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

M Radhakrishna Reddy, K Mohana Raju & K Hussain Reddy* Department of Chemistry, Sri Krishnadevaraya University, Anantapur 515 003

Received 2 November 1995; revised 23 January 1996

Macrocyclic cobalt(II) complexes with varying ring sizes (12-14 membered) have been synthesized by using template method with bis(benzil)ethylenediamine 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 B_{12} is in part due to the presence of unsymmetrical and flexible equatorial ligand system^{1,2}. Although the macrocyclic metal complexes using acetylacetone³⁻⁵ and 2,6-diacetylpyridine^{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)ethylenediamine.

Materials and Methods

All the solvents used were of AR grade. Ethylenediamine and $CoCl_2 6H_2O$ 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 Schimadzu UV-160 A spectrophotometer. The electrical conductivity measurements were made in DMF (*ca.* 10^{-3} *M*) at room temperature ($27 \pm 2^{\circ}$ 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

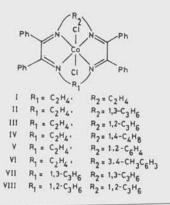
In a 100 ml short-necked round-bottomed flask, benzil (5 g, 24 mmol) was taken in ethanol (30 ml) and to this was added 1,2-diaminoethane (0.80 ml, 12 mmol) in ethanol (20 ml) and heated under reflux for 3h. The reaction mixture was cooled and the reddish yellow coloured compound obtained was recrystallized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

Synthesis of complexes (I-VI)

The reaction mixture containing bis(benzil) ethylenediamine (2 g, 4.3 mmol), diamine (4.3 mmol) and $CoCl_2 \cdot 6H_2O$ (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, $CoCl_2 \cdot 6H_2O$ and 1,3-diaminopropane, (or) 1,2-diaminopropane. The analytical data for all complexes are given in Table 1.

[†]Presented at the 6th symposium on Modern Trends in Inorganic Chemistry, held at the University of Hyderabad.



| Table Complex | 1—Analytical data of Mol. formula | f macrocyclic cob Colour Fo | alt complexes ound (Calcd.), % | | | |
|------------------|--|--------------------------------|-----------------------------------|----------------|--|--|
| | | (Yield, %) | С | Н | | |
| 1 | $[Co(C_{32}H_{28}N_4)Cl_2]$ | Brownish Green (35) | 64.10 (64.22) | 4.65 (4.68) | | |
| П | $[\mathrm{Co}(\mathrm{C}_{33}\mathrm{H}_{30}\mathrm{N}_4)\mathrm{Cl}_2]$ | Green (58) | 64.66 (64.72) | 4.92 (4.90) | | |
| Ш | $[{\rm Co}({\rm C}_{33}{\rm H}_{30}{\rm N}_4){\rm Cl}_2]$ | Pale Green (40) | 64.90 (64.72) | 4.84 (4.90) | | |
| IV | $[{\rm Co}({\rm C}_{34}{\rm H}_{32}{\rm N}_4){\rm Cl}_2]$ | 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 4 (67.28) (4 | | | |
| VII | $[Co(C_{34}H_{32}N_4)Cl_2]$ | Blackish Green (36) | 65.22 (65.19) | 5.14 (5.11) | | |
| vш | $[Co(C_{34}H_{32}N_4)Cl_2] \\$ | Green (35) | 65.09 (65.19) | 5.05 (5.11) | | |

Results and Discussion

All the complexes are stable at room temperature, non-hygroscopic, sparingly soluble in methanol or ethanol and readily soluble in acetonitrile (CH₃CN), 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 (v_1), 14598-16000 (v_2) and 18691-20000 cm⁻¹ (v_3) which can be assigned to ${}^{4}T_{1g} \rightarrow {}^{4}T_{2g}$, ${}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}(F)$ and ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(P)$ 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 v_2/v_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.

| omplex | $(cm^{+1})^{\nu_{+1}^{*}}$ | (cm^{-1}) | v ₃ (cm ⁻¹) | \mathbf{B}^{\dagger} | B ⁺ ₃₅ | 10 Dq | $\nu_2 - \nu_1$ | ν_2/ν_1 | LFSE (kcal/mol) |
|--------|----------------------------|-------------|---------------------------------------|------------------------|------------------------------|-------|-----------------|---------------|--------------------|
| 1 | 6805 | 16000 | 20000 | 863 | 0.89 | 8315 | 9195 | 2.35 | 23.75 |
| | 7082 | 15540 | 18180 | 762 | 0.78 | 8083 | 8418 | 2.18 | 23.10 |
| п | 5995 | 14925 | 18690 | 621 | 0.64 | 6825 | 8930 | 2.49 | 19.50 |
| | 6308 | 14598 | 19417 | 799 | 0.82 | 7255 | 8290 | 2.31 | 20.60 |
| Ш | 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 |

