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REACTIVITY PATTERNS OF COBALT MACROCYCLIC COMPLEXES. METAL PROMOTED REACTIONS OF DIOXYGEN

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ABSTRACT. The dynamics of the reaction of oxygen with cobalt tetraaza macrocyclic complexes were investigated. The formation of dioxygen, superoxo, and peroxo adducts of cobalt complexes are reported. The reaction is believed to proceed in two steps: Formation of the superoxo complex, which is a fast step, followed by reaction with another cobalt(II) complex in the medium to form the peroxo compound.

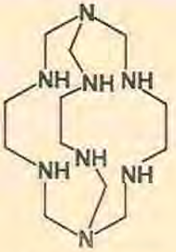
The reactivity of the superoxo complex with different reducing agents was investigated. Effect of these reducing agents on oxygen uptake and formation of peroxo cobalt(II) macrocyclic complexes are reported. Outer-sphere electron transfer turned out to be reasonably facile with the strong reducing agent $Co(sep)^{2+}$. The end product of these reactions is $Co(N_4)(OH_2)(O_2H)^{2+}$. The inner-sphere reactions of Co-O_2 species to form meta-stable μ-peroxo adducts proceed efficiently with very mild reducing agents such as Fe^{2+} and $Co(N_4)^{2+}$. In the reduction of $Co(N_4)(OH_2)O_2^{2+}$ with Fe^{2+} the formation of Fe-O-O-Co intermediate was detected. This intermediate appears to decay into Fe^{3+} and $Co(N_4)(OH_2)(O_2H)^{2+}$.

INTRODUCTION

The chemistry of the formation of dioxygen, superoxo and peroxo adducts of transition metal complexes has received widespread attention because of its relevance to oxygen transport and catalytic activation as in the heme O_2 carriers, oxygenases and hydroxylases. The advantage of studying such simple one-electron transfer reactions of dioxygen moieties [1-5] is that one can make use of electron-transfer chemistry [6-14] to gain insight into the reactivity patterns of dioxygen species.

The reactions of cobalt(II) complexes with oxygen have been well investigated [15-19]. However, cobalt-mediated oxygenations are varied and generally complex, due to variations of the coordination sphere of the metal. Tetraaza macrocyclic ligands have provided a convenient means for minimizing these complexities by defining four coordination sites. This permitted us to examine the reactivity of metals in relatively well defined coordination environments. Moreover, variation of functional groups on the equatorial macrocyclic ligand has provided a means for manipulating the reactivity of the metal centre. Herein, the dynamics of the reaction of oxygen with cobalt tetraaza macrocyclic complexes are reported. The complex investigated was $Co([16]aneN_4)^{2+}$, hereafter abbreviated as $Co(N_4)^{2+}$ [20]. It is important in catalytic redox reactions of molecular oxygen.

[16]aneN$_4$



sepulchrate

EXPERIMENTAL

Synthesis: Literature procedures were employed for the synthesis of most of the materials used in this study. The ligand 1,5,9,13-tetraaza cyclohexadecane was obtained from Strem Chemical Co. Solutions of the $Co(N_4)^{2+}$ complexes were prepared by mixing a 10% stoichiometric excess of the ligand with deaerated solutions of cobaltous perchlorate. Ferrous perchlorate solutions were deaerated over Zn-Hg to remove any Fe(III). The cobalt(III) complex of sepulchrate, $Co(sep)Cl_3$, was prepared as described in the literature [22]. $Co(sep)^{2+}$ was conveniently prepared by the Zn-Hg reduction of $Co(sep)^{3+}$.

