

Synthesis, characterization and electrochemistry of unsymmetrical macrocyclic cobalt(II) complexes derived from bis(benzil)ethylenediimine[†]

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Macrocyclic cobalt(II) complexes with varying ring sizes (12-14 membered) have been synthesized by using template method with bis(benzil)ethylenediimine precursor. These complexes have been characterized by elemental analyses, conductance, IR and electronic spectra. The spectral data suggest octahedral geometry for all the complexes. Various ligand field parameters have been calculated. The CV results suggest that the cobalt complexes derived from aromatic diamines are reduced at more negative potentials.

The catalytic activity of vitamin B₁₂ is in part due to the presence of unsymmetrical and flexible equatorial ligand system^{1,2}. Although the macrocyclic metal complexes using acetylacetonone³⁻⁵ and 2,6-di-acetylpyridine^{6,7} have been reported, the studies on unsymmetrical macrocyclic cobalt(II) complexes with varying ring sizes are limited⁸. Further electrochemical studies on macrocyclic metal complexes are infrequently made. It led us to synthesize and characterize the following unsymmetrical macrocyclic cobalt complexes using bis(benzil)ethylenediimine.

Materials and Methods

All the solvents used were of AR grade. Ethylenediimine and CoCl₂·6H₂O were of Qualigens make. 1,3-Diaminopropane, 1,2-diaminopropane, 1,4-diaminobutane, 1,2-diaminobenzene (recrystallised from toluene before use) and 3,4-diaminotoluene were of Fluka AG make.

The elemental analysis were performed by the HERAEUS (Mikro standard 8304071, available at IISc, Bangalore) carbon and hydrogen analyzer. The IR spectra were recorded in the range 4000-400 cm⁻¹ using KBr discs with Perkin-Elmer 983 G spectrophotometer. The electronic spectra for all complexes in the UV and visible region (180-1100 nm) were recorded with Shimadzu UV-160 A spectrophotometer. The electrical conductivity measurements were made in DMF (ca. 10⁻³ M) at room temperature (27 ± 2°C) using

a Systronic 303 direct reading conductivity bridge. The cyclic voltammetry was performed with a BAS model CV-27 controller and a conventional three electrode configuration with glassy carbon working electrode, silver/silver chloride reference electrode and platinum counter electrode. Nitrogen was used as a purge gas and all solutions were 0.1 M concentration in TBAPF₆.

Synthesis of bis(benzil)ethylenediimine⁹

In a 100 ml short-necked round-bottomed flask, benzil (5 g, 24 mmol) was taken in ethanol (30 ml) and to this was added 1,2-diaminoethane (0.80 ml, 12 mmol) in ethanol (20 ml) and heated under reflux for 3h. The reaction mixture was cooled and the reddish yellow coloured compound obtained was recrystallized from ethanol. m.pt. 86-88°C, yield, 65%.

Synthesis of complexes (I-VI)

The reaction mixture containing bis(benzil) ethylenediimine (2 g, 4.3 mmol), diamine (4.3 mmol) and CoCl₂·6H₂O (1.02 g, 4.3 mmol) in methanol (25 ml) was heated under reflux for 4 h. The reaction mixture was cooled and transferred to evaporating dish and set aside for few hours, whereupon a dark green-coloured compound separated out. It was collected, washed with hot water, then with cold methanol and dried *in vacuo*.

Complexes (VII and VIII) were prepared by the cyclocondensation of 1:1:1 molar (4 mmol) quantities of benzil, CoCl₂·6H₂O and 1,3-diaminopropane, (or) 1,2-diaminopropane. The analytical data for all complexes are given in Table 1.

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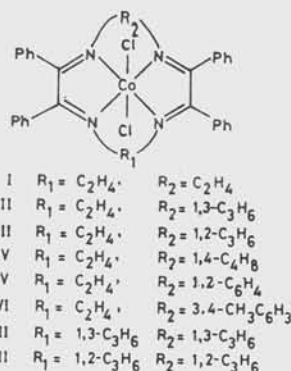


