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Application of the Marcus Theory to the Electron-Transfer Reactions of Metal-Bound Dioxygen

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The reductions of the "μ-superoxo" species $[Co_2(NH_3)_8(\mu\text{-}O_2NH_2)]^{4+}$ and $[Co_2(NH_3)_{10}(\mu\text{-}O_2)]^{5+}$ by $Co(trpy)_2^{2+}$, $Co(bpy)_3^{2+}$, and $Co(phen)_3^{2+}$ are reported. The Marcus theory adequately describes the kinetics of all these reactions. Values of reduction potentials and self-exchange rates for bound O_2 are reported for the first time. For $[Co_2(NH_3)_8(\mu\text{-}O_2,NH_2)]^{4+}$, $E° = +0.75$ V and $k_{11} = 1.0 \times 10^{-5}$ M^{-1} s^{-1} while for $[Co_2(NH_3)_{10}(\mu\text{-}O_2)]^{5+}$, $E° = + \sim 1.0$ V and $k_{11} = 6 \times 10^{-7}$ M^{-1} s^{-1}. The relative values of these self-exchange rates cannot be explained in purely structural terms but appear to depend on charge-dependent differences in forming the precursor complex as estimated by an electrostatic work function.

Introduction

The biological importance of metal–dioxygen interactions has stimulated considerable work in the development of inorganic metal–dioxygen model systems.[1-3] As a result of this work, the basic concepts controlling M–O_2 bonding and equilibria are reasonably well understood. The presently accepted model invokes considerable transfer of electron density from metal to dioxygen in bond formation, so that (in the limit) the metal is formally oxidized and O_2 is formally reduced: $M^{n+} + O_2 \rightleftarrows M^{n+1}\text{–}O_2^-$. As an indication of this formalism, such adducts (for $M^{n+} = Co^{2+}$) are conventionally designated as "superoxo" complexes. Reaction with a second metal may yield a "μ-peroxo" complex $M^{n+1}\text{–}O_2^- + M^{n+} \rightleftarrows M^{n+1}\text{–}O_2^{2-}\text{–}M^{n+1}$ which can be oxidized to a "μ-superoxo" adduct. The electronic structure and bonding of mononuclear and binuclear superoxo species have been compared at length elsewhere[4] and found quite similar.

While much is known about the bonding and equilibria of such complexes, their reaction chemistry is far less well characterized. The redox reactivity of metal-bound O_2 is of particular (biochemical) interest since >90% of all O_2 utilized in vivo is reduced to H_2O in electron transport.

Given the well-defined behavior of the cobalt μ-superoxo complexes, several previous investigations of the reduction kinetics of these species have been reported.[5-8] However, these studies are incomplete in several important regards. While an outer-sphere mechanism has been postulated for the superoxo → peroxo conversion, the reagents previously used, particularly Fe^{2+}, have sufficiently high ligand-exchange rates that an inner-sphere pathway could not be rigorously excluded. A much more informative mechanistic test would be to attempt to apply Marcus' theory to characterize the reductions.[10] Such an approach also yields values for the self-exchange rates (k_{11}) of bound O_2, which make possible estimation of the reaction rates with virtually any reaction partner and may provide valuable information about the relation of physical and electronic structure to reactivity. Unfortunately, this approach is generally not feasible for previous studies since the reagents used (Fe^{2+}, U^{3+}, Eu^{2+}, Cr^{2+}) have poorly characterized self-exchange rates (k_{22}) so that calculated values of k_{11} vary by several orders of magnitude. Furthermore, up to now reliable values of the reduction potentials of μ-superoxo species have not been available.