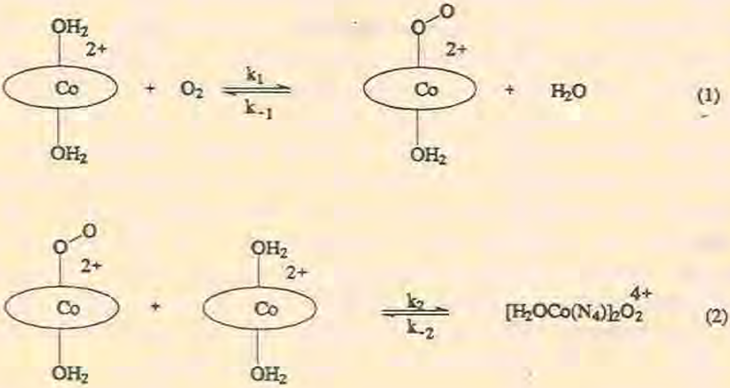
Kinetic measurements: Rate measurements were performed with thermostated Aminco or Durrum stopped-flow instruments. The reducing agents employed in this work (Fe^{2+} and $Co(sep)^{2+}$) have lower rates of reaction with O_2 than does $Co(N_4)(OH_2)_2^{2+}$. Consequently, the mixing of a solution containing $Co(N_4)(OH_2)_2^{2+}$ and a reducing species with solutions containing O_2 resulted in a very rapid formation of $Co(N_4)(OH_2)O_2^{2+}$. Thus, to an equilibrated solution of cobaltous perchlorate and [16]aneN$_4$ ligand (1:1.1) premixed in a Hamilton air-tight syringe, Fe^{2+} solution or $Co(sep)^{2+}$ solution in $HClO_4$ medium was introduced and mixed well. Mixing and deaeration was done in argon atmosphere. Another syringe was used to take oxygen-saturated-solvent (H_2O, ionic strength was adjusted by $LiClO_4$ or $NaClO_4$). These two syringes were fitted into a stopped flow machine and the absorbance decay of $Co(N_4)(OH_2)O_2^{2+}$ was observed at 380 nm in the screen of the oscilloscope.

RESULTS AND DISCUSSION

Rapid mixing of a cobalt(II) macrocyclic complex and a solution containing O_2 resulted in the formation of a strongly absorbing intermediate species. This species then decayed to a final product whose absorption spectrum was indistinguishable from that of an authentic sample of $[H_2OCo(N_4)]_2O_2^{4+}$.

Three stages of the reaction were distinguished: 1) rapid reaction of cobalt(II) macrocyclic complex with O_2 to form a very reactive intermediate, the superoxo complex; 2) rapid reaction of this superoxo complex with another molecule of cobalt(II) macrocyclic complex to form meta stable adducts $[H_2OCo(N_4)]_2O_2^{4+}$, μ-peroxo complex; and 3) slow decomposition of this μ-peroxo product.

These results are most conveniently discussed in terms of the traditional [15,17,23-25] reaction shown in Scheme 1.



Scheme 1

As shown in Scheme 1, Equation 2, the superoxo complex reacts with another molecule of cobalt(II) macrocyclic complex in the medium to form the meta-stable μ-peroxo adduct. Oxidation of ruthenium(II) macrocyclic complexes by molecular oxygen was also reported to proceed via an outer-sphere formation of superoxide ion followed by its reaction with a second ruthenium(II) complex to yield hydrogen peroxide and two ruthenium(III) molecules [26,27]. A similar mechanism was also proposed for the oxidation of $Ru(NH_3)_6^{2+}$ by molecular oxygen [1] to yield hydrogen peroxide and two molecules of $Ru(NH_3)_6^{3+}$.

The reactivity of the cobalt superoxo complex with foreign compounds was investigated to study the effects of such compounds on oxygen uptake and consequent peroxo formation of the cobalt(II) macrocyclic complex. Mild reducing agents with labile coordination position such as $Fe(H_2O)_5^{2+}$ react with the coordinated superoxo ligand of the cobalt(II) macrocyclic complex. Kinetic parameters are shown in Table 1 and Figure 1. The presence of this mild, inner-sphere reducing agent in the reaction medium accelerates the rate of $Co(N_4)(OH_2)O_2^{2+}$ decay. For sufficiently large concentrations of the Fe^{2+}, the apparent first-order rate constant for the formation of the mixed metal-μ-peroxo complex, $[H_2OCo^{II}(N_4)\text{-O-O-}Fe(H_2O)_5]^{4+}$, became proportional to the concentration of Fe^{2+}. The data show that there is a competitive reaction of Fe^{2+} with the superoxo species. This competitive reaction can be represented by Equations 1 and 2 (Scheme 1) and Equation 3.

$$\mathrm{Co(N_4)O_2^{2+} + Fe(H_2O)_6^{2+} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [Co(N_4){-}O{-}O{-}Fe(H_2O)_5]^{4+}} \tag{3}$$

The slopes of the plots of k_{obs} *vs* [Fe^{2+}] correspond to the second order rate constants. These second order rate constants are results of the combination of the above rates (Scheme 1) due to the two predominant reactions (1) and (2).

