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Formation, Electronic and Solution Structure, and Reactions of Mononuclear Dioxygen Complexes: [Bis(*N,N'*-dimethylethylenediamine)chlorosuperoxocobalt(III)] and Related Compounds

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The charge-transfer and electron spin resonance spectra of the 1:1 complexes $[Co(s\text{-}Me_2en)_2X(O_2)]^{n+}$, where X may be chloride or a solvent molecule, are reported. A band near 340 nm is assigned to the $O_2^- \rightarrow Co(III)$ LMCT transition. In the chloride complex, the $Cl \rightarrow Co(III)$ LMCT transition is observed at 236 nm, providing a unique example to adduce the nature of the cobalt oxidation state.

Introduction

The complexation of molecular oxygen by transition metals has generated considerable interest, centered primarily on studies of cobalt–dioxygen bonding as a model for biological processes.[2a] These complexes may form with 1:1 and 2:1 metal–dioxygen stoichiometries:

$$ML + O_2 \rightleftharpoons MLO_2 \underset{-ML}{\overset{+ML}{\rightleftharpoons}} MLO_2ML \qquad (1)$$

A wealth of physical data supports the assignment of a formal oxidation state of Co(III) to the metal, with concomitant formal reduction of dioxygen to "superoxide" and "peroxide" for the 1:1 and 2:1 complexes, respectively. For most ligands, the binuclear μ-peroxo complexes are readily formed at room temperature (and one-electron oxidation gives dinuclear superoxo species), whereas mononuclear complexes tend to form with sterically hindered ligands (e.g., vitamin B_{12}[2b]), nonaqueous solvents ($[Co(CN)_5O_2]^{3-}$ in DMF[3]), and low temperatures or some combination of the above.[2a,4] One of us has recently demonstrated[5] the formation of mononuclear bis(*N,N'*-disubstituted ethylenediamine)superoxocobalt(III) complexes. These simple amine complexes differ from the bulk of previously reported mononuclear superoxo complexes,[2] which generally incorporate ligand systems with considerable π-acceptor character. The *N,N'*-dialkylethylenediamines posses no low-lying π^* orbitals, and the basicity of the amine donors is quite high. Thermodynamically stable mononuclear superoxo complexes can be formed at room temperature in polar nonaqueous solvents, in contrast to the lower temperatures required to stabilize the porphine and Schiff-base systems.[2a,4] The simplicity of these systems has thus made them attractive candidates for studies of reactivity and electronic structure. Accordingly, we have examined the electronic spectra and some reactions of [(*N,N'*-dimethylethylenediamine)chlorosuperoxocobalt(III)] and of several analogous complexes, in an attempt to establish what differences, if any, exist between the mononuclear superoxo complexes and dinuclear μ-superoxo analogues.

Experimental Section

Reagent grade *N,N'*-dimethylethylenediamine (s-Me$_2$en) was obtained from K&K Laboratories. The complexes $[Co(s\text{-}Me_2en)_2X_2]$ ($X^- = Cl^-, Br^-, I^-, NO_3^-$) were prepared as described previously.[6] Dissolving $[Co(s\text{-}Me_2en)_2X_2]$ in deaerated ethanol gives a light pink solution, which on exposure to oxygen turns dark red-brown, corresponding to $[Co(s\text{-}Me_2en)_2X(O_2)]^+$. The oxygen adducts themselves are moderately soluble in the lower alcohols. However, the cobalt(II) precursor complexes in the s-Me$_2$en series are not very soluble. Only when $X^- = Cl^-$ or NO_3^- can a moderately concentrated solution be obtained.