We have therefore examined the reduction kinetics of several μ-superoxo complexes with well-characterized outer-sphere reagents: $Co(bpy)_3^{2+}$, $Co(phen)_3^{2+}$, $Co(trpy)_2^{2+}$,[9] for which k_{22} values are well-known.[10] These studies are designed to answer several basic questions. First, what are the reduction potentials of the μ-superoxo adducts? Second, do the reductions of μ-superoxo cobalt species proceed via a simple outer-sphere pathway that can be described by Marcus' theory? Third, if this description is valid, what are the intrinsic self-exchange rates for metal-bound O_2, and is there a structural basis for this reactivity? Fourth, to what extent can *differences* in reactivity between μ-superoxo adducts (e.g., the monobridged and dibridged species (I and II)) be explained on a structural (or other) basis?

Experimental Section

Materials and Methods. The μ-superoxo complexes $[Co_2(NH_3)_{10}(\mu\text{-}O_2)]Cl_5$ (I), $[Co_2(NH_3)_8(\mu\text{-}O_2,NH_2)](NO_3)_4$ (II), and $K_5[Co(CN)_{10}(\mu\text{-}O_2)]$ (III) and their corresponding μ-peroxo complexes were synthesized and purified by standard literature methods.[11] Elemental analyses were satisfactory. Visible spectra of the peroxo and superoxo species agree well with the reported values.[1] $Co(trpy)^{2+}$, $Co(bpy)_3^{2+}$, and $Co(phen)_3^{2+}$ were prepared in situ by stoichiometric addition of ligand (G. Frederick Smith) to standardized solutions of cobalt(II) nitrate. For some reactions, the pyridyl reagents were isolated and recrystallized as ClO_4 salts, but no rate differences were found. All solutions were prepared in doubly distilled water. KNO_3 was used to control ionic strength. In a few cases $LiClO_4$ was substituted to test for specific ion effects. Only small differences in rates were observed.

Reduction Potentials. The reduction potentials were estimated for species I–III by analytical potentiometry. Where possible, they were checked by rapid-scan cyclic voltammetry, using a PAR 370 electrochemical system.

Potentiometric readings were obtained by using a Beckman 4500 Research pH meter fitted with Pt and calomel electrodes. Millivolt readings were standardized by using $Fe(CN)_6^{3-,4-}$ and $Co(trpy)_2^{3+,2+}$ couples. Measurements were made in a thermostated cell protected from light.

For the potentiometric measurements, μ-superoxo solutions were prepared in dilute HNO_3 ($[H^+] = 10^{-4}$ M), while the μ-peroxo species were dissolved in weak base (10^{-4} M OH^- or NH_3) so that neutral solutions were obtained on mixing.

Under these conditions the μ-superoxo systems were found to be highly stable. The superoxo spectral measurements of MLCT[1] show a decomposition half-life $t_{1/2} > 8$ h for I and II and pH ≤4 (HNO_3, $\mu = 0.05$ M (KNO_3), 25 °C) and $t_{1/2} > 1$ h at $[H^+] \simeq 10^{-7}$ M. They undergo more rapid decomposition upon exposure to light or in the presence of excess base or certain buffers.

However, the peroxo analogues, particularly of I, are far less stable. Even under measurement conditions, some decomposition occurs, which is mirrored in a potential drift. This decomposition was monitored by the potential drift, spectral measurements, and O_2 release (YSI

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(1) G. McLendon and A. Martell, *Coord. Chem. Rev.*, **19**, 1 (1976).
(2) F. Basolo, B. Hoffman, and J. Ibers, *Acc. Chem. Res.*, **8**, 384 (1975).
(3) J. Collman, *Acc. Chem. Res.*, **10**, 265 (1977).
(4) G. McLendon, S. Pickens, and A. Martell, *Inorg. Chem.*, **16**, 1551 (1977).
(5) A. Sykes, *Chem. Br.*, **10**, 170 (1974).
(6) A. Sykes and J. Weil, *Prog. Inorg. Chem.*, **13**, 1 (1970).
(7) A. Hoffman and H. Taube, *Inorg. Chem.*, **7**, 1971 (1968).
(8) G. McLendon and A. Martell, *Inorg. Chem.*, **15**, 2662 (1976).
(9) Abbreviations used are bpy = bipyridyl, phen = 1,10-phenanthroline, and trpy = terpyridyl.
(10) S. Wherland and H. Gray, *Biol. Aspects Inorg. Chem.*, [*Symp.*], 323 (1978); see Table I.
(11) R. Davies, M. Mori, A. Sykes, and J. Weil, *Inorg. Synth.*, **12**, 199 (1970).

