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LETTER

Synthesis, structure and electrochemistry of a novel dinuclear cobalt(II) complex containing pyrrole units: an unusual reductive electropolymerization of the dinuclear cobalt(II) complex

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Mononuclear metal complexes bearing a pyrrole unit have been the subject of much current interest [1–12] because of their potential use in obtaining polymer film-modified electrodes for specific applications (e.g. electrocatalysis, electrochromics and photosensitizers), but, hitherto, dinuclear metal complexes bearing pyrrole units have not been described. In general, pyrrole [13] and pyrrole bearing mononuclear metal complexes undergo oxidative electropolymerization [1–12]. We now report the synthesis, structure and electrochemical results of one dinuclear cobalt(II) complex bearing pyrrole units, **3**, where the dinuclear cobalt(II) complex **3** undergoes metal-mediated electropolymerization; this

reductive electropolymerization of the dinuclear cobalt(II) complex **3** is unprecedented to the best of our knowledge.

Dinuclear cobalt centers are known to be required for the electrocatalytic activation of small molecules such as oxygen and carbon dioxide [14–17]. The electrocatalytic reduction of molecular oxygen to H_2O_2 by compound **2** is remarkable. In view of the interesting electrocatalytic properties of **2** [14] and other dinuclear cobalt(II) complexes [15–17], we have synthesized the pyrrole bearing dinucleating ligand, **1**, whose dinuclear cobalt(II) complex **3** is used as a precursor to produce electroactive polymer film-modified electrodes.

4-(1H-pyrrole-1-yl)-3,5-bis(pyridine-2-yl)-1,2,4-triazole (**1**) was prepared by refluxing a mixture of 4-amino-3,5-bis(pyridine-2-yl)-1,2,4-triazole [18–20] (4.76 g, 0.02 mol) and 2,5-dimethoxy-2,5-dihydrofuran (3.3 g, 0.025 mol) in acetic acid (25 ml) and dioxane (20 ml) for 24 h. The solution was evaporated to dryness on a rotary evaporator and the solid residue obtained was dissolved in chloroform, washed with 10% aqueous ammonia and dried over sodium sulfate, filtered, and then chromatographed over neutral alumina with chloroform; **1** was obtained in 80% yield as a white crystalline solid. Mass spectrometric data and spectroscopic data were consistent with the structure of **1****.

Compound **3** was prepared by mixing stoichiometric amounts of **1** and $CoCl_2 \cdot 6H_2O$ in methanol/H_2O (80:20). On slow evaporation the dinuclear cobalt(II) complex crystallized from the reaction mixture in good (60–70%) yield as air-stable orange crystals. Complex **3** gave good elemental analyses†.

Data for **1: ^1H NMR (CDCl$_3$). $\delta = 6.23$ (2H, t, 3-H and 4-H of pyrrole), 6.88 (2H, t, 2-H and 5-H of pyrrole), 7.32 (2H, m, 4-H of pyridine), 7.82 (4H, m, 3-H and 5-H of pyridine), 8.52 (2H, d, 6-H of pyridine); MS, *m/e* 288; m.p. 200–202 °C. *Anal.* Calc for **1**, $C_{16}H_{12}N_6$: C, 66.66; H, 4.20; N, 29.16. Found: C, 66.41; H, 4.32; N, 29.98%.

†*Anal.* Calc. for **3**, $[C_{32}N_{12}H_{24}Co_2 \cdot (H_2O)_4]Cl_4 \cdot 2MeOH \cdot 2H_2O$: C, 40.49; H, 4.40; N, 16.67. Found: C, 40.27; H, 4.22; N, 16.82%.
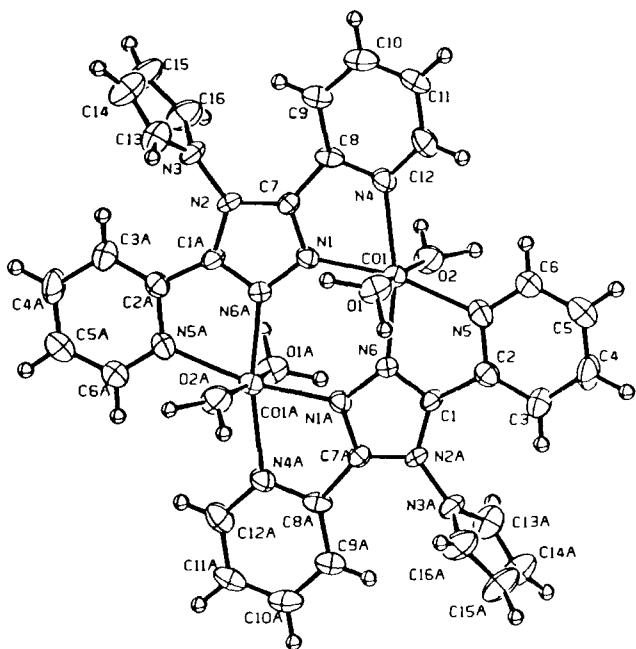