The kinetic stability of each of the mononuclear complexes was monitored by following the decrease in intensity with time of the EPR signal, measured on a Varian AS-100 spectrometer, using a flat quartz cell. Low-temperature EPR spectra were obtained with an Air Products Model LTD-3-11-Liquid Transfer Heli-Tran refrigerator and a 12-in. magnet E-line Varian spectrometer. As a check on the EPR data, analogous measurements were made of the change in optical density at 330 nm (λ_{max} for an intense absorption of the superoxo complex) as a function of time. Visible spectra were obtained at room temperature, at 78 K, and at about 10 K on Cary 14 and 17 spectrophotometers. Low-temperature spectra were obtained in a quartz Dewar (78 K) or Cryogenic Technology "Cryocooler" (liquid He), the complexes being dissolved in 4:1 EtOH–MeOH glasses. We have noted that the rate of conversion of a 1:1 adduct to a dinuclear species is both X and temperature dependent. To inhibit the dimerization reaction, solutions were generally made up and maintained at ice temperature. For low-temperature spectra, solutions were cooled rapidly to 0 °C, followed by slow cooling to 78 K to obtain a good glass.

Kinetic measurements of complex formation were obtained on a Durrum-Gibson D1 110 stopped-flow spectrophotometer, measuring absorbance change at 360 nm on mixing ethanolic $[Co(s\text{-}Me_2en)_2Cl_2]$ with aerated ethanol. The fact that the chlorosuperoxo complex is sufficiently stable toward dinuclear complex formation at room temperature allowed us to obtain the second-order rate constant for 1:1 adduct formation.

Results and Discussion

On exposing a cooled pink solution of $[Co(s\text{-}Me_2en)_2Cl_2]$ to air, the solution turns dark brown essentially instantaneously. The original pink color may be recovered by warming, by nitrogen degassing, or by several freeze–thaw–evacuate cycles, consistent with reversible oxygenation (eq 2). The kinetics

$$Co(s\text{-}Me_2en)_2Cl_2 + O_2 \underset{EtOH}{\overset{k_1}{\rightleftharpoons}} [Co(s\text{-}Me_2en)_2Cl(O_2)]^+ + Cl^- \qquad (2)$$

of this reaction were measured, yielding a value of k_1 of 6.2×10^3 M^{-1} s^{-1} at 25 °C. This rate constant is comparable to those measured for other cobalt(II) polyamines[8] but is considerably smaller than those estimated for the corresponding reactions with cobalt porphyrins[9] and some iron proteins.[10,11]

The 1:1 oxygenated complexes usually decay according to eq 1 at a rate that depends on solvent, temperature, and the nature of X. A qualitative study of this decay has been undertaken to ensure that the spectra reported here do arise specifically from the 1:1 species. At ice temperature there is no difficulty in maintaining a solution of the 1:1 species with $X^- = Cl^-$, Br^-, or NO_3^-. With iodide, data must be collected rapidly, as the solution of the 1:1 complex, even at ice temperature, has a fairly short lifetime (minutes). The ESR spectra of the bromide, iodide, or nitrate complexes dissolved in acetonitrile are all identical (Table I), implying substitution of the anion by solvent to form the species $[Co(s\text{-}Me_2en)_2(CH_3CN)(O_2)]^{2+}$. Indeed, the nitrate ion appears readily to be substituted by solvent to provide access to a range of solvated species having varying ESR spectra. In contrast, the chloride complex has a unique spectrum which is independent of solvent (methanol, ethanol, acetonitrile, dimethylacetamide),

Table I. EPR and Electronic Spectral Data for $[Co(s\text{-}Me_2en)_2X(O_2)]^+Y^-$ Complexes

X^a	Y^-	$g_\parallel$	$A_\parallel$, G	$g_\perp$,[b]	$A_\perp$, G[b]	ν_{max}, nm
CH_3CN	NO_3^-	2.067	23	2.008	~17	308
CH_3CN	Br^-	2.068	22	2.006	~18	341
MeOH	NO_3^-	2.072	28	2.009	~21	327
Cl[c]	Cl^-	2.075	26	2.011	~19	344
		(2.077)[d]	(~30)	(2.011)	(~19)	

[a] The solvent is CH_3CN or MeOH as indicated. For the chloride species, the spectrum is independent of solvent. [b] $g_\perp$ and $A_\perp$ values are averages estimated from spectra with apparent rhombic distortion. [c] $g_{iso} = 2.029$, $\langle A_{iso}\rangle = 15.60$. [d] Numbers in parentheses are approximate parameters from the Q-band spectrum for $[Co(s\text{-}Me_2en)_2Cl(O_2)]Cl$. The Q-band spectrum of this compound does not reveal a strong rhombic distortion. The apparent rhombic distortion in the X-band spectra and our inability to obtain a satisfactory computer simulation out of numerous permutations of the g and A values may be due in part to a different orientation for the G tensor than for the A tensor.

