



Polarographic studies of Pd (II), Pt (II) and Co (III) complexes of Polyaza Ligands

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Abstract

The polarographic technique gives a convenient method for studying redox reactions. The complexes studied give well defined, diffusion controlled one electron transfer reduction waves. The waves are irreversible in behavior. In case of P+(II) complexes, a regular cathodic shift in half wave potential of changing over from the trans structural macro cycle to the cis is observed. The redox properties of polyaza macrocyclic ligands have been of continued interest. As a result of these studies several macro cyclic complexes have been used as oxidant, reductants and electro catalysts. Earlier work on the redox behavior of macrocyclic complexes had mainly dealt with unsaturated systems. Later studies have dealt with many types of saturated systems also. It is important to study the effect of ligand structure, chelate ring size, donor unsaturation, substituent pattern and relative position of five and six membered chelate rings. It has been shown that a decrease in the ligand field strength of the macrocyclic ligands conclude in an anodic shift in the oxidant and reduction potentials. A change in the nature of the ring substituents changes the redox potential. The changes in the redox potential in these complexes are influence the substituents on the metal nitrogen interaction. In this we discuss the polarographic behavior of the complexes of (L1) Me₂ (ET4) (14) diene (C₂₀H₄₀N₄), Me₂ (ET4) (14) ane (C₂₀H₄₄N₄), (L3) Me₆ (ET4) (14) diene (C₁₆H₃₅N₄) and, (L4) Me₂ (14) ane (C₁₆H₃₆N₄). The polarograms of the complexes in aqueous solution were marked on a Metrohm Polarecord 50 using a dropping mercury electrode (d.m.e.) as the working device. To choose a correct supporting electrolyte, polarographic wave of a few complexes were recorded in different electrolytes. It was observed that the best waves were prepared in 0.1 M sodium perchlorate. The one electron transfer irreversible waves related to the reduction of Pt (II) to Pt (I) and Pd (II) to Pd (I). It is reasonable to assume that the Pt – N distance is the significant factor. It has been seen that a change in the symmetry of the ligand result in change in the ligand field strength.

Key words: Polarographic technique, unsaturated systems, Redox potential.

Introduction

Polarographic technique gives a convenient procedure for on the redox behavior of macro cyclic complexes has significantly dealt with 14 membered unsaturated system but later work (Keene, 1998; Winkler, 1992) have dealt with many types of saturated system also. All the known complexes give diffusion controlled one electron transfer reduction waves. The waves are irreversible. The low values of $k^{\circ}f_1h_1$ the formal rate of reduction also favour this result. In case of Pt (II) complexes, a regular cathodic shift in half wave potential of changing over from the trans-structured macrocycle to the cis ones is seen. This type of nature has been related with the basicity of the do no nitrogen (Barigelletti and Flamigni, 2000;

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Sorell, 1989; Gomez *et al.*, 1990). The polarography technique of considering the reduction of metal complexes is an easy method of investigating their redox reactions. The redox qualities of polyaza macrocyclic ligands have been of continued interest (wang *et al.*, 1993) since the formation of such complexes (Nag and Chakravorty, 1980). The conclusion of these studies is that macro cyclic complexes have been used as oxidant (Olson and Vasilevskis, 1969; McAuley *et al.*, 1984), reductants (Whitburn and Laurence, 1979; McAuley *et al.*, 1983) and electrocatalysts (Raghuraman *et al.*, 2003). The prior work on the redox nature of macro cyclic complex is had with 14-membered unsaturated systems, which a few statements have addressed with even such systems as imine-carbinolamine and dicarbinolamine systems (Barefield *et al.*, 1976). Later studies have



addressed with many types of saturated systems. It has been probable to gain a broad picture about the influence of ligand structure (Balasubramanian, 1987), chelate ring size donor unsaturation donor unsaturation, configuration of donor unsaturation, substituent pattern and relative position of five and six membered chelate rings (Jubran *et al.*, 1985). It has been given that reductions in the ligand field strength of the macrocyclic ligands conclude in an anodic shift in the oxidation and reduction potentials (Kalyanasundaram, 1982). Changes in the behavior of the ring substituents also to a certain limit effects the redox potentia. It shows that the alteration in the redox potential in these complexes, primarily due to the effect of the substituent's on the metal nitrogen interaction. It is of interests to investigate the influence of nature and relative position of ring substituents on the redox nature. We discuss the complexes of (L1).