(L)

1   2   3

2
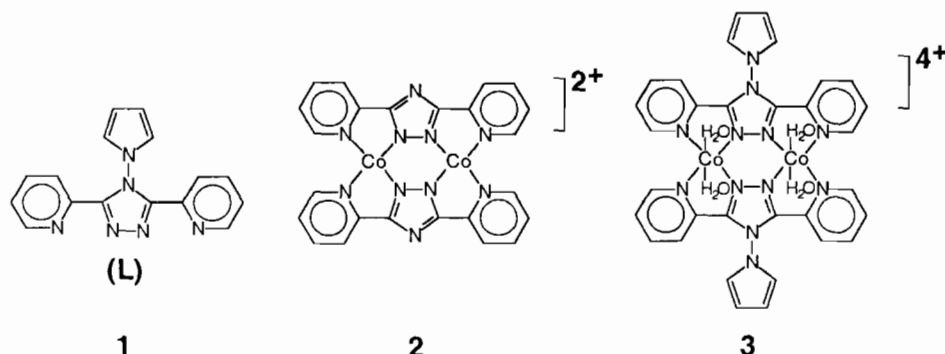
Fig. 1. View of the molecular shape of the dinuclear complex [Co₂L₂(H₂O)₄]Cl₄·2MeOH·2H₂O with atomic numbering system. Lattice methanol molecules, water molecules and the chlorides ions are omitted for clarity.

Figure 1 shows the X-ray crystal structure* of **3**, which consists of the $[Co_2L_2(H_2O)_4]^{4+}$ cation, four chloride anions, two solvent methanol molecules and two solvent water molecules. There is an inversion center in the center of the cation thereby making the two Co atoms crystallographically equivalent in the solid state. Each cobalt is coordinated by two triazole nitrogen atoms, two pyridine nitrogen atoms and two water molecules completing a CoN_4O_2 chromophore. The two cobalt centers are separated by 4.226(2) Å. All Co–O bond lengths are approximately equal at c. 2.06 Å, and the variation in the Co–N distances of the triazoles and pyridyl nitrogen atoms is quite large (c. 0.12 Å).

Reductive electropolymerization was carried out in a nitrogen atmosphere at room temperature, using a one compartment cell equipped with three electrodes. Complex **3** was dissolved (0.5×10^{-3} M) in acetonitrile together with the supporting electrolyte (0.1 M, Et₄NClO₄). Typically, film formation was achieved on

a glassy carbon electrode by cyclical potential scans between 0 and -1.70 V versus SCE at 100 mV s⁻¹.

A thin uniform, presumably metal-bound polymeric film is formed on the glassy carbon electrode by cyclic scanning of potentials between 0 and -1.70 V (versus SCE). The electrode surface becomes conducting as reduction proceeds. The increase in size of the cathodic and anodic peaks clearly indicates the deposition of an electroactive [21] polymer film on the electrode surface. A typical CV is shown in Fig. 2, curve A. After ten cyclical scans, the electrode is rinsed with acetone and dipped into fresh 0.1 M Et₄NClO₄/acetonitrile solution and cycling the potential between 0 and -1.70 V gives the cyclic voltammetry as shown in Fig. 2, curve B. The thickness of the deposited polymer can be controlled by varying the number of cyclical potential scans. The polymer film thus formed is insoluble in commonly used solvents.

In situ measurement of conductivity by twin electrode arrangements indicates that the polymer is fairly conductive (c. 2×10^{-6} Ω^{-1} cm⁻¹ at -1.40 V versus SCE). The polymer film formation is strongly dependent on solvents and supporting electrolytes. Polymer dissolves slowly on exposure to O_2-saturated solution of DMF or DMSO. However, the color of the dry film remains unchanged in air for several days, which indicates that the film is stable on exposure to O_2 in the absence of solvents. This film is polymeric; the polymeric behavior is inferred from its insolubility in a variety of common solvents such as CH_3COCH_3, CH_3CN and CH_2Cl_2. The dinuclear cobalt(II) complex **3** does not form a polymeric film on the electrode surface on anodic polymerization.
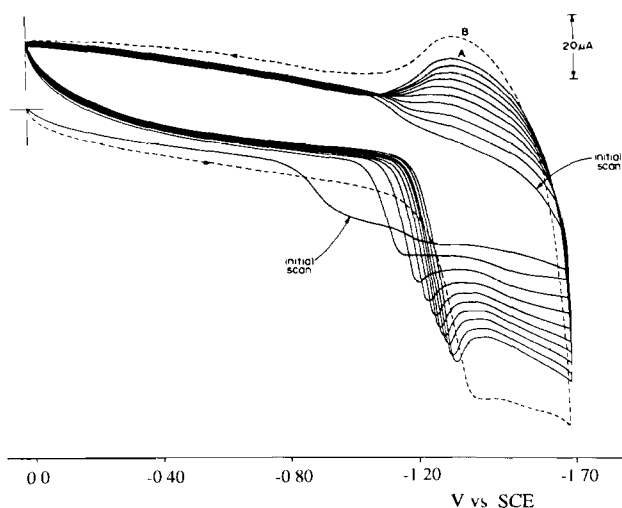

Fig. 2. Cyclic voltammograms in 0.1 M Et₄NClO₄/CH₃CN Curve A: ten cyclic potential scans from first scans between 0 and -1.70 V vs. SCE of a glassy carbon electrode in a 0 5 mM solution of **3** at 100 mV s⁻¹. Increasing size of the peaks represent growth of film Curve B· modified electrode in 0 1 M Et₄NClO₄/CH₃CN.