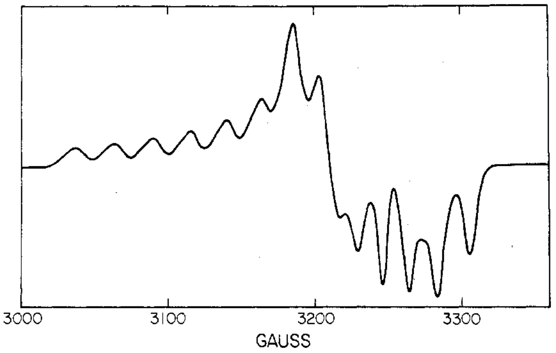

Figure 1. ESR spectrum of $[Co(s\text{-}Me_2en)_2Cl(O_2)]^+$ in EtOH at liquid nitrogen temperature ($h\nu$ = 9.096 GHz, power 2 mW, modulation amplitude 8 G, gain 4 × 10^2).

implying that the chloride ion remains bound to cobalt. An illustrative spectrum at liquid nitrogen temperature is shown in Figure 1. There is marked rhombic distortion as expected for the proposed cis configuration.[5]

A cis configuration is also easier to reconcile with the relative insensitivity of the ESR spectra to the nature of X.[5] Furthermore, it is well established that $Co-O_2$ binding is enhanced by the presence of a strongly σ donating trans ligand.[12,13] In the complexes under consideration here, a cis configuration would place the more basic amine nitrogen atom trans to dioxygen. Parameters obtained from a fluid ESR spectrum of $[Co(s\text{-}Me_2en)_2Cl(O_2)]^+Cl^-$ (Table I) are not comparable with the frozen spectrum. Evidently there is some kind of structural change upon freezing or there is very fast exchange with the deoxygenated species in the fluid state. The lability of the X group cis to the superoxide group also provides access to a range of substrate substituted species, e.g., X = phenolate, which are under further study.[14]

All these 1:1 dioxygen adducts display an intense band in the range 310–340 nm. This band is attributable to an $O_2^- \rightarrow Co(III)$ charge-transfer transition by analogy to an interpretation of the electronic spectra of μ-superoxo-dicobalt(III) discussed in detail previously.[15] The question of intensities of oxygen to metal LMCT's is discussed in detail elsewhere.[16] In addition to the LMCT band, the $[Co(s\text{-}Me_2en)_2(Cl)O_2]^+$ complex exhibits a very intense feature at 236 nm, as well as a low-energy absorption (480 nm) that is resolved at 4 K in a 4:1 EtOH–MeOH glass (Figure 2). The 236-nm band is reasonably assigned to $Cl^- \rightarrow Co(III)$ charge transfer, as examination of the electronic spectrum of $[Co(s\text{-}Me_2en)_2(CH_3CN)O_2]^+$ has revealed no evidence for any LMCT bands other than $O_2^- \rightarrow Co(III)$ down to 210 nm. A band at 270 nm is observed in some solutions of the bromide complex. However, it does not increase in intensity in parallel with the 330-nm band seen with this species. Thus, if a room-temperature solution of the bromide complex is cooled, the 330-nm band ($O_2^- \rightarrow Co(III)$) increases in intensity as the equilibrium concentration of 1:1 adduct increases, but the 270-nm band does not increase in concert. A reasonable possibility, therefore, is that the 270-nm band is due to $Br^- \rightarrow Co(III)$ charge transfer in a dinuclear species. A fresh ice cold solution of the iodide complex exhibits a shoulder at 287 nm and a peak at 330 nm. On standing or upon warming of the solution, the 330-nm band shifts to 356 nm (with loss of the ESR signal), whereas the 287-nm band intensifies to a peak but does not shift. We infer, therefore, that the 287-nm band represents an $I^- \rightarrow Co(III)$ charge-transfer transition in a dinuclear iodo complex. Both the bromide and freshly prepared iodide complexes exhibit the band near 330 nm, which is, therefore, assigned as the $O_2^- \rightarrow Co(III)$ charge-transfer transition.

