

SYNTHESIS AND ELECTROCHEMISTRY OF BINUCLEAR LEAD (II) AND COBALT (II) TETRAPYRROLE MACROCYCLES

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ABSTRACT. Lead (II) and Cobalt (II) complexes of the ligand 4,16,20,32 tetraethyl-15,21,31-tetramethyl-8,12,24,28,33,34,35,36-octaazapentacyclo-[28.2.1.1^{3,6}.1^{4,17}.1^{19,22}]hexatricula-1,3,5,7,12,14(35),15,17,19,21,23,28,30(33),31-tetradecane (bi-dptmd, 6H) have been synthesized. Electrochemical studies using cyclic voltammetric techniques on Pb₂ (bi-dptmd) (SCN)₂ indicate two well defined irreversible ligand oxidation waves at +0.74 V and at +0.98 V vs SCE and two lead (II) centered reduction waves at -0.80 V and -1.03 V vs SCE. In addition Pb²⁺/Pb⁰ couple wave is observed at -0.45 V vs SCE.

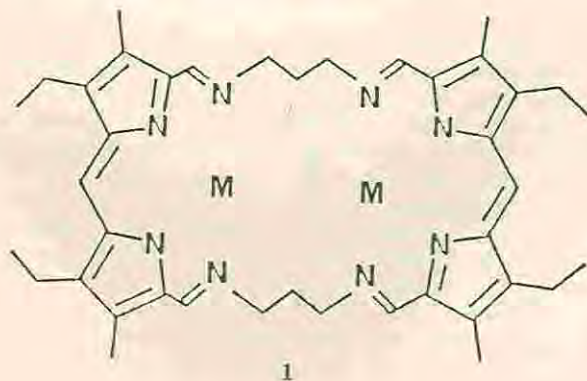
INTRODUCTION

The synthesis of binuclear complexes in which a ligand structure maintains the metal centers in close proximity represents an important area in the study of transition metal complexes.

The interest in these complexes derives in part from their ability to serve as simple models for multi-metal centred catalysts (1), as in the reaction involving oxygen activation.

Binuclear complexes of cofacial diporphyrins (2,3) or face-to-face porphyrins (4,5) have been reported. It has been found that several of the dicobalt (II) complexes of the cofacial diporphyrins catalyze the four-electron reduction of dioxygen to water (6-10).

In our laboratories we have synthesized a hybrid porphyrin-like ligand **1** that allows the incorporation of two metals within one macrocyclic system.



Since redox behaviour is so important in the chemical properties of transition metal complexes, the electrochemical means of assessing the chemical significance of the multi-metal centers was undertaken.

EXPERIMENTAL

Physical Measurements. IR spectra were recorded from 4000 to 600 cm^{-1} on an IBM IR-32 spectrophotometer. MS were run by Dr. C. Judson of the mass spectrometer laboratory, University of Kansas, using Ribermag R 10-10 spectrometer. Elemental analyses for carbon, hydrogen and nitrogen were performed at the microanalytical laboratory, University of Kansas, by Dr. T. Nguyen and at Mic Anal-Organic Microanalysis, Tucson, AZ. Electrochemical measurements were obtained on a PAR 173 potentiostat/galvanostat equipped with a PAR 179 digital coulometer and a PAR 175 universal programmer. A three electrode glass cell was used with a glassy carbon working electrode, a platinum wire counterelectrode and saturated calomel as reference electrode. Data were collected at room temperature, and no correction was made for junction potentials. Controlled potential electrolyses (CPE) were performed at a rotating platinum mesh working electrode using the same instrumentation.

Synthesis. The abbreviation used for the ligand derive from its component parts, i.e. bi for two, dp for dipyrromethene and tmd for 1, 3-propanediamine (trimethylenediamine).

The free base-ligand 4,16,20,32-tetraethyl-5,15,21,31-tetramethyl-8,12,24,28,33,34,35,36-octaazapentacyclo[28.2.1.1^{3,6}.1^{4,17}.1^{19,22}]hexatriaconta-3,5,7,12,14,16,19,23,28,30,32-dodecaene (bi-dptmd. 6H) and Pb_2 (bi-dptmd) $(\text{SCN})_2$ were synthesized and characterized according to our reported methods (11,12).