It may be considered important to note that 10 Dq varies strongly with ring size for constant donor atoms and axial ligands^{12,13}. The effect is large and parameters change over to ~ 15% of its value. The idea that a constant set of donor atoms should yield same ligand field is certainly wrong with present macrocyclic cobalt complexes. The cobalt complexes containing smaller (12-membered) ring show abnormally high 10 Dq values. If the ring size is too small it must be stretched to accommodate the metal ion. This distortion exerts a force that serves to enhance the metal donor interactions which increase the magnitude of 10 Dqvalue. Thus constrictive effect of small ring is felt by the cobalt complexes.

In the IR spectra of the complexes, the stretching and deformation vibrations of the NH₂ groups are absent. Strong bands appearing in the range 1615-1600 cm⁻¹ are assigned¹⁴⁻¹⁸ to the coordinated vC=N stretching vibrations in all the complexes. The bands at 1473-1495 cm⁻¹ (v_{asym} C - C₆H₅) and 1375-1390 cm⁻¹ (v_{sym} C - C₆H₅) characteristic of the benzil moiety are present in all the complexes. In the far IR spectra of all the complexes, additional bands are observed in the 440-485 cm⁻¹ region assigned to v(Co-N) vibrations which substantiate the participation of azomethine nitrogen in coordination¹⁹.

The cyclic voltammograms for the cobalt complexes are recorded in acetonitrile, DMF and DMSO in tetrabutylammonium hexafluorophosphate (TBAPF₆) supporting electrolyte vs. Ag/AgCl reference electrode (Table 3). In DMSO most of the complexes gave reversible peaks corresponding to Co(III)/Co(II) redox couple. In other solvents (acetonitrile and DMF), such reversible peaks are not observed. The cyclic voltammograms of III, V and VIII in DMSO has cathodic peak at -0.61 V vs Ag/AgCl (with $E_{1/2} = -0.54$ V) due to reversible cathodic-anodic peak systems that correspond to Co(III)/Co(II) couple. The CV of I and VIII in DMSO had an irreversible Co(II)/Co(I) couple at $E_{pc} = -1.27$ V and -1.53 V respectively.

The CV of **I**, **II**, **III** and **VII** in DMF show reversible Co(II)/Co(I) couple with $E_{1/2} = -1.1$ V. Similarly, in acetonitrile, compounds **I**, **II**, **IV**, **V** and **VII** show cathodic/anodic peak system at $E_{1/2} = -1.12$ V. The one-electron reduction of all cobalt(II) species is responsible for the reversible wave at ca - 1.1 V. The Co(II)/Co(I) $E_{1/2}$ values for all the complexes studied are similar to the value reported for aquocobalamin $(-1.02 \text{ V})^{20,21}$.

The first reduction system $Co(III) \rightarrow Co(II)$ depends on the nature of axial ligand. The reduction to cobalt(I) depends on the ability of equatorial ligands to stabilize the Co(I) oxidation state. Complexes V and VI are reduced from Co(II) to Co(I) at $E_{1/2}$ values of -1.49 and -1.48 V vs Ag/AgCl. The corresponding 12-membered macrocyclic tetraaza cobalt complexes (I and II) are reduced at less negative potentials. These results in-

Table 3—Cyclic voltammetric data of cobalt complexes ($\sim 10^{-1} M$) in DMF, DMSO and CH₃CN containing 0.1 *M* TBAPF₆ at 1.0 V/s at glassy carbon electrode, temp. = 25°C