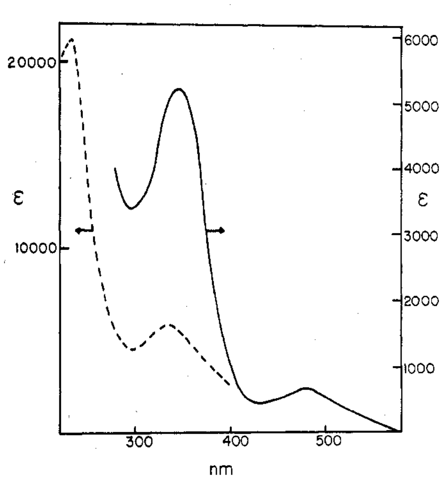

Figure 2. Electronic spectrum of $Co(s\text{-}Me_2en)_2Cl(O_2) + Cl^-$: solid line, solution in 4:1 EtOH–MeOH at liquid helium temperature; hatched line, room-temperature spectrum in acetonitrile (λ_{max} 236, 344, 480 nm).

The position of the LMCT transition in the series $[Co(s\text{-}Me_2en)_2(X)(O_2)]^{n+}(Y^-)_n$ is dependent upon both X and Y. The dependence upon X is to be expected; dependence upon Y is more unusual (see Table I). We believe that this is due to a strong hydrogen bonding interaction between the counterion and the amine protons. This will change the charge distribution on the cation and certainly modify charge-transfer energies. Evidence for such hydrogen bonding was previously presented[5] and has been further supported by the x-ray structure of the analogous complex $[Ni(s\text{-}Et_2en)_2(ONO)]^+NO_2^-$. The anionic nitrite group is shown in this study[17] to interact with the amine protons. Such protons would be even more acidic in a cobalt(III) complex than in this nickel(II) derivative because of polarization by the central positive metal ion.

Both MLCT ($Co(III) \rightarrow O_2^-$) and d–d transitions should occur at low energies in $[Co(s\text{-}Me_2en)_2Cl(O_2)]^+$. The band at 480 nm is very broad and moderately intense (ϵ ~600 M^{-1} cm^{-1}), which suggests that it could be due to overlapping MLCT and d–d absorptions. At the very least, then, we may conclude that $Co(III) \rightarrow O_2^-$ charge transfer is more energetic in $[Co(s\text{-}Me_2en)_2Cl(O_2)]^+$ than it is in the closely related dinuclear species $[Co_2(NH_3)_{10}O_2]^{5+}$ where it falls at 670 nm.[15] Such a blue shift of the MLCT transition is not unreasonable, as the removal of a cobalt(III) center from one end of the superoxide ion should destabilize the half-filled "vertical" π^* orbital.

The chloro complex is unique in that both oxygen and halogen to metal charge-transfer bands may simultaneously be observed. Comparison with *cis*- and *trans*-$\mathrm{Co(en)_2Cl_2^+}$ is profitable. The lowest energy chloride to cobalt(III) charge-transfer transition in *cis*-$\mathrm{Co(en)_2Cl_2^+}$ occurs[18] at about 256 nm, blue-shifted as expected from the analogous band in the trans isomer[19] (305 nm). A further blue shift of approximately one-tenth of an optical electronegativity unit[7,20] occurs with the superoxide complex (Figure 2). This reflects some small contribution of cobalt(II) character to the ground state of the superoxide complex.

Intense ligand absorption in the 300–400-nm region has made it difficult to identify $\mathrm{O_2^-} \rightarrow$ Co(III) CT bands in the spectra of 1:1 cobalt(II)–dioxygen complexes containing π-conjugated nitrogen donors. Nevertheless, there is a shoulder near 320 nm in the spectrum of low-temperature-oxygenated vitamin $\mathrm{B_{12}}$[21] and an extra peak in the Soret region of the MCD spectrum of oxygenated (dimethylmesoporphyrin IX ato)(pyridine)cobalt(II).[22] To equate these bands as charge transfer from bound superoxide would be premature; however, the possibility certainly warrants further study.