0020-1669/80/1319-0012$01.00/0

Table I. Reduction Potentials of μ-Superoxo Species (25 °C; $\mu = 0.05$ M)

complex	$E°$, V vs. NHE[a]
$[Co_2(NH_3)_{10}(\mu\text{-}O_2)]^{5+}$	~0.9[b] (0.95)
$[Co_2(NH_3)_8(\mu\text{-}O_2,NH_2)]^{4+}$	0.75 (0.60)
$[Co_2(CN)_{10}(\mu\text{-}O_2)]^{4-}$	0.09 (0.06)

[a] First values listed are the voltammetric values (CV): values in parentheses are obtained by potentiometry corrected for complex decomposition. [b] E_p reduction; oxidation wave obscured by solvent breakdown.

O_2 electrode). Under the potentiometric conditions, it was found that over short times the degradation was approximately pseudo first order and amounted to less than 15% of the total species over 10 min. Thus an approximate potential for the μ-superoxo/μ-peroxo couple may be estimated by extrapolation of the potential to $t = 0$.

On varying the relative concentrations of the μ-superoxo and μ-peroxo systems, we found that $E°$ values calculated from the Nernst equation showed a high degree of self-consistency.

Given the uncertainty in these measurements, independent electrochemical characterization of the potentials has been attempted. Previous voltammetric measurements,[13,14] of this potential were unreliable because of sample decomposition[23] and electrode adsorption phenomena. These problems were found minimal under the conditions of the present study ($T = 25$ °C, $\mu = 0.1$ M (KNO_3), $[H^+] = 10^{-3}$ M (HNO_3), [μ-superoxo] $\simeq 10^{-3}$ M added as a solid sample).

A PAR 370 electrochemistry system, incorporating Pt working and auxiliary electrodes and a calomel reference, was used for the CV measurements. Scan rates were varied from 200 mV/s to 1 V/s. Reversible behavior was found for compound II, and quasi-reversible behavior, for compound III. The observed peak potentials agree well with the potentials estimated by potentiometry. The potentials of compound I cannot be estimated accurately by voltammetry, since solvent breakdown begins to occur at ~1 V. A reduction-peak shoulder on the solvent-breakdown current is observed at ca. 1 V, but the more anodic oxidation peak is obscured. Thus, some degree of uncertainty remains for the potential of I. Given the correspondence between potentiometric and voltammetric values observed for complexes II and III, the potentiometric value for I appears to provide a reasonable estimate, which is supported by its chemical reactivity (vide infra).

Kinetics were followed on a Durrum D-110 stopped flow. Reactions were carried out with temperature control to ±0.1 °C and rigorous protection of the reagents from light (the μ-superoxo species are photosensitive). KNO_3 was used as the supporting electrolyte, and H^+ concentration was $\sim 10^{-4}$ M. (Higher H^+ concentrations led to some decomposition of the $Co(bpy)_3^{2+}$ species with irreproducible results, whereas lower H^+ concentrations led to slow decomposition of the superoxo species.) All reactions were carried out under pseudo-first-order conditions with reductant in excess by 6- to 60-fold. Rate constants were adjusted by the method of Corbett.[12] In all cases excellent reproducibility was obtained.

