
$[Cd(Me_4)\ [32]\ tetraeneN_4]\ (NO_3)_2$	[a]	1636	–	458	1460, 1385, 1029, 829
$[Cd(Ph_4)\ [12]\ tetraeneN_4]\ (NO_3)_2$	88	1635	1590 1560	450	1480, 1385, 829, 740, 720
$[Cd(Ph_4)\ [14]\ tetraeneN_4]\ (NO_3)_2$	90	1640	1585 1590	455	1385, 829, 740, 720
$[Cd(Ph_4)\ [16]\ tetraeneN_4]\ (NO_3)_2$	89	1630	1580 1590	455	1475, 1385, 1029, 829, 720
$[Cd(Ph_4)\ [20]\ tetraeneN_4]\ (NO_3)_2$	[a]	1615	1575 1550	455	1460, 1385, 829, 740, 720
$[Cd(Ph_4)\ [24]\ tetraeneN_4]\ (NO_3)_2$	[a]	1625	1595 1555	460	1470, 1385, 829, 740, 720
$[Cd(Ph_4)\ [32]\ tetraeneN_4]\ (NO_3)_2$	[a]	1620	1585 1560	450	1450, 1385, 829, 740, 720

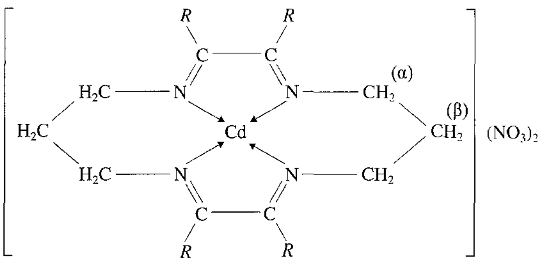
[a] Insoluble

Table 3. Chemical shifts (δ, ppm) of Cd(II) macrocyclic complexes

Complex	$-CH_3$[a]	α-CH_2	$-CH_2$ (β and others)	$-C_6H_5$
$[Cd(Me_4)\ [12]\ tetraeneN_4]\ (NO_3)_2$	0.88t	2.15s	–	–
$[Cd(Me_4)\ [14]\ tetraeneN_4]\ (NO_3)_2$	0.88t	2.99t[b]	1.71q[b]	–
$[Cd(Me_4)\ [16]\ tetraeneN_4]\ (NO_3)_2$	0.88t	2.42t[b]	1.49m	–
$[Cd(Me_4)\ [24]\ tetraeneN_4]\ (NO_3)_2$	0.88t	2.55t[b]	1.32m	–
$[Cd(Me_4)\ [32]\ tetraeneN_4]\ (NO_3)_2$	0.88t	2.50t[b]	1.29m	–
$[Cd(Ph_4)\ [14]\ tetraeneN_4]\ (NO_3)_2$	–	2.81t[b]	1.58q[b]	7.5–7.9m
$[Cd(Ph_4)\ [16]\ tetraeneN_4]\ (NO_3)_2$	–	2.46t[b]	1.63m	7.6–7.9m
$[Cd(Ph_4)\ [20]\ tetraeneN_4]\ (NO_3)_2$	–	3.16t[b]	1.28m	7.4–7.8m

[a] Coupling constant $J \sim 3$ Hz
[b] Coupling constant $J \sim 6$ Hz

complexes. In the complex $[Cd(Me_4)\ [14]\ tetraene\ N_4]\ (NO_3)_2$ (**2**) the α-CH_2 protons and β-CH_2 protons appear at δ 2.99 ppm (triplet) and δ 1.71 ppm (quintet), respectively. In free 1,3-diaminopropane the α-CH_2 protons appear at δ 2.79 (triplet) and the β-CH_2 protons at δ 1.60 ppm (quintet) [21]. Downfield shifting of α-CH_2



2 $R = CH_3$

3 $R = C_6H_5$

and β-CH_2 protons supports the formation of a macrocyclic complex via $C=N$ linkage. Methyl protons give a triplet at δ 0.88 ppm due to long range coupling with the α-CH_2 protons. In free 2,3-butanedione the methyl protons appear at δ 1.46 ppm. Upfield shifting of methyl protons supports the coordination of the metal atom to the macrocycle. Similarly, in the complex [Cd(*Ph*$_4$) [14] tetraeneN_4] $(NO_3)_2$ (**3**) the aromatic protons are observed at δ 7.2 – 7.9 ppm and the α-CH_2 and β-CH_2 protons appear at δ 2.81 ppm (triplet) and δ 1.58 ppm (quintet), respectively.

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