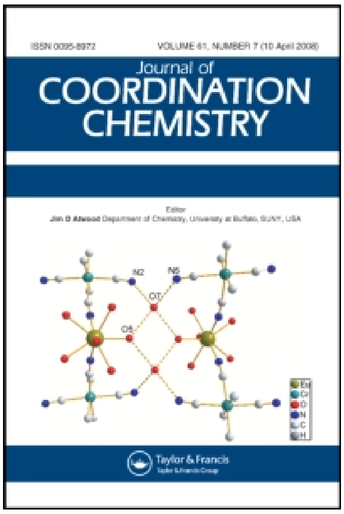

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OXYGENATED COBALT COMPLEXES WITH SIMPLE TETRAAZAMACROCYCLIC LIGANDS

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Binuclear oxygenated cobalt complexes with 5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene (Me_4[14]dieneN_4) and 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene (Me_6[14]dieneN_4) with axial ligands (NCO^-, NCS^-, $NCSe^-$, N_3^-, OH^-, NO_2^-, $ON{-}C(CN)_2^-$, Im) have been isolated and characterised by physical and chemical methods, including derivatography, electronic, IR and X-ray photoelectron spectroscopy, magnetic measurements and EPR. The electronic structure of the cobalt ion-dioxygen fragment conforms to the scheme Co(III)–O_2–Co(III). The coordinated dioxygen species is activated owing to the transfer of an appreciable electron density to it. Irreversible oxidation in aqueous solution is illustrated by $[\mu O_2\{Co(Me_4[14]dieneN_4)(H_2O)\}_2](ClO_4)_4$. Activation parameters for this process are $E^* = 54 \pm 4\,kJ\,mol^{-1}$ and $\Delta S^* = -140 \pm 16\,J\,mol\,K^{-1}$. A possible mechanism is proposed.

INTRODUCTION

Basic systematic studies of water-soluble synthetic oxygen carriers, cobalt complexes with polychelating ligands of different nature, were performed under the guidance of A.E. Martell.[1] Cobalt coordination compounds with synthetic tetraazamacrocyclic ligands may be used as the simplest models of biocomplexes, natural carriers and activators of molecular oxygen.

A variety of cobalt compounds with molecular oxygen of this type have been examined and characterized in solution.[2–7] The number of investigations dealing with the synthesis and isolation of individual compounds is limited.[8–10] We also observed reversible oxygenation of the cobalt(II) complexes with 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (Me_6[14]anN_4) and 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene (Me_6[14]dieneN_4)[9] simultaneously with Martell.[1] The oxygenated cobalt complexes within these ligands are liable to relatively rapid, irreversible oxidation in aqueous solution.[10]

Accordingly, the present study was undertaken to isolate oxygenated cobalt complexes with 5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene (Me_4[14]dieneN_4) and Me_6[14]dieneN_4 with various axial ligands, and to determine their structure, the electronic structure of the cobalt ion-dioxygen fragment, as well as the axial ligand *trans* effect.

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EXPERIMENTAL

Syntheses of the oxygenated cobalt complexes $[\mu O_2\{Co(Me_4[14]dieneN_4)(H_2O)\}_2](ClO_4)_4 \cdot 4H_2O$ and $[\mu O_2\{Co(Me_6[14]dieneN_4)(X)\}_2](ClO_4)_n$, where X = NCO^-, NCS^-, $NCSe^-$, N_3^-, OH^-, NO_2^-, $ON\text{–}C(CN)_2^-$ (n = 2), Im (n = 4) hav been described in our earlier papers.[10,11] These compounds have been synthesized b crystallization from oxygenated aqueous or aqueous-ethanol solutions of the corresponding cobalt(II) complexes and NaX.

Derivatograms were recorded on an OD-103 derivatograph (Hungary). Electroni absorption spectra were measured using Specord UV VIS and CF-20 spectrophotometers. IR spectra were obtained using UR-20 and Perkin-Elmer 325 spectrometers. X-ray photoelectron spectra were measured on an IEE-15 photoelectro spectrometer. Mass spectrometric measurements indicate that solid samples of th complexes examined underwent deoxygenation with maximal rates at 373–391K (10^{-5} Pa). Therefore, X-ray photoelectron spectra were recorded at 78K under vacuum of 1.3×10^{-5} Pa using AlK_α radiation. Spectra were calibrated usin $E_B C1s = 285$ eV for the hydrocarbons of adsorbed diffusion oil (close to the C1 binding energy in polyazamacrocyclic complexes).[12] The binding energies wer measured with an accuracy of 0.1–0.2 eV with respect to the Fermi level of th spectrometer. EPR spectra were recorded using a JEOL-JES-3x-Me. Magneti parameters were determined by the Gouy technique.