Results and Discussion

Reduction Potentials. Values for the reduction potentials of the μ-superoxo species are presented in Table I. No previous potentiometric values are available for comparison, but the voltammetric values reported by Vleck[13] do not agree with the present report. Other studies,[14,23] have indicated that Vleck's results are complicated by the decomposition of the peroxo species studied (vide supra). Such decomposition may also limit the reliability of the present potentiometric studies. As a check, rapid-scan CV studies of the superoxo adducts were carried out. Unlike the μ-peroxo adducts the superoxo complexes do not decompose under the measurement conditions, and the peroxo reduction product may be sufficiently stable to be detected by rapid scan. This situation indeed occurs, as exemplified in the CV of complex II, which exhibits a reversible redox couple at ~0.76 V (vs. NHE) (Figure 1). This potential is in good agreement with that estimated by potentiometry, suggesting that the limited peroxo decomposition which occurs during the potentiometric measurement does not greatly influence the reliability.

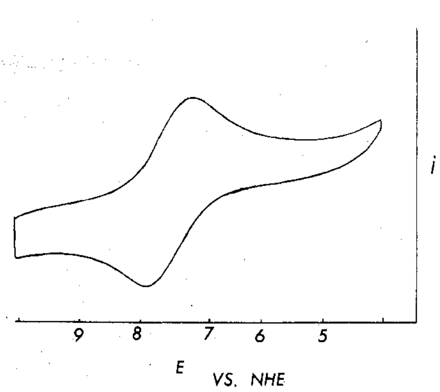

Figure 1. Cyclic voltammogram of $[Co_2(NH_3)_8(\mu\text{-}O_2,NH_2)]^{4+}$ ($[HNO_3] = 10^{-3}$ M, $[KNO_3] = 0.1$ M, $T = 25$ °C). Scan rate is 200 mV/s.

Similar agreement is found for the μ-superoxo-bis(pentacyanocobalt) species (0.08 V by CV, 0.06 V by potentiometry). A corresponding check of the superoxo adduct I is not feasible. Its potential is sufficiently anodic that it is largely obscured by the onset of solvent breakdown, so that reversibility cannot be assessed. An apparent reduction peak is observed at 0.9 V, which is close to the potentiometric value of +0.95 V. It should be noted that the potentiometric and voltammetric values are not only consistent with one another but also with the known chemical reactivity of the μ-superoxo complexes. For example Fe^{2+} is well-known to reduce I and II but not III as predicted by the presently reported potentials. By contrast, Vleck's previously reported potentials (0.36 V for I) would suggest I should *not* oxidize Fe^{2+}. Similar chemical studies by Sykes[6] had suggested an approximate potential of 0.9 V for I, in good agreement with the electrochemical value reported here. While the values for II and III may be taken as well established, some residual error must be assumed for species I. Given the high correspondence between potentiometric, voltammetric, and chemical estimates of $E°$ for these species, any such error should be sufficiently small that it will not adversely effect the conclusions drawn herein.

There are no obvious structural differences among the complexes which should lead to the 0.8-V potential spread. It is not unreasonable to suppose that much of this difference is purely electrostatic, since the most highly oxidizing complex carries a 5+ charge, whereas the least oxidizing is highly negatively charged.

In the present format, the primary importance of these potentials is that they allow assessment of the utility of Marcus' theory in describing the superoxo reduction kinetics.

Kinetics. The reduction of I and II by the cobalt polypyridyl chelates exhibited clean pseudo-first-order kinetics. Typical data are shown in Figure 2. The validity of Marcus' theory for describing these data is tested as follows. The self-exchange rate, k_{11}, for reduction of bound O_2 is obtained from the relation[15] $k_{11} = k_{12}^2/k_{22}K_{12}f$ where k_{12} is the measured reaction rate, k_{22} the self-exchange rate of the reductant (e.g., $Co(trpy)_2^{2+}$), K_{12} the equilibrium constant for the reaction ($\log K_{12} = nE°/0.059$) and $\ln f = (\ln K_{12})^2/[4 \ln (k_{11}k_{22}/Z^2)]$.

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(12) J. Corbett, *J. Chem. Educ.*, **49**, 663 (1972).

(13) A. Vleck, *Collect. Czech. Chem. Commun.*, **25**, 3036 (1960).