Co_2 (bi-dptmd) $(\text{Cl})_2$: A 100 ml 3-neck flask was equipped with a magnetic stirrer, a condenser, a heating mantle and a nitrogen gas inlet adapter. To this flask, the free ligand bi-dptmd. 6H (118.5 mg, 0.173 mmol) and 75 ml of methanol were added. The suspension was stirred vigorously under nitrogen and cobalt (II) chloride (163.5 mg, 0.692 mmol) was added. The mixture, which turned blue instantly, was brought to reflux for 10 h under nitrogen and cooled to room temperature. The sky-blue microcrystalline product was filtered through a fine glass crucible under nitrogen, rinsed with deaerated methanol and dried in vacuo (18). Yield 124.2 mg (75%). MS: $m/z = 760$ (M-2Cl).

RESULTS AND DISCUSSION

Synthesis. The synthesis of the free-base ligand and its lead (II) zinc (II) and copper (II) complexes have been reported (11,12). In the synthesis of binuclear cobalt (II) complexes Co_2 (bi-dptmd) Cl_2 , utilization of $\text{Co}(\text{BF}_4)_2$, $\text{Co}(\text{OAC})_2$ and CoBr_2 were not successful. The isolation of the chloride complex may be attributed to the fact that Cl^- can bridge the two metal ions, thereby stabilizing the tetrahedral, four coordinate cobalt (II) complex. The IR of the complex shows a very strong $\nu_{\text{C}=\text{N}}$ at 1653 which is consistent with uncoordinated $\text{C}=\text{N}$ stretching frequency (16). The cobalt complex, Co_2 (bi-dptmd) $(\text{Cl})_2$ has a magnetic moment of 4.50 B.M./metal center. This is consistent with three unpaired electrons per cobalt (d^7 high spin) in a tetrahedral geometry (17).

Electrochemistry. Bi-dpmtd. 6H: From the cyclic voltammogram of the free ligand (Fig. 1), it is clear that the ligand undergoes an irreversible two-electron oxidation at 1.03 V vs SCE. There is no reduction wave in the region 0 to -2.00

V. The oxidation wave is quite broad which is probably due to two sequential one-electron oxidation steps at very close potentials.

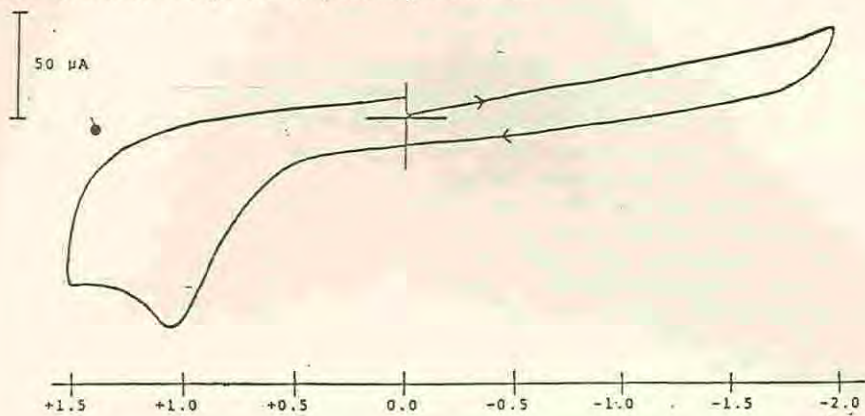


Fig. 1. Cyclic voltammogram of 1.00×10^{-3} M bi-dptmd. 6H in CH_2Cl_2 at 200 mV/s; supporting electrolyte (TBA) ClO_4 (0.1 M).

Pb_2 (bi-dptmd) (SCN) $_2$: The cyclic voltammogram for the complex is shown in Fig. 2. An initial sweep starting at 0.0 V between -1.50 and +1.50 V showed two well-defined irreversible ligand oxidation waves at +0.74 V and +0.98 V vs SCE and two lead (II) -centered reductions at -0.80 V and -1.03 V vs SCE. On the second reversal sweep of the potential from -1.50 V to +1.50 V vs SCE, a large oxidation peak appeared at -0.45 V vs SCE, which was not evident on the first sweep.