The kinetics of the irreversible oxidation of $[\mu O_2\{Co(Me_4[14]dieneN_4)(H_2O)\}_2](ClO_4)_4$ in aqueous solution was studied in air-tight quartz cells by th procedure developed earlier and reported in ref. [13]. The reaction rate was measure spectrophotometrically through monitoring the change in the absorption intensity i the region of the charge transfer $1\pi^*_g\, O_2 \rightarrow d_{z^2}\, Co$ ($\lambda = 318$ nm) band maximum.

RESULTS AND DISCUSSION

Heating the binuclear oxygenated $[\mu O_2\{Co(Mc)(X)\}_2](ClO_4)_n$ complexes (Mc is tetraazamacrocyclic ligand) to a temperature not higher than 140°C leads to quantitative endothermal deoxygenation. As a result, the corresponding five-coordinate low-spin cobalt complex is formed. The unsplit signal in the EPR spectra o oxygenation solid products ($g \sim 2.4$), as well as magnetic moments, *e.g.* in $[Co(Mc)(NCS)(ClO_4)]$ $\mu = 2.1$ B.M., characterize them as compounds containing on unpaired electron. The temperature of deoxygenation for these macrocyclic complexes ($Mc = Me_6[14]dieneN_4$) depends on the nature of the *trans* ligand in th sequence OH^- (80°C) < N_3^- (106°C) < $ON\text{–}C(CN)_2^-$ (108°C) < NCS^- (130°C which presumably characterizes the increase in stability of the oxygenated complexe

The stretching vibration bands $\nu_{Co\text{–}O_2}$(520, 515, 490 cm^{-1}) and ν_{O-O}(830, 83 827 cm^{-1}) were determined for the above oxygenated coordination compound where X = NCS^-, $ON\text{–}C(CN)_2^-$ and N_3^-, respectively. These are within the range c corresponding frequencies characteristic of other binuclear oxygenated cobalt complexes with histidinate ion and salen.[17] The bands were identified by comparison c the vibrational spectra for the solid oxygenated complexes with those for corresponding deoxygenated compounds.

The IR spectra of all the oxygenated complexes under study contain intense ν_C stretching vibrations at 1665–1660 cm^{-1}, as well as ν_{NH} (3200–3170 cm^{-1}), ν_{C}

(2900–2970 cm^{-1}). These bands usually characterize equatorial Me$_4$- and Me$_6$-[14]dieneN$_4$ ligands bound in a complex.

The coordination of axial ligands may be determined from the increase in the frequency of stretching vibrations on binding: NCS$^-$ ($\nu_{CN} = 2110\,cm^{-1}$), NCO$^-$ ($\nu_{CN} = 2265\,cm^{-1}$), NCSe$^-$ ($\nu_{CN} = 2117\,cm^{-1}$), ON–C(CN)$_2^-$ ($\nu_{CN} = 2230\,cm^{-1}$) and N$_3^-$ ($\nu_{as} = 2050\,cm^{-1}$) as compared to the free ligands (2053, 2155, 2070, 2185, 2041 cm^{-1}, respectively).[14]

The coordination of isothiocyanate, azide and hydroxyl ions in the inner sphere is confirmed by $\nu_{Co-N} = 334$, 304 and $\nu_{Co-O} = 202\,cm^{-1}$. The nitrosodicyanomethanide ion is bound to cobalt *via* a nitroso oxygen, $\nu_{Co-O} = 202\,cm^{-1}$; as in [M{ON–C(CN)$_2$}$_2py_4$] complexes.[15]

TABLE I

Core electron binding energies (E_B) in the cobalt complexes.