(14) W. Harris, R. Bess, G. McLendon, and A. Martell, submitted for publication in *Inorg. Chem.*

(15) k_{11} values calculated from Taube's work[7] are of the same order of magnitude as those reported here but are lower. For reaction of I with Cr^{2+}, $k_{11} = 1 \times 10^{-5}$ M^{-1} s^{-1}, with V^{2+}, $k_{11} \simeq 10^{-3}$ M^{-1} s^{-1}, and with Eu^{2+}, $k_{11} \simeq 10^{-4}$ M^{-1} s^{-1}. This may reflect the poorly defined k_{22} values of these reagents or may actually reflect a slowing of overall rate at very large driving force.[21]

Table II. Parameters from Marcus' Theory Fit of Superoxo Reduction (25 °C; $\mu = 0.05$ M (KNO_3))

complex	reactant	$K_{12}{}^a$	$k_{22}{}^b$ reactant	k_{12} obsd, M^{-1} s^{-1}	k_{11} calcd, M^{-1} s^{-1}
$[Co_2(NH_3)_{10}(\mu\text{-}O_2)]^{5+}$	$[Co(trpy)_2]^{2+}$	7.3×10^{11}	1940	$6000^c \pm 500$	6.3×10^{-7}
	$[Co(bpy)_3]^{2+}$	6×10^{11}	18	380 ± 20	6.0×10^{-7}
	$[Co(phen)_3]^{2+}$	1.4×10^{10}	45	188 ± 15	5.6×10^{-7}
$[Co_2(NH_3)_8(\mu\text{-}O_2,NH_2)]^{4+}$	$[Co(trpy)]^{2+}$	4×10^{8}	1940	$1025^d \pm 90$	1.0×10^{-5}
	$[Co(bpy)_3]^{2+}$	4×10^{7}	18	90 ± 8	1.2×10^{-5}
	$[Co(phen)_3]^{2+}$	6×10^{6}	45	32 ± 2	9×10^{-6}

[a] Reduction potentials for reactants: $[Co(trpy)_2]^{3+,2+}$, 0.27 V; $[Co(bpy)_3]^{3+,2+}$, 0.3 V; $[Co(phen)_3]^{3+,2+}$, 0.37 V. [b] From ref 10. [c] $\Delta H^{\ddagger} = 4.5$ kcal/mol. [d] $\Delta H^{\ddagger} = 4.2$ kcal/mol.

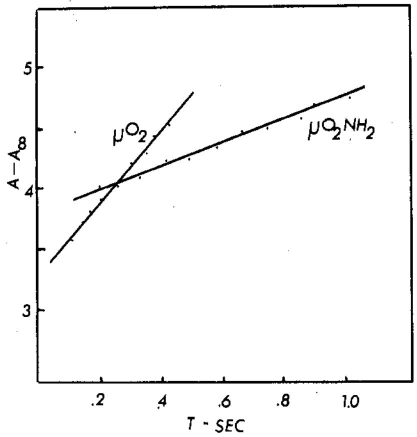

Figure 2. Pseudo-first-order plots of the reduction of μ-superoxo-bis(pentaamminecobalt(III)) (μO_2) and μ-superoxo-μ-amido-bis-(tetraamminecobalt(III)) (μO_2NH_2) by bis(terpyridyl)cobalt(II). Ionic strength is 0.05 M (KNO_3); $T = 25$ °C.

Table III. Comparative Structural Data for μ-Superoxo and μ-Peroxo Adducts

complex	O-O,[a] Å	Co-O-O-Co,[b] deg	Co-O,[a] Å	ref
$[Co_2(NH_3)_{10}\text{-}(\mu\text{-}O_2)]^{5+}$	1.31	10	1.88	18
$[Co_2(NH_3)_{10}\text{-}(\mu\text{-}O_2)]^{4+}$	1.47	40	1.88	18
$[Co_2(NH_3)_8\text{-}(\mu\text{-}O_2,NH_2)]^{4+}$	1.32	10	1.87	19
$[Co_2(en)_4\text{-}(\mu\text{-}O_2,NH_2)]^{4+}$	1.35	20	1.87	17
$[Co_2(en)_4\text{-}(\mu\text{-}O_2,NH_2)]^{3+}$	1.46	60	1.88	17

[a] Bond length. [b] Torsion angle.

