

The Study of Electrochemical Behavior of Mono and Dinuclear Co(III) Complexes, $\text{trans-[pyCo((DO)(DOH)pn)(L)]PF}_6$ and $[\{\text{pyCo((DO)(DOH)pn)}\}_2(\mu\text{-dicyd})](\text{PF}_6)_2$

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ABSTRACT: *Electrochemical behavior of the new mono and dinuclear Co (III) complexes of the types $\text{trans-[pyCo((DO)(DOH)pn)(L)]PF}_6$ and $[\{\text{pyCo((DO)(DOH)pn)}\}_2(\mu\text{-dicyd})](\text{PF}_6)_2$ have been studied in acetonitrile solution. All the mono nuclear complexes show two quasi-reversible reduction couples associate to Co(III/II) and Co(II/I). Each of these redox couples split to two one electron waves in dinuclear complex.*

KEY WORDS: *Phenycyanamide, Co(III) complex, Comproportionation equilibrium constant, Oxime.*

INTRODUCTION

Much attention has been paid to the intramolecular electron transfer between metal ions in ligand-bridged di or oligonuclear complexes with regard to the design of photochemical molecular devices[1-3] or mimetic models of the photosynthetic systems in biology[4-5]. The control of signal transfer (electron) from one metal site to another obviously depends on control of metal-metal coupling. The degree of metal-metal coupling in dinuclear complexes is affected by both the inner-coordination sphere as well as the outer-coordination sphere (solvent)[6-31]. The strength of donor-acceptor coupling can range from nonexist (class I) to weak (class II) to very strong (class III). For a class III complex, there is no thermal barrier for electron transfer between metal ions and, thus the odd electron exists in a

delocalized state. Metal-metal coupling give rise to a metal-to-metal charge transfer (MMCT) transition in the complex's electronic absorption spectrum. The stability of a mixed-valence complex(III,II) relative to its oxidized and reduced forms can be quantified by the comproportionation equilibrium constant(K_c)[6].



$$K_c = [\text{III,II}]^2 / [\text{III,III}][\text{II,II}]$$

The larger K_c is, the greater the electronic coupling. K_c is usually deduced from the difference in potential between metal center reduction couples, $\text{Log } K_c = 16.9(\Delta E)$.

In order to explore the effect of the inner and outer-coordination sphere on the redox couples, electrochemical

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behavior of a series of mono and dinuclear Cobalt (III) complexes, *trans*-[pyCo((DO)(DOH)pn)(L)]⁺, *trans*-[pyCo((DO)(DOH)pn)₂(μ-dicyd)]²⁺, where L = monoanion of phenylcyanamide (pcyd⁻), 2-chlorophenylcyanamide (2-Clpcyd⁻), 4-methylphenylcyanamide (4-Mepcyd⁻) and dicyd²⁻ = 1,4-dicyanamidobenzene dianion and (DO)(DOH)pn = N², N^{2'}-propanediylbis(2,3-butanedione 2-imine 3-oxime) which have previously been synthesized and characterized [29,31], were studied by cyclic voltammetry.

EXPERIMENTAL

Materials

All of the chemicals and solvents used were analytical grade. Acetonitrile, diethylether, acetone and toluene were purchased from Merck (Darmstadt, Germany).

Tetrabutylammoniumhexafluorophosphate (TBAH) and alumina(WA-1, 150 mesh) were purchased from Aldrich and used without further purification. Syntheses of the thallium salts of phenylcyanamide ligands has been previously described [8].

Measurements

Cyclic voltammograms were recorded by using a Metrohm 694 apparatus. Three electrodes were utilized in this system, a platinum disk working electrode (RDE), a platinum wire auxiliary electrode and Ag/AgCl reference electrode. The platinum disk working electrode was manually cleaned with 1- μm diamond polish prior to each scan.

The supporting electrolyte, tetrabutylammoniumhexafluorophosphate(TBAH), was recrystallized twice from ethanol-water (1/1) and vacuum-dried at 110 °C overnight. Acetonitrile was distilled over alumina and degassed under vacuum prior to use in cyclic voltammetry. The solutions were deoxygenated by purging with argon(Ar) for 15 min and blanketed with argon prior to each scan.

All voltammetric measurements were carried out using a 10⁻³ M solution of the complex in acetonitrile containing 0.1 M (TBAH).

RESULTS AND DISCUSSION

The electrochemical data are given in Table 1 and a representative voltammogram of mononuclear complex, *trans*-[pyCo((DO)(DOH)pn)(4-Mepcyd)]⁺ and that of the