Complex	E_B, eV			
	Co2p$_{3/2}$	N1s	Cl2p$_{3/2}$	O1s
1. [μO_2{CoMe$_6$[14]dieneN$_4$(NCS)}$_2$](ClO$_4$)$_2$	781.3	399.7 398.2 sh	207.5	532.1
2. [μO_2{CoMe$_6$[14]dieneN$_4$(N$_3$)}$_2$](ClO$_4$)$_2$	781.3	399.7 402.6 sh	207.9	532.8
3. [μO_2{CoMe$_6$[14]dieneN$_4$(NCO)}$_2$](ClO$_4$)$_2$	781.6	399.8 397.9 sh	207.5	532.0
4. [μO_2{CoMe$_6$[14]dieneN$_4$(OH)}$_2$](ClO$_4$)$_2$	781.7	400.1	208.1	532.7
5. [μO_2{CoMe$_6$[14]dieneN$_4$(Im)}$_2$](ClO$_4$)$_4$	782.0	399.8	208.1	532.3
6. [μO_2{CoMe$_4$[14]dieneN$_4$(H$_2$O)}$_2$](ClO$_4$)$_4$	781.6	400.1		
7. Co(II)Me$_6$[14]dieneN$_4$(NCS)(ClO$_4$)	780.3	400.1 398.2 sh	207.8	532.3
8. Co(II)Me$_6$[14]dieneN$_4$(N$_3$)(ClO$_4$)	780.6	399.8 402.5	207.9	532.8
9. Co(II)Me$_4$[14]dieneN$_4$(H$_2$O)(ClO$_4$)$_2$	780.1	399.9		
10. Co(II)salen	779.9	398.9		
11. Co(III)Me$_6$[14]dieneN$_4$(NCS)$_2$]ClO$_4$	781.8	399.6 398.0		
12. Co(III)Me$_6$[14]dieneN$_4$(N$_3$)$_2$]ClO$_4$	781.4	399.9 403		
13. Co(III)Me$_6$[14]dieneN$_4$(NCO)$_2$]ClO$_4$	781.6	399.7		

X-ray electron spectroscopy (E_B = Co2p$_{3/2}$, N1s, Cl2p$_{3/2}$, O1s) can provide information about the structure of the complexes under study and in particular of the electronic structure of the "cobalt ion-dioxygen" fragment. The N1s binding energy of Me$_4$- and Me$_6$[14]dieneN$_4$ in transition metal complexes is close to 400 eV.[12] It was found to be 400.1–399.7 eV (Table I) in the examined compounds. Deconvolution of the N1s peak for compounds 1 and 3 (Table I) yields E_BN1s(NSC$^-$) = 398.2 eV and E_BN1s(NCO$^-$) = 398.4 eV. The first E_B value resembles the corresponding value in an analogous cobalt(III) compound (398.0 eV) containing an isothiocyanate ion.[12] The N1s binding energy of free ligands in NaNCS and NaNCO amounts to 397.8 and 397.9 eV, respectively.[16] This is lower than for NCS$^-$ and NCO$^-$ coordinated to metal complexes. Such a comparison shows that these ligands acting as electron donors, axially coordinated *via* the nitrogen atom, in the examined complexes. A broad N1s band for the imidazole-containing complex (5, Table I) indicates a close resemblance of the N1s binding energies of an equatorial tetraazamacrocycle and an axial heterocyclic ligand (imidazole).

The $\mathrm{Cl2p}_{3/2}$ binding energy for all compounds under study (208.1–207.3 eV) is lower than that for sodium perchlorate (208.7 eV[16]) and is close to the energy of inner-sphere perchlorate in other 3d transition metal complexes.[16] The O1s binding energy, listed in Table I, characterizes the inner-sphere perchlorate oxygen atom.

It was of interest to compare the $\mathrm{Co2p}_{3/2}$ binding energies of the oxygenated cobalt complexes with the corresponding cobalt(II) and cobalt(III) coordination compounds. It follows from Table I that the $\mathrm{Co2p}_{3/2}$ values for the cobalt(II) complexes (7–9) are equal to 780.4 ± 0.2 eV.

The $\mathrm{Co2p}_{3/2}$ binding energies in Co(III) compounds with the same equatorial and axial ligands (11–13) are 781.6 ± 0.2 eV. Analogous binding energies in oxygenated cobalt complexes amount to 781.5 ± 0.2 eV (1–4,6) and coincide with the latter. A slightly higher $\mathrm{Co2p}_{3/2}$ binding energy ($E_B = 782.0$ eV) in complexes containing the electroneutral axial ligand imidazole is attributed to the effect of the greater (4+, 5; 2+, 1–4,6) positive charge of the complex ion. Comparison suggests that the oxidation state of cobalt is equal to three and that the electronic structure of the cobalt ion-dioxygen fragment conforms to the scheme Co(III)-O_2-Co(III). Such a coordinated dioxygen species is activated owing to the transfer of an appreciable electron density to it. The species may react with various reductants of organic and inorganic nature.[17]

In the electronic absorption spectra of the oxygenated complexes in aqueous solution one can observe intense absorption bands at 330 nm (Table II).

TABLE II
The position and intensity of the charge transfer band in the oxygenated complexes.