Values of these parameters and the associated calculated values of k_{11} are contained in Table II. Several features of the data require particular comment. First, it is clear that the invariance of the calculated k_{11} values is consistent with and offers strong evidence for a simple outer-sphere mechanism indeed operating in the reduction of bound superoxides as previously proposed. Second, at 0.05 M ionic strength the rate of reaction of the monobridged species with the cobalt chelate reductants is higher than that of the dibridged. This represents a reversal in relative reactivity from that observed by Sykes in the reaction of these adducts with Fe^{2+}. These earlier studies were explained by (reasonably) assuming that the dioxygen moiety was sterically more accessible in the dibridged species than in the monobridged. However, the present data are clearly inconsistent with this explanation. The greater bulk of the cobalt pyridyl reductants should accentuate the relative reactivity of the dibridged species. Instead, it reacts less rapidly with these reagents than the monobridged complex. In light of Marcus' theory, such a reversal of relative reactivity is indeed predicted, since the rate k_{12} depends on both K_{12} and k_{11}. In the reaction with Fe^{2+}, K_{12} is small for both I and II, and the differences in k_{11} between these reactants dominate the relative values of k_{12}. Thus the monobridged adduct, with a lower self-exchange rate, reacts more slowly. As the driving force (K_{12}) increases, however, differences in K_{12} for the two species are much larger than the differences in k_{11}, and the monobridged adduct reacts more rapidly, as shown in Table II. Thus, while a simple steric model cannot explain all the cross-reaction results, they are easily interpreted in the framework of Marcus' theory.[15]

Activation parameters for the cross reactions are reported in Table II. These fall in the same general range as previously observed for superoxo reductions[5-8] and thus merit no particular comment. Finally, the absolute and relative magnitudes of the self-exchange rates of I and II should be discussed. There rates are rather low (10^{-6}–10^{-5} M^{-1} s^{-1}) compared with those of the cobalt pyridyl reductants (10–10^3 M^{-1} s^{-1}). This is not unreasonable since a large change in geometry, centered on the dioxygen bridge, occurs during reduction. The O–O bond length increases by 0.15 Å (1.32 Å for μ-superoxo, 1.48 Å for μ-peroxo). Such a large geometry change creates a large Franck–Condon barrier to electron transfer, consistent with the low self-exchange rate. The situation is highly analogous to the well-known slow exchange rates when "eg" electrons are involved in redox reactions of transition metals.[16]

Although the generally low reactivity of the μ-superoxo adducts thus has a structural basis, the reason for the reactivity difference between the mono- and dibridged species is less obvious. Crystallographic data[17-19] for oxidized and reduced mono- and dibridged species are compared in Table III. It is clear from these data that there are no significant differences in superoxo → μ-peroxo bond-length changes or torsional-angle changes. Since the degrees of structural change required on reduction are essentially identical for both monobridged and dibridged species, qualitative Franck–Condon arguments cannot explain the reactivity differences observed.

An alternative explanation lies in the charge differences of the reactants. In formation of a precursor complex electrostatic work is required to bring the two charged species into sufficiently close contact for electron exchange. The required work will clearly be larger for the more highly charged 5+ complex, I, than for the 4+ complex, II. A more quantitative estimate of this difference can be obtained by using a simple Coulombic work function:[20]

$$\ln k = \ln k_0 - 3.6\left[\frac{e - IR_1}{1 + R_1} + \left(\frac{e - IR_2}{1 + R_2}\right)\left(\frac{Z_1 Z_2}{R_1 + R_2}\right)\right]$$

$\ln k_0$ is the rate at infinite ionic strength, $I = 0.33\mu^{1/2}$, R_1 and R_2 are the radii of oxidized and reduced species (for the self-exchange $R_1 \simeq R_2$), and Z_1 and Z_2 are the charges of the oxidized and reduced species.