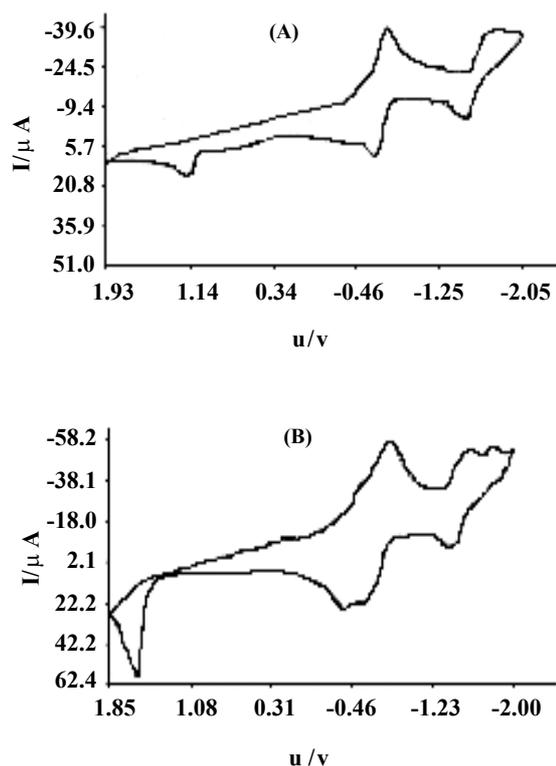


Fig.1: Cyclic voltammograms of (A) [pyCo((DO)(DOH)pn)(4-Mepcyd)]⁺ and (B) [pyCo((DO)(DOH)pn)₂(μ-dicyd)]²⁺ in acetonitrile solution (0.1 M TBAH) at the scan rate of 200 mV/s.

dinuclear complex, *trans*-[pyCo((DO)(DOH)pn)₂(μ-dicyd)]²⁺ is compared in Fig.1. Since the phenylcyanamide ligands behave like pseudo halogens, the voltammograms of the mono-nuclear complexes presented in this paper, show two subsequent cathodic-anodic peak systems corresponding to the two Co(III)/Co(II) and Co(II)/Co(I) reduction couples. This behavior is in accord with that observed for *trans*-[pyCo((DO)(DOH)pn)Cl]⁺ [32]. These two reduction couples are quasi-reversible and generally possess invariant anodic to cathodic peak separation ranging from 120 to 150 mV, respectively at scan rates between 100 and 500 mV/s in acetonitrile. In comparison to the other Schiff-base Co(III) complexes previously described [31,33-35], the Co(II/I) reduction waves for the mono-nuclear complexes *trans*-[pyCo((DO)(DOH)pn)(L)]⁺, where L = monoanion of phenylcyanamide (4-Mepcyd⁻) [1], (pcyd⁻) [2], (2-Clpcyd⁻) [3] appear at -1684, -1686 and -1692 mV, respectively vs Ag/AgCl as a reference electrode. This redox couple is relatively

Table 1: Electrochemical data(mV vs Ag/AgCl) for mono and dinuclear cobalt(III) complexes in 0.1 M TBAH acetonitrile solution with scan rate of 200 mV/s.

Complex	Redox Couple	E _{pc}	E _{pa}	E _{1/2}
[pyCo((DO)(DOH)pn)(4-Mepcyd)] ⁺	III/II	-771	-652	-711
	II/I	-1856	-1513	-1684
	L ⁰ /L ⁻	-	1175	-
[pyCo((DO)(DOH)pn)(pcyd)] ⁺	III/II	-800	-583	-691
	II/I	-1869	-1504	-1686
	L ⁰ /L ⁻	-	1187	-
[pyCo((DO)(DOH)pn)(2-Clpcyd)] ⁺	III/II	-712	-568	-640
	II/I	-1881	-1503	-1692
	L ⁰ /L ⁻	-	1273	-
[₂ {pyCo((DO)(DOH)pn)} ₂ (μ-dicyd)] ²⁺	III,III/III,II	-576	-453	-514
	III,II/II,II	-821	-605	-713
	II,II/II,I	-1582	-1430	-1506
	II,I/I,I	-1806	-1702	-1754
	L ⁻ /L ²⁻	-	1590	-

insensitive to the nature of axial ligands and is mainly influenced by the equatorial chelate. On the other hand, the Co (III/II) reduction waves for the complexes 1-3 appear at -711, -691 and -640 mV vs Ag/AgCl, respectively which depend on the exact axial ligation.

The anodic wave at positive potential is assigned to the oxidation of the coordinated phenylcyanamide anion ligand. Both the Co(III/II) reduction couples and ligand oxidation waves shift to more positive potentials as the electron-withdrawing ability of the substituents on the phenyl ring increase from Me to Cl. This is consistent with the expected decrease in the basicity of phenyl cyanamide ligands [6-21,31].

In comparison to the mononuclear complexes, the cobalt redox couples in the dinuclear complex occur in approximately the same region as the Co(III/II) and Co(II/I) of trans-[pyCo((DO)(DOH)pn)(L)]⁺.

However, these reduction couples are split into four one electron waves at -514, -713, -1506 and -1754 mV vs Ag/AgCl which correspond to Co(III,III/III,II), (III,II/II,II), (II,II/II,I) and (II,I/I,I), respectively, and is indicative of significant metal-metal coupling. These redox couples seem to be quasi-reversible with an average separation between cathodic and anodic waves of

73 mV that is largely independent of scan rate between 100-500 mV/s. Cyclic voltammetry of the free dicyd²⁻ molecule in acetonitrile showed two redox couples corresponding to dicyd^{-2/-} and dicyd^{0/-} [6,13,16,20,31]. In this dinuclear Co(III) complex between scanning rates 100-500 mV/s, we only see one anodic wave for the coordinated dicyd²⁻ due to decomposition of bridging ligand after oxidation. The value of K_c for the formation of Co(III)-Co(II) mixed-valence complex was determined to be 1.7 × 10⁴. In comparison to other dinuclear complexes, this magnitude of K_c support a class II assignment for the trans-[₂{pyCo((DO)(DOH)pn)}₂(μ-dicyd)]²⁺.

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