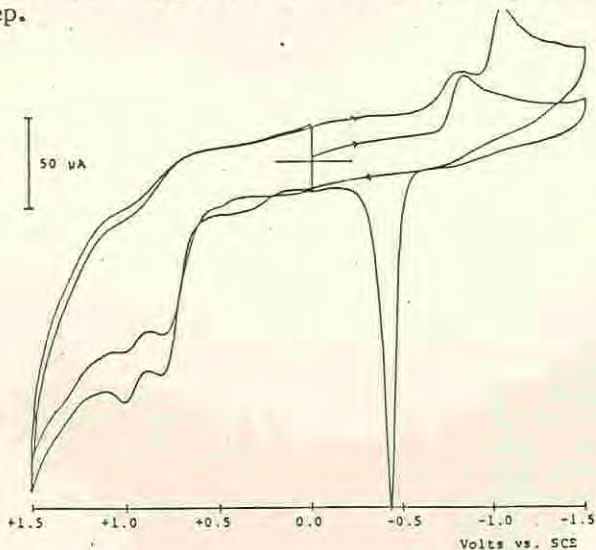


Fig. 2. Cyclic voltammogram of 3.07×10^{-4} M Pb_2 (bi-dptmd) (SCN) $_2$ in DMF at 200 mV/s; supporting electrolyte 0.1 M TBAP, scanning from 0.0 V to -1.5 V and then to +1.5 V.

Fig. 3 shows three repetitive scans from 0.0 V to -1.5 V back to +1.5 V vs SCE. It is observed that the two ligand centered oxidation peaks at +0.78 V and +0.98 V diminish as the number of scans increases. This is due to the fact that the ligand oxidation is irreversible. On the other hand for the lead centered peaks, we see that on the second scan, the Pb^{2+} reduction peak at -0.80 V diminishes and the peak at -1.08 V increases; and the reoxidation peak at -0.45 V increases. The peak at -0.80 V is attributed to complexed lead and that at -1.08 V to uncomplexed lead.

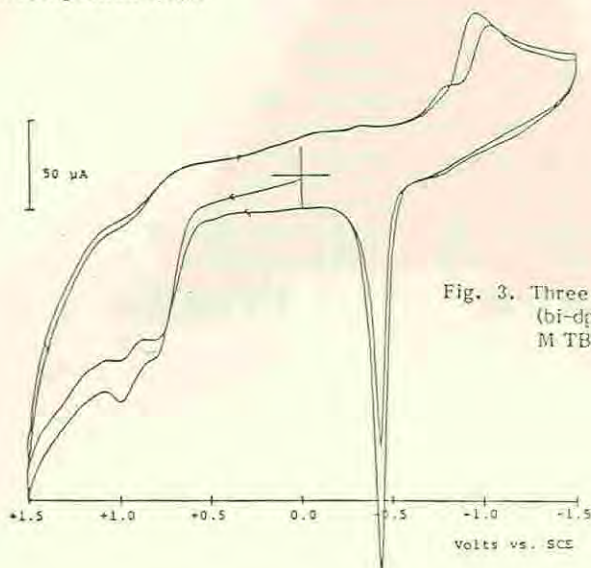


Fig. 3. Three repetitive scans of 3.07×10^{-4} M Pb_2 (bi-dptnd) $(SCN)_2$ in DMF at 200 mv/s; 0.1 M TBAP as supporting electrolyte.

Fig. 4 shows two scans, the first sweep is from 0 to +1.5 V. On the first sweep, the reduction peak at -0.80 V now appears as a shoulder to the peak of -1.08 V due to the presence of fewer complexed Pb^{2+} ; and on the second sweep we only see a single reduction peak at slightly less than -1.08 V corresponding to the reduction of uncomplexed Pb^{2+} ions. These results are probably attributed to the presence of two lead ions at different environments in the macrocyclic ligand.