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(16) F. Basolo and R. Pearson, "Inorganic Reaction Mechanisms", Wiley, New York, 1968.

(17) U. Thewalt, *Z. Anorg. Allg. Chem.*, **393**, 1 (1972).

(18) L. Lindblom, W. Schaefer, and R. Marsh, *Acta Crystallogr., Sect. A*, **24**, 1461 (1971).

(19) G. Cristoph, R. Marsh, and W. Schaefer, *Inorg. Chem.*, **8**, 291 (1969).

(20) R. Alberty and G. Hammes, *J. Chem. Phys.*, **62**, 154 (1958).

(21) C. Kreutz and N. Sutin, *J. Am. Chem. Soc.*, **99**, 241 (1977).

Calculating from data for $\mu = 0.05–2.5$ gives values of $k_0 = 1.0 \times 10^{-3}\ M^{-1}\ s^{-1}$ for $[Co(NH_3)(\mu\text{-}O_2)]$ and $k_0 = 3.2 \times 10^{-3}\ M^{-1}\ s^{-1}$ for $[Co_2(NH_3)_8(\mu\text{-}O_2,NH_2)]$. Within the accuracy of this model, then, most of the large self-exchange difference between the monobridged and dibridged species can be explained by the charge differences of these complexes.

Finally, it is interesting to compare the values for the self-exchange rates derived here with those for free superoxide. Literature data are available for the reaction of O_2^- with several substrates.[23] From these data, a self-exchange rate for O_2^- of $\sim 10^{-3}\ M^{-1}\ s^{-1}$ can be derived.[22]

This rate is quite similar to that of metal-bound "superoxide" reported here. Thus, the reactivity of bound O_2 reinforces the structural evidence for a superoxide description. The common reactivity of free O_2^- and metal-bound O_2 might also suggest that a self-exchange rate of $\sim 10^{-3}\ M^{-1}\ s^{-1}$ may serve as a good approximation for many metal–O_2 systems (e.g., oxidases, superoxide dismutase). Studies to test this proposition are in progress.

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Registry No. $[Co_2(NH_3)_{10}(\mu\text{-}O_2)]^{5+}$, 12259-09-5; $[Co_2(NH_3)_8(\mu\text{-}O_2,\mu\text{-}NH_2)]^{4+}$, 12381-36-1; $[Co_2(CN)_{10}(\mu\text{-}O_2)]^{5-}$, 12374-80-0; $[Co(trpy)_2]^{2+}$, 18308-16-2; $[Co(bpy)_3]^{2+}$, 15878-95-2; $[Co(phen)_3]^{2+}$, 16788-34-4.

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[22] For the cross reaction of O_2^- with cyt c $k_{12} = 5 \times 10^5\ M^{-1}\ s^{-1}$. Taking $k_{22} = 5 \times 10^3\ M^{-1}\ s^{-1}$ and $K_{12} = 10^{13.5}$ gives $k_{11} = 10^{-3}\ M^{-1}\ s^{-1}$.

[23] R. Rao and C. Hayon, *J. Phys. Chem.*, **79**, 397 (1975).

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Electronic Structures of μ-Peroxo-bis[(pentadentate polyamine)cobalt(III)] Complexes