	Complex	λ_{max}, nm	ε, $M^{-1}cm^{-1}$
	$[\mu O_2\{CoMe_6[14]dieneN_4(X)\}_2]^{2+}$		
X: 1	NCO^-	329	5520
2	NCS^-	330	4300
3	$NCSe^-$	330	4000
4	N_3^-	338	5600
5	OH^-	329	4000
6	NO_2^-	330(sh)	2000
7	$ON{-}C(CN)_2^-$	344(sh)	4000
8	$[\mu O_2\{CoMe_6[14]dieneN_4(Im)\}_2]^{4+}$	331	3640
9	$[\mu O_2\{CoMe_4[14]dieneN_4(H_2O)\}_2]^{4+}$	330	5770
10	$[\mu O_2\{CoMe_2[14]dieneN_4(H_2O)\}_2]^{4+}$	320(sh)	3870

These charge transfer bands are characteristic of the formation of cobalt coordination compounds with molecular oxygen, and for oxygenated complexes with tetraazamacrocyclic ligands (Table II) may, with a high probability, be assigned to a $\pi_h^* \rightarrow d\sigma^*$ transition (if the cobalt–dioxygen–cobalt group is flat.[18] The spectra permit one to follow the change in the state of a complex in oxygenation–deoxygenation cycles (alternate coordination and liberation of O_2 by the complex on changing the partial pressure of oxygen and temperature).

The ability to binding molecular oxygen to the examined complexes in aqueous solution disappears after 3–10 oxygenation–deoxygenation cycles. This phenomenon may be attributed to an irreversible oxidation whose nature has been studied earlier using a cobalt histidinate complex.[13]

It should be noted that a cobalt complex with Me_4[14]dieneN_4, described in ref. [19] as a compound containing molecular oxygen, does not contain the characteristic charge transfer band in the near UV region. Prolonged contact with the synthesis solution used for its isolation results in a Co(III) complex.

When dissolved in dimethylformamide, the binuclear oxygenated complexes undergo a reversible dissociation to give mononuclear oxygenated forms, as shown below.

$$[(X)(Mc)CoO_2Co(Mc)(X)]^{2+} \rightleftharpoons [(X)(Mc)CoO_2]^{+} + [Co(Mc)(X)]^{+} \tag{1}$$

$$[(X)(Mc)CoO_2]^{+} \rightleftharpoons [(X)(Mc)Co]^{+} + O_2 \tag{2}$$

Depending on the partial pressure, temperature and stability of the oxygenated complexes, the formation of only low-spin tetraazamacrocyclic complexes of cobalt(II), oxygenated mononuclear forms or mixtures may be observed in dimethylformamide solution using the EPR technique. Reactions (*1*) and (*2*) were found to be reversible. EPR spectra for these macrocyclic complexes in dimethylformamide, measured at room temperature, are isotropic and contain eight components (superhyperfine splitting from the ^{59}Co nucleus (I = 7/2)). The corresponding spectra measured at 77K are anisotropic and described by the parameters listed in Table III.

TABLE III
EPR spectral parameters for $[O_2Co(Me_6[14]dieneN_4)(X)]^+$ complexes in dimethylformamide solution at 77K.

				A_1	A_2	A_3
X	g_1	g_2	g_3		$(10^{-4}), cm^{-1}$	
1 OH^-	2.088	2.000	1.989	26.9	16.4	13.8
2 N_3^-	2.000	2.000	1.989	26.8	16.5	14.0
3 $ON\text{–}C(CN)_2^-$	2.086	2.000	1.996	22.7	14.2	11.6
4 NCS^-	2.085	2.000	1.990	20.4	12.4	7.6

The superhyperfine splitting parameters (Table III) are much lower than for corresponding values characterizing the analogous cobalt(II) complexes: for $[Co(Me_6[14]dieneN_4)(OH)]^+$ $A_1 = 93.1 \times 10^{-4}$ cm^{-1}, $g = 2.481$, $A_2 = 69.2 \times 10^{-4}$ cm^{-1}, $g_2 = 2.324$, $A_3 = 124.6 \times 10^{-4}$ cm^{-1}, $g_3 = 2.016$.

The superhyperfine splitting parameters decrease in the series of oxygenated cobalt complexes with various axial ligands (X): $OH^- > ON\text{–}C(CN)_2^- > NCS^-$. Thus an unpaired electron in the oxygenated complexes is, to a great extent, delocalized relative to the cobalt nucleus. Its delocalization correlates with axial ligand field strength.