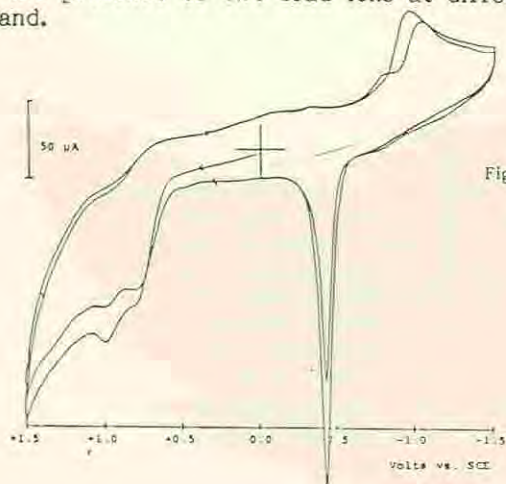
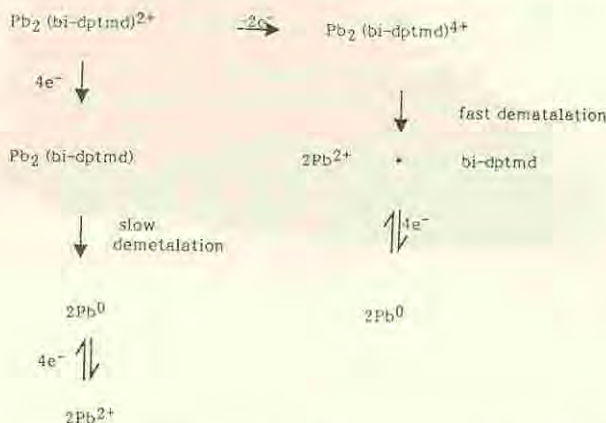


Fig. 4. Cyclic voltammogram of 3.07×10^{-4} m Pb_2 (bi-dptnd) $(SCN)_2$ in DMF at 200 mv/s, 0.1 M TBAP as supporting electrolyte. Initial scan from 0.0 V to +1.5 V and then to -1.5 V.

To ascertain the origin of the new wave, the electrochemistry of uncomplexed $\text{Pb}(\text{ClO}_4)_2$ was examined under analogous conditions. The reduction of Pb^{2+} to Pb^0 occurred at -0.74 V vs SCE and the oxidation of Pb^0 to Pb^{2+} at -0.40 V vs SCE.

These results suggest that the large oxidation peak at -0.45 V is due to anodic stripping where lead (0) is oxidized to lead (II). The two lead cation reduction which occur after the oxidation of the ligand can be rationalized as follows. The Pb^{2+} cations are probably in different environments and are expelled from the macrocyclic ligand due to the reduced affinity of Pb^{2+} cation for the neutral ligand. That the liberated Pb^{2+} is reduced to Pb^0 at the same potential observed for the reduction of free Pb^{2+} (-0.40 V vs SCE) further confirms the $\text{Pb}^{2+}/\text{Pb}^0$ couple. It is also shown in Fig. 4 that after the oxidation of the ligand, the demetalation step is very fast. Scanning n sweeps between 0 and -1.5 V did not result in the big anodic stripping peak indicating that demetalation occurs only after the ligand oxidation.

The oxidation of the ligand and the reduction-oxidation of the lead (II) ions, when combined with the demetalation reaction, lead to the overall oxidation-reduction scheme shown below (Scheme 1).



Scheme 1. Proposed mechanism of the demetalation of $\text{Pb}_2(\text{bi-dptmd})(\text{SCN})_2$ complex during electrolysis.

The above mechanism differs from the mechanism for the demetalation of lead (II) phthalocyanine, where the ligand is reduced fast followed by a slow demetalation process (13). Nor is it similar to the demetalation mechanism of silver and thallium porphyrins, where the central cation is reduced and then expelled owing to the large increase in its size, which the ligand cannot accommodate (14). Here we observe that the lack of affinity of the lead (II) ion for the neutral ligand formed on oxidation is responsible for the demetalation of the cations. In this study, there is no evidence for the formation of $\text{Pb}(\text{IV})$ complexes as has been postulated for lead porphyrins (15).

Electrochemical studies for the $\text{Co}_2(\text{bi-dptmd})(\text{Cl})_2$ have not been successful because of solubility problems.

Of interest to us also is the catalytic oxidation of organic substrates with the cobalt complexes. Preliminary results show that cobalt complex in coordinating solvents such as methanol catalyzes the oxidation of 2,6-di-tert-butylphenol

to the corresponding benzoquinone and the diphenoquinone. These studies will be reported in detail elsewhere.

ACKNOWLEDGEMENT

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18. IR (KBr) ν_{C-H} , 2961, 2928, 2866, $\nu_{C=N}$, 1653, pyrrol ring vibrations, 1581, 1539, cm^{-1} Anal. Calcd. for $Co_2(bi-dptmd)(Cl)_2 \cdot 3H_2O$: C, 54.24; H, 6.33; N, 12.66; Found: C, 53.48; H, 6.30; N, 12.47.