Table 1—Analytical data of macrocyclic cobalt complexes

Complex	Mol. formula	Colour (Yield, %)	Found (Calcd.), %	
			C	H
I	$[Co(C_{32}H_{28}N_4)Cl_2]$	Brownish Green (35)	64.10 (64.22)	4.65 (4.68)
II	$[Co(C_{33}H_{30}N_4)Cl_2]$	Green (58)	64.66 (64.72)	4.92 (4.90)
III	$[Co(C_{33}H_{30}N_4)Cl_2]$	Pale Green (40)	64.90 (64.72)	4.84 (4.90)
IV	$[Co(C_{34}H_{32}N_4)Cl_2]$	Green (22)	64.95 (65.19)	5.02 (5.11)
V	$[Co(C_{36}H_{28}N_4)Cl_2]$	Brown (45)	66.82 (66.90)	4.28 (4.34)
VI	$[Co(C_{37}H_{30}N_4)Cl_2]$	Green (36)	66.90 (67.28)	4.59 (4.55)
VII	$[Co(C_{34}H_{32}N_4)Cl_2]$	Blackish Green (36)	65.22 (65.19)	5.14 (5.11)
VIII	$[Co(C_{34}H_{32}N_4)Cl_2]$	Green (35)	65.09 (65.19)	5.05 (5.11)

Table 2—Electronic spectral data and ligand field parameters of cobalt complexes in chloroform/pyridine

Complex	ν_1^* (cm^{-1})	ν_2 (cm^{-1})	ν_3 (cm^{-1})	B^1	B_{35}^1	10 Dq	$\nu_2 - \nu_1$	ν_2/ν_1	LFSE (kcal/mol)
I	6805	16000	20000	863	0.89	8315	9195	2.35	23.75
	7082	15540	18180	762	0.78	8083	8418	2.18	23.10
II	5995	14925	18690	621	0.64	6825	8930	2.49	19.50
	6308	14598	19417	799	0.82	7255	8290	2.31	20.60
III	6568	15625	21980	899	0.93	7585	9057	2.38	21.67
	6768	16260	24255	950	0.98	7833	9492	2.40	22.38
IV	7061	16130	20833	861	0.89	8114	9069	2.28	25.19
	5706	14492	22988	930	0.96	6649	8786	2.54	25.10
V	6795	15873	21505	884	0.91	7834	9078	2.34	25.94
	7312	17241	23810	976	1.01	8437	9929	2.36	28.36
VI	6026	14598	21276	867	0.89	6975	8572	2.42	24.49
	6728	16260	23530	959	0.99	7792	9532	2.42	27.23
VII	6219	15503	19417	643	0.66	7078	9284	2.49	26.53
	6776	16129	22727	930	0.96	7827	9353	2.38	26.72
VIII	6269	15150	21990	897	0.92	7255	8881	2.42	25.37
	6263	14814	20833	852	0.88	7192	8591	2.38	24.55

*Calculated value; $B = 1/510 [8\nu_3 - 2\nu_2] \pm 3[81\nu_3^2 - 16\nu_2(\nu_2 - \nu_3)]^{1/2} B/971$

Results and Discussion

All the complexes are stable at room temperature, non-hygroscopic, sparingly soluble in methanol or ethanol and readily soluble in acetonitrile (CH_3CN), DMF and DMSO. The analytical data are consistent with the proposed molecular formulae, $[Co(mac)Cl_2]$ where, mac is a macrocyclic ligand with varying ring size (Table 1). The molar conductivity data show that the present complexes are non-electrolytes. The presence of chloride is evident only after the chemical decomposition of complexes suggesting the presence of chloride in coordination sphere.

The electronic spectra of the present complexes were recorded in chloroform and pyridine. In the electronic spectra of cobalt tetraaza macrocyclic complexes, three bands are observed at 5995-7061 (ν_1), 14598-16000 (ν_2) and 18691-20000 cm^{-1} (ν_3) which can be assigned to ${}^4T_{1g} \rightarrow {}^4T_{2g}$, ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions respectively, in an octahedral geometry^{11,12}. Various ligand field parameters for the cobalt complexes are given in Table 2. The high values of 10 Dq and interelectronic repulsion (B) are consistent with the nitrogen coordination of macrocyclic ligands. The ratio ν_2/ν_1 calculated is as required for the octahedral cobalt(II) complexes.

Comparison of electronic spectral parameters in chloroform and pyridine solvents suggests the coordination of latter to cobalt by displacing at least one chloride ligand present in axial position. The LFSE values for most of the complexes are relatively high in pyridine solvent.

dicates that the equatorial ligands of **I** and **II** have greater ability to stabilize the Co(I) oxidation state. This trend is observed in DMF and acetonitrile solvents. As the ring size increases, $E_{1/2}$ values for Co(II)→Co(I) couple shifts towards less negative potentials.

Acknowledgement

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