| Complex | Co-redox couple | $-E_{pr}(\mathbf{V})$ | | $-E_{pa}(\mathbf{V})$ | | $-E_{1/2}(\mathbf{V})$ | | | $E(\mathbf{mV})$ | | | | |
|---------|--------------------|-----------------------|------|-----------------------|------|------------------------|--------------------|------|------------------|--------------------|-----|------|--------------------|
| | | DMF | DMSO | CH ₃ CN | DMF | DMSO | CH ₃ CN | DMF | DMSO | CH ₃ CN | DMF | DMSO | CH ₃ CN |
| 1 | $\Pi I / \Pi$ | 0.65 | - | | | - | | - | | — | | - | 7 |
| | II/I | 1.42 | 1.27 | 1.19 | 1.08 | - | 1.17 | 1.25 | - | 1.18 | 325 | _ | 20 |
| П | $\Pi I / \Pi$ | | | | | - | | | - | | | - | - |
| | Π/I | 1.06 | 1.03 | 1.16 | 0.98 | 0.80 | 1.04 | 1.02 | 0.92 | 1.10 | 80 | 227 | 120 |
| ш | 111/11 | | 0.64 | - | | 0.50 | | | 0.50 | - | | .43 | - |
| | Π/I | 1.08 | 1.55 | 1.22 | 0.98 | 0.85 | 1.09 | 1.02 | 1.20 | 1.11 | 10 | 70 | 130 |
| IV | III/II | 1.55 | 1.02 | 1.13 | - | 0.82 | 1.07 | - | 0.92 | 1.10 | | 200 | 60 |
| VI | 111/11 | | | _ | | - | - | | - | - | | | |
| | Π/I | - | 1.53 | 0.98 | - | 1.36 | 0.87 | | 1.45 | 0.93 | - | 170 | 110 |
| v | H1/11 | | 0.60 | — | | 0.48 | _ | | 0.54 | | - | 125 | - |
| | 11/1 | | | 1.52 | _ | - | 1.46 | | - | 1.49 | | - | 60 |
| | 11/1 | 1.57 | - | 1.53 | 1.44 | - | 1.42 | 1.51 | - | 1.48 | 133 | _ | 110 |
| VI | Ш/П | | - | - | | — | | | | - | | | _ |
| VII | HI/II | | _ | _ | | | _ | | _ | _ | | | - |
| | Π/I | 1.05 | 1.05 | 1.14 | 0.96 | 0.92 | 1.07 | 1.01 | 0.99 | 1.11 | 150 | 133 | 70 |
| VIII | III/II | | 0.59 | - | - | 0.48 | - | | 0.54 | | | 110 | _ |
| | 11/1 | - | 1.53 | 1.15 | - | - | - | | - | - | | - | - |

dicate 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) \rightarrow Co(I) couple shifts towards less negative potentials.

Acknowledgement

We are thankful to the DST, New Delhi (Grant No. SP/S₁/F-07/92) for financial support.

References

- Pratt J M, The Inorganic chemistry of vitamin B₁₂ (Academic Press, New York) 1972; Chem Soc Rev, (1985) 161.
- 2 Schrauzer G N, Acc chem Res, 1 (1968) 97 and references therein.
- 3 Truex J J & Holm R H, J Am chem Soc, 94 (1972) 4529.
- 4 Goedken V L, Pluth J J, Panq S S & Bursten B, J Am chem Soc, 98 (1976) 8014.
- 5 Chipperfield J R, Woodward S, J Chem Edn, 71 (1994) 75.
- 6 Lindoy L F, Tokel N E, Anderson C B & Busch D H, J Coord chem, 1 (1971) 7.

- 7 Rana V B, Singh D P, Singh P & Teotia M P, Trans Met Chem, 6 (1981) 36.
- 8 Hussain Reddy K, Krishnaiah G & Sreenivasulu Y, Polyhedron, 10 (1991) 2785.
- 9 Costes J P. Polyhedron, 6 (1987) 2169.
- 10 Geary M J, Coord chem Rev, 7 (1971) 81.
- 11 Lever A B P, Inorganic electronic spectroscopy (Elsevier, New York) 1984.
- 12 Martin L Y, DeHayee L J, Zomps L J & Busch D H, J Am chem Soc, 96 (1974) 4046.
- 13 Martin L Y, Sperati C R & Busch D H, J Am chem Soc, 99 (1977) 2968.
- 14 Eggleston D S & Jackhls S C, Inorg Chem, 19 (1980) 1953.
- 15 Coltrain B K & Jackhls S C, Inorg Chem, 20 (1991) 2032.
- 16 Baldwin D A, Peiffer R M, Richqott D W & Rose N A, J Am chem Soc, 95 (1975) 515.
- 17 Jackhls S C, Farmery K, Barefield E K, Rose N J & Busch . D H, Inorg Chem, 11 (1972) 2893.
- 18 Rana V B, Singh P, Singh D R & Teotia M P, Polyhedron, 4 (1982) 177.
- 19 Ferraro J R, Low frequency vibrations of inorganic and coordination compounds (Plenum Press, New York) 1972.
- 20 Costa G, Puxeddu A & Tauzer G, Inorg nucl chem Lett, 4 (1968) 319.
- 21 Lexa D & Saveant J M, Acc chem Res, 16 (1983) 235.