It is possible that other reactions occur simultaneously with the formation of the mixed metal-μ-peroxo complex. Protonation or deprotonation of the species present in the medium can take place. However, it is interesting to note that the slopes of the plots of k_{obs} *vs* [Fe^{2+}] at different pHs (Table 1) practically fall in the same range. This may lead to the conclusion that the reaction of $Co(N_4)O_2^{2+}$ with Fe^{2+} is pH independent.

The chemical behaviour of $Co(N_4)O_2$ towards strong reducing agent such as Co(sep)$_{2+}$ has been investigated. The Co(sep)$^{2+}$ has inert coordination positions which react readily with coordinated superoxo ligand of the cobalt(II) macrocyclic complex. Kinetic parameters are shown in Table 2 and Figure 1. The presence of this strong, outer-sphere reducing agent in the medium greatly accelerated the rate of decay of the coordinated superoxo ligand of $Co(N_4)(H_2O)_2O_2^{2+}$. For sufficiently large concentrations of Co(sep)$^{2+}$, the apparent first-order rate constant for the decay of the intermediate became proportional to the concentration of Co(sep)$^{2+}$ (Figure 1).

The effect of hydrogen ion concentration as well as the cobalt(II) macrocyclic complex concentration on the apparent second order rate constant are also shown in Table 2. The reactions that must be considered in this case are shown in Equations 1 and 2 (Scheme 1) and 4 and 5.

$$\mathrm{Co(N_4)(OH_2)O_2^{2+} + Co(sep)^{2+} \xrightarrow{k_4} Co(N_4)(OH_2)O_2^{+} + Co(sep)^{3+}} \tag{4}$$

$$\mathrm{Co(N_4)(OH_2)O_2^{+} + H^{+} \rightleftharpoons Co(N_4)(OH_2)O_2H^{2+}} \tag{5}$$

The end product of these reactions is $Co(N_4)(OH_2)(O_2H)^{2+}$, but protonation appears to follow electron transfer. This indicates that Co-O_2 is a weak oxidant with only a small reorganization barrier to electron transfer.

Thus, these results suggest that coordination of O_2 slightly increases its oxidizing potential but greatly decreases its intrinsic barrier to electron transfer. This stands in contrast to both the O_2/O_2^- and μ-peroxo/μ-superoxo couples. Further work is required to determine the validity and generality of these results.

Table 1. Reactivity of $Co(N_4)O_2^{2+}$ with $Fe(H_2O)_6^{2+}$. Summary of kinetic parameters[a].

$[H^+]$ (M)	$[Co(N_4)]^{2+}$ X 10^4 (M)	$[Fe^{2+}]$ X 10^2 (M)	k_{obs} X 10^{-1} (s^{-1})	$t_{1/2}$ X 10^{-1} (s)
0.10	5.950	0.000	2.75	2.52
0.10	5.990	0.505	2.73	2.54
0.10	6.009	1.101	2.80	2.48
0.10	6.009	1.705	2.75	2.52
0.10	6.005	2.503	2.79	2.48
0.10	5.998	2.755	2.82	2.46
0.10	6.001	3.505	2.90	2.39
0.10	6.001	4.050	3.14	2.21
0.10	5.995	4.502	3.19	2.17
0.10	5.995	5.201	3.25	2.13
0.10	6.005	6.005	3.50	1.98
0.10	6.108	6.501	3.66	1.89
0.10	5.995	6.998	3.70	1.87
0.10	5.998	8.005	3.85	1.80
0.10	5.998	9.089	4.19	1.65
0.01	6.050	4.051	3.20	2.17
0.01	6.050	4.910	3.30	2.10
0.01	6.005	5.851	3.43	2.02
0.01	6.005	6.550	3.61	1.92
0.01	6.115	7.250	3.76	1.84
0.01	6.115	8.150	3.85	1.80
0.15	5.985	4.101	2.95	2.35
0.15	5.985	4.550	3.01	2.30
0.15	5.985	5.201	3.11	2.23
0.15	6.080	6.050	3.30	2.10
0.15	6.080	6.850	3.45	2.01
0.15	6.080	7.551	3.60	1.93

[a] λ = 380 nm, t = 25.0 ± 0.20°,
μ = 0.2 ($LiClO_4$) and $[O_2]$ 6.3 X 10^{-4} M.

Table 2. Reactivity of $Co(N_4)O_2^{2+}$ with $Co(sep)^{2+}$. Summary of Kinetic parameters[a].