The metal free ligand **1** undergoes oxidation (at +1.20 V) and reduction (at −1.70 V) but it does not form a polymeric film on the electrode surface by either method; however, only reductive electropolymerization of the dinuclear cobalt(II) complex **3** is possible. This finding clearly indicates that the dinuclear cobalt(II) centers appear to be an important factor for reductive electropolymerization. The reductive process is probably ligand localized, because the dinuclear zinc complex also forms a non-conductive film by cyclical potential scans between 0.0 and −1.70 V versus SCE, but the free ligand **1** does not form a polymer. Therefore, the metal centers are important for polymerization. Analytical results of the polymer suggest that the pyrrole is not involved in the electropolymerization process, but it acts as a leaving group. Further work in this area is in progress.

Unlike compound **2**, the Co(III/II) couple has not been observed in either the monomer **3** in solution or in the polymer-modified electrode in the range 0.0 to +1.0 V versus SCE. The difference in the electrochemical properties between compounds **2** and **3** may be due to the ligand difference. The ligand in compound **2** is anionic because it has one ionizable proton per ligand whereas the ligand in compound **3** is neutral. Thus the dinuclear complex **3** is more cationic than compound **2**; therefore, compound **3** will be difficult to oxidize purely on electrostatic grounds.

This new polymer film-modified electrode might have scope for applications in industry, especially in the field of electro-reductive reactions; indeed reduction of CO_2 is observed in solution using complex **3** in DMSO and also by the modified electrode. Figure 3, curve a, shows the response of the modified electrode in the presence of N_2. Figure 3, curve b, shows the reduction of CO_2 by the modified electrode. The increase in current between −1.4 and −1.7 V versus SCE (Fig. 3, b) in a CO_2-saturated solution indicates that the film is functioning as an electron mediator and reducing CO_2.

The formation of dinuclear cobalt centers is observed when CO_2 is reduced electrochemically using the mononuclear cobalt complex suggesting that the dinuclear cobalt complexes might be suitable for the electrocatalytic reduction of small molecules such as O_2 and CO_2 [22]. The chemical reactivity, particularly the electrochemical and catalytic properties, of the dinuclear metal complexes is significantly different from that of simple mononuclear or isolated dinuclear metal complexes. These reactivity differences are probably associated with the metal–metal and metal–ligand–metal electronic interactions. Such interactions are absent in mononuclear metal complexes. It is therefore logical to examine the behavior of polymer modified electrodes using dinuclear metal complexes as monomer.
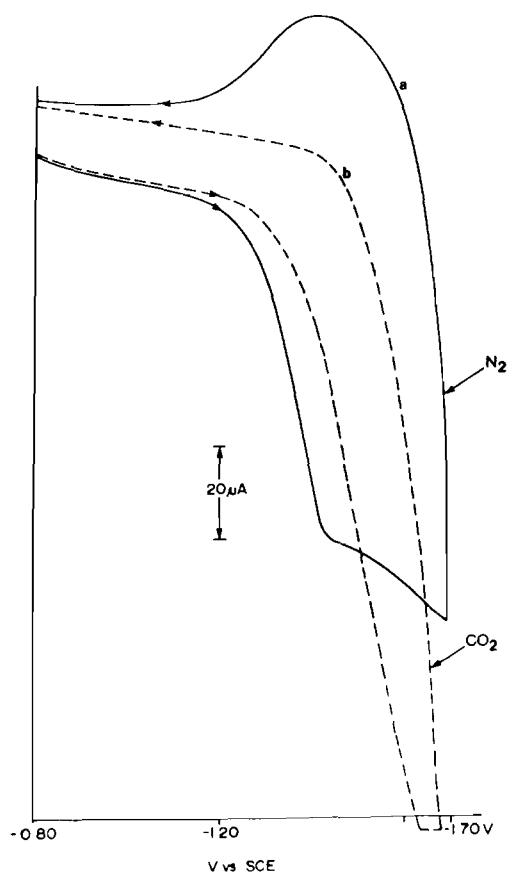

Fig. 3. Cyclic voltammograms of 0.1 M Et_4NClO_4/CH_3CN solution at 100 mV s^{-1}: (a) glassy carbon modified electrode in an N_2-saturated solution, (b) glassy carbon modified electrode in a CO_2-saturated solution.

Acknowledgements

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