Me₂ (ET₄) (14) diene (C₂₀H₄₀N₄)

Me₂ (ET₄) (14) ane (C₂₀H₄₄N₄)

(L3) Me₆ (ET₄) (14) diene (C₁₆H₃₅N₄) and

And (L4) Me₂ (14) ane (C₁₆H₃₆N₄)

Methods and Materials

The polarograms of the complexes in aqueous solutions were marked on a Metrohm polarecord 50 using a dropping mercury electrode (dme) as the working electronic device. A graphite electrode was used an auxillary electrode. The saturated calomel electrode taken as reference electrode was obtained with a saturated solution of NaCl. All estimates were made at 25°C. The solution was deaerated by bubbling analytical grade nitrogen through them for about 10 min prior to marking the waves. The DME is an electrode made of mercury and is helpful in polarography experiments with mercury electrodes are known as forms of polarography. But the experiments are very identical to related voltammetry experiments which is useful in solid working electrodes. Auxiliary electrode is also called counter electrode. Electrochemical cell for voltammetry or any other reactions in which an electric current flows. Reference electrode has a stable and commonly known electrode potential. The good stability of the electrode potential is generally achieved by a redox system with constant concentration of every component of the redox reaction.

Results and Discussions

In order to choose a correct helping electrolyte, polarographic wave of few complexes were marked in different helping electrolytes. It was observed that the best waves were prepared in 0.1M sodium perchlorate and so subsequent studies were executed in this electrolyte. Since formation of potassium perchlorate attains in the reference electrode brit due to the combination of potassium chloride and sodium perchlorate, the reference S.C. was obtained with sodium chloride, Potassium perchlorate due to its less solubility tends to clog the frit. The polarograms of the complexes of Pd (II), Pt (II) with (L1) Me₂ (Et₄) [14] diene (C₂₀H₄₀N₄), (L2) (C₂₀H₄₀N₄) Me₂ (Et₄) [14] ane, (L3) (C₁₆H₃₅N₄) Me₆ [14] diene and (L4) (C₁₆H₃₆N₄) Me₆ [14] ane show well defined waves. These waves are diffusion controlled since plots of *i*_d against 'h^{1/2}' are straight. The half wave potential of these complexes are listed. The half wave potential of same other macro cyclic complexes are also possessed for comparison. The polarographic waves of these complexes indicate irreversible nature since plots of -*E*_{d,e} against log *i* / (*i*_d - 1) produces fractional value of *n*, the number of electrons included in the electrode process. This is helped by the low values of *k*_{*f*,*n*}^o. The value of *k*_{*f*,*n*}^o were estimated from the given below current - voltage relationship (30, 31).

$$E.d.e. + 0.2412 = (0.0591/dn) \log 1.349 k_{f,n}^{\circ} / d^{1/2} - 0.0542 / \alpha n [\log (i/i_d - i) - 0.546 \log t]$$

Where αn are the transfer coefficient and thus the drop time. A plot of *E*_{d,e} against [log (*i*/*i*_d - *i*) - 0.546 log *t*] produces a slope equal to 0.0542 / αn and an intercept equal to (0.0591) $\alpha n \log (1.34 k_{f,n}^{\circ} / d^{1/2} - 0.2412$. The one electron transfer irreversible waves related to the reduction of Pt (II) to Pt (I) and Pd (II) to Pd (I). An examination of the half wave potential values indicates that reduction of the Pt (II) complexes of the cis-ligands is very tough as compared to that of the more symmetrical trans ligands. The cathodic shift of the Pt (II)/Pt (I) that exists on hanging from a cis to trans geometry of the ligand is assumed in view of the likely raised basicity of the adjoining nitrogen donor. The unsymmetrical behavior of the macrocyclic ring will lead to a rise in the Pt-N bond length will conclude in a higher energy of this



orbital. Similar nature is noted where an anodic shift is seen when the Pt-N bond length is raised to than increase in ring size (Meites and Israel, 1961). The anodic shift in the reduction potential has also been relegated to steric interactions (Priya *et al.*, 2003). This result was based on the conclusion given by N-alkylating the macrocycles. Whereas N-alkylation may have a direct steric interaction, the relative position of the C-substituent's is too far off to be associated in any such steric interactions. So it is reasonable to acquire that the Pt – N distance is the deciding factor. It has been seen that a change in the symmetry of the ligand conclude in a change in the ligand field strengths (Priya *et al.*, 2003; Mostafa and Aicha, 2002).

Conclusion

The anodic shift in the reduction potential has also been relegated to steric interactions (35). This result was based on the conclusion given by N-alkylating the macrocycles. Whereas N-alkylation may have a direct steric interaction, the relative position of the C-substituent's is too far off to be associated in any such steric interactions. So it is reasonable to acquire that the Pt – N distance is the deciding factor. It has been seen that a change in the symmetry of the ligand conclude in a change in the ligand field strengths.

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