$[H^+]$ (M)	$[Co(N_4)]^{2+}$ X 10^4 (M)	$[Co(sep)]^{2+}$ X 10^3 (M)	k_{obs} X 10^{-1} (s^{-1})	$t_{1/2}$ X 10^2 (s)
0.01	6.090	0.461	3.41	2.03
0.01	6.090	0.805	3.50	1.98
0.01	6.090	1.201	3.70	1.87
0.01	6.110	1.602	4.00	1.73
0.01	6.110	2.015	4.10	1.69
0.01	6.110	2.205	4.15	1.67
0.20	3.015	0.000	2.20	3.15
0.20	3.080	3.495	6.20	1.12
0.20	3.050	4.005	6.45	1.07
0.20	3.050	5.205	7.90	0.88
0.20	6.090	0.441	3.00	2.31
0.20	6.090	0.842	3.31	2.09
0.20	6.095	1.201	3.70	1.87
0.20	6.095	1.605	4.01	1.73
0.20	6.110	2.450	4.95	1.40
0.20	6.110	2.601	5.10	1.36
0.20	6.110	2.910	5.50	1.26
0.20	5.998	2.001	4.75	1.46
0.20	5.998	4.667	7.25	0.96

[a] λ = 380 nm, t = 25.0 ± 0.20°,
μ = 0.2 ($LiClO_4$) and $[O_2]$ 6.3 X 10^{-4} M.

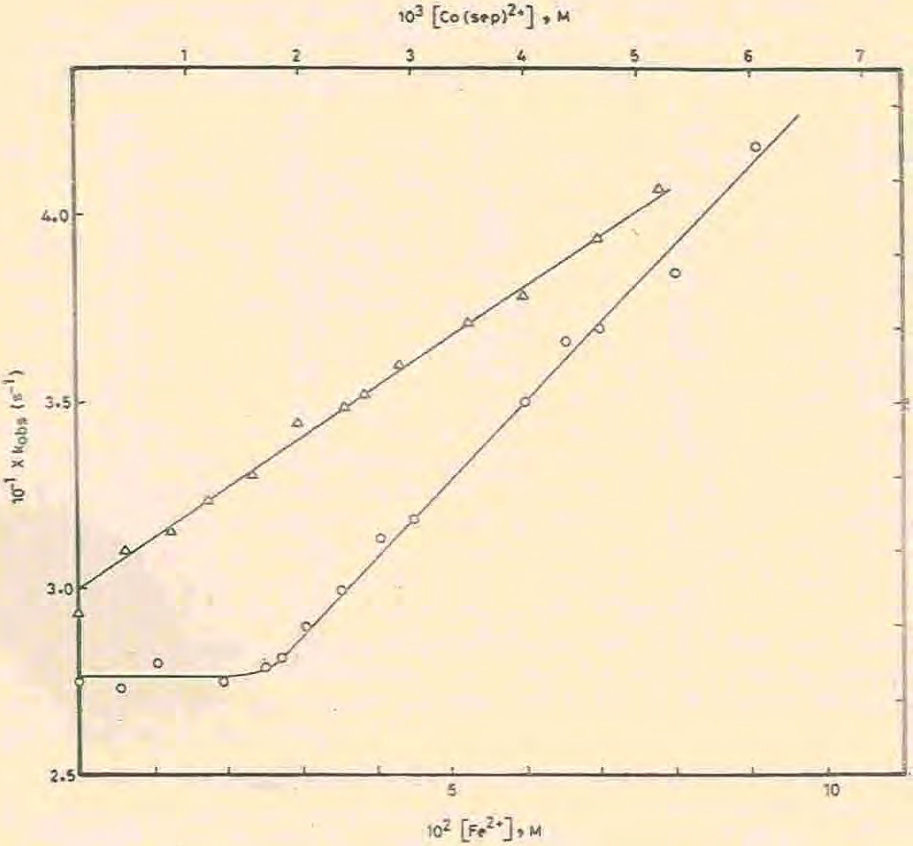


Fig. 1. The rate of decay of Co([16]aneN$_4$)(OH$_2$)O$_2^{2+}$ in the presence of reducing agents. Left scale: O, Fe(H$_2$O)$_6^{2+}$; right scale: △, Co(sep)$^{2+}$. [O$_2$] = 6.3 X 10^{-4} M; ionic strength = 0.2 M (NaClO$_4$ + HClO$_4$). Temperature = 25°.

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