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Electronic spectral studies of $[CoLO_2CoL]^{4+}$ and $[CoLCl]^{2+}$, where L is 1,4,7,10,13-pentaazatridecane (tetren), 2,6-bis(5-(1,4-diazahexyl))pyridine (epyden), 1,9-bis(2-pyridyl)-2,5,8-triazanonane (pydien), 1,11-bis(2-pyridyl)-2,6,10-triazaundecane (pydpt), 1,9-bis(4-imidazolyl)-2,5,8-triazanonane (imdien), and 1,11-bis(4-imidazolyl)-2,6,10-triazaundecane (imdpt) are reported. Chelate ring size has a noticeable influence on the ligand field strength, Dq ranging from 2630 to 2410 cm^{-1} in the series pydien > imdien > epyden $\gtrsim$ tetren $\sim$ imdpt > pydpt. A propensity for splitting of the $^1T_{1g}$ band in solutions containing high concentrations of weak field ligands seems to imply that the position transaxial to the peroxide moiety is rather labile. This is observed particularly for the pydien and pydpt complexes. The frequencies of the oxygen to cobalt charge-transfer bands are linearly related to the redox potentials of the complexes and to log K_{O_2}. While the base strength of the ligand is the major factor influencing the magnitude of K_{O_2}, ligand field strength may introduce a sizable perturbation.

Introduction

The past few decades have seen a growing interest in the study of cobalt–dioxygen complexes as models for biological oxygen carriers such as hemoglobin, hemerythrin, and hemocyanin.[2] Not only are the cobalt complexes more chemically tractable than the copper- and iron-containing systems they model but also they yield more easily interpreted electronic spectra. While considerable insight has been gained from the relatively few electronic spectral studies that have been conducted,[3–8] virtually no studies have been conducted on complexes that have been well characterized in terms of oxygen affinity, redox potentials, or the like. Thus any correlations between electronic structure and chemical behavior have, to date, been somewhat speculative.

Recently a series of pentadentate polyamine ligands consisting of 1,4,7,10,13-pentaazatridecane (tetren), 2,6-bis(5-(1,4-diazahexyl))pyridine (epyden), 1,9-bis(2-pyridyl)-2,5,8-triazanonane (pydien), 1,11-bis(2-pyridyl)-2,6,10-triazaundecane (pydpt), 1,9-bis(4-imidazolyl)-2,5,8-triazanonane (imdien), and 1,11-bis(4-imidazolyl)-2,6,10-triazaundecane (imdpt) have been extensively characterized in these laboratories in terms of stability constants with various metals, oxygen affinities of the cobalt(II) complexes, redox potentials of the cobalt(II) and μ-peroxo-dicobalt(III) complexes,[9,10] and X-ray crystal structures of the μ-peroxo $(Co^{III}pydien)_2$ and $(Co^{III}pydpt)_2$ complexes.[11] The cobalt(II) complexes of these ligands cover a fairly wide range of oxygen affinity and yet are simple enough to allow spectral studies of the dioxygen complexes without extensive interference from intraligand or charge-transfer bands not involving the dioxygen.

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[1] Abstracted in part from a dissertation submitted by S. R. Pickens to the faculty of Texas A&M University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] See, for example, G. McLendon and A. E. Martell, *Coord. Chem. Rev.*, **19**, 1 (1976).

[3] B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, **5**, 1514 (1966).

[4] G. N. Schrauzer and L. P. Lee, *J. Am. Chem. Soc.*, **92**, 1551 (1970).

[5] Y. Sasaki, J. Fujita, and K. Saito, *Bull. Chem. Soc. Jpn.*, **44**, 3373 (1971).

[6] V. M. Miskowski, J. L. Robbins, I. M. Treitel, and H. B. Gray, *Inorg. Chem.*, **14**, 2318 (1975).

[7] A. B. P. Lever and H. B. Gray, *Acc. Chem. Res.*, **11**, 348 (1978).

[8] S. R. Pickens, G. McLendon, A. B. P. Lever, H. B. Gray, and A. E. Martell, *Inorg. Chem.*, **17**, 2190 (1978).

[9] W. R. Harris, I. Murase, J. H. Timmons, and A. E. Martell, *Inorg. Chem.*, **17**, 889 (1978).

[10] J. H. Timmons, W. R. Harris, I. Murase, and A. E. Martell, *Inorg. Chem.*, **17**, 2192 (1978).

[11] J. H. Timmons, R. H. Niswander, A. Clearfield, and A. E. Martell, *Inorg. Chem.*, **18**, 1042 (1979), for pydpt; for pydien the manuscript has been submitted for publication.