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Registry No. $\mathrm{[Co(\textit{s}\text{-}Me_2en)_2Cl_2]}$, 42590-61-4; $\mathrm{[Co(\textit{s}\text{-}Me_2en)_2Br_2]}$, 42590-63-6; $\mathrm{[Co(\textit{s}\text{-}Me_2en)_2I_2]}$, 42590-65-8; $\mathrm{[Co(\textit{s}\text{-}Me_2en)_2(NO_3)_2]}$, 42534-16-7; $\mathrm{[Co(\textit{s}\text{-}Me_2en)_2(CH_3CN)(O_2)](NO_3)_2}$, 66119-81-1; $\mathrm{[Co(\textit{s}\text{-}Me_2en)_2(CH_3CN)(O_2)]Br_2}$, 66119-79-7; $\mathrm{[Co(\textit{s}\text{-}Me_2en)_2(MeOH)(O_2)](NO_3)_2}$, 66119-78-6; $\mathrm{[Co(\textit{s}\text{-}Me_2en)_2Cl(O_2)]Cl}$, 66119-76-4; $\mathrm{[Co(\textit{s}\text{-}Me_2en)_2(CH_3CN)(O_2)]I_2}$, 66119-75-3.

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Stabilities of Metal Chelates of Imidazolyl-Containing Pentadentate Polyamines and Their Dioxygen Complexes[1a]

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The synthesis of the new imidazolyl containing polyamines 1,9-bis(4-imidazolyl)-2,5,8-triazanonane (4-IMDIEN), 1,11-bis(4-imidazolyl)-2,6,10-triazaundecane (4-IMDPT), and 1,11-bis(2-imidazolyl)-2,6,10-triazaundecane (2-IMDPT) is described. Ligand protonation constants, the stability constants of the Co(II), Ni(II), Cu(II), and Zn(II) chelates, and the oxygenation constants ($K_{\mathrm{O_2}} = \mathrm{[MLO_2ML]/[ML]^2[O_2]}$) of the cobaltous chelates have been determined. The cobaltous chelates form stable oxygen complexes below pH 4, 5.5, and 5, respectively. Equilibrium data are compared with those of aliphatic polyamines and with those of the analogous pyridyl-containing ligands previously described. The imidazolyl ligands are found to be slightly more effective than their pyridyl analogues at coordinating molecular oxygen and are also more stable to irreversible oxidation to Co(III)-containing species. These results are discussed in terms of differences between pyridyl and imidazolyl donors. Differences in the equilibria of the isomeric IMDPT's are also discussed.

Introduction

The reactions of metal chelate compounds, especially cobaltous chelates, with dioxygen have received considerable attention over the past few years, and recent reviews of the field are available.[2] In a recent paper,[3] the chelating tendencies of some pentadentate ligands with pyridyl donor groups and the oxygenation equilibria of the cobaltous complexes of these ligands were discussed. The present paper continues the investigation of pentadentate ligands having potential π-bonding donor groups with a discussion of the imidazolyl-containing ligands 1,9-bis(4-imidazolyl)-2,5,8-triazanonane (4-IMDIEN), 1,11-bis(4-imidazolyl)-2,6,10-triazaundecane (4-IMDPT), and 1,11-bis(2-imidazolyl)-2,6,10-triazaundecane (2-IMDPT), shown schematically (formulas I–III).

The imidazole group is of special interest due to the presence of histidine at the active site of the biological oxygen carriers hemoglobin and myoglobin. Thus, imidazole-containing ligands were used in model studies of biological oxygen carriers,[4,5] and the reactions of dioxygen with cobalt complexes of histidine and peptides containing histidine have been extensively studied.[2a,6] Gruenwedel[7] has already described a tetradentate ligand having two imidazolyl groups (BIMEDA), for which he determined the protonation constants and stability constants with several transition-metal cations. The oxygenation equilibrium for the cobaltous complex of this ligand, however, is complicated by

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