The results obtained confirm the observation that binuclear oxygenated complexes are predominantly formed in polar solvents with high dielectric permeability. These have a stronger polar metal ion–dioxygen bond than that in mononuclear compounds. The formation of mononuclear oxygenated complexes is facilitated by low dielectric permeability of the solvent.[20]

Irreversible oxidation in aqueous solution is illustrated by the $[\mu O_2\{Co(Me_4\text{-}[14]dieneN_4)(H_2O)\}_2](ClO_4)_4$ complex. The reaction kinetics are characterized by a direct dependence in the semilogarithmic lgD_t/D_o- time coordinates (D_t is the optical density in the region of the maximum of the charge transfer band for time, t; D_o is the optical density at $t = 0$, obtained by extrapolation; Fig. 1. The effective rate constants are independent of the concentration of oxygenated complex in the range 5×10^{-5} to 2×10^{-3} mol dm^{-3} (Table IV).

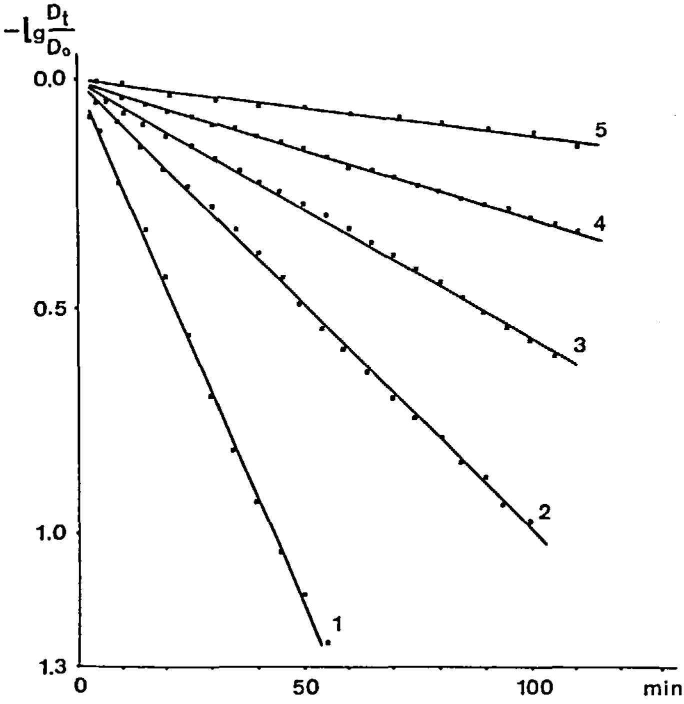

FIGURE 1 Kinetic dependencies for irreversible oxidation of $[\mu O_2\{Co(Me_4[14]dieneN_4)(H_2O)\}_2](ClO_4)_4$ in water (concentration, C, of complex = 1.5×10^{-4} mol dm^{-3}); 1: 40°C, pH = 9.2; 2: 30°C, pH = 9.5; 3: 20°C, pH = 9.2; 4: 14.5°C, pH = 9.25; 5: C = 1×10^{-4} mol dm^{-3}, 20°C, pH = 12.5.

The kinetic equation has the form (*3*); water molecules are omitted in the formula.

$$d[\mu O_2Co_2(Mc)_2]/dt = K_{eff}[\mu O_2Co_2(Mc)_2] \qquad (3)$$

Activation parameters for the process were found to be $E^{\neq} = 54 \pm 4$ kJ mol^{-1}, $\Delta S^{\neq} = -140 \pm 16$ J mol^{-1} K^{-1}, from the temperature-dependence of the effective rate constant using least-squares techniques. The absorption spectrum of the reaction products contains an absorption band characteristic of d–d transitions in the corresponding octahedral Co(III) complexes ($\lambda_{max} = 514$ nm, $\varepsilon = 80$ M^{-1} cm^{-1}.[18] The Clark electrode was useful in determining some 12% of the deoxygenated form of the complex in aqueous solution; the concentration of dissolved oxygen was 2.8×10^{-4} mol dm^{-3} (20 ± 0.5°C).

TABLE IV

Effective rate constants for irreversible oxidation of $[\mu O_2\{Co(Me_4[14]dieneN_4)(H_2O)\}_2](ClO_4)_4$.

Starting concentration of complex, mol dm^{-3}	pH	T, °C	$k_{eff} \times 10^4$, s^{-1}
5×10^{-5}	9.25	20.0	2.4
1×10^{-4}	9.25	21.0	3.1
2×10^{-4}	9.15	21.0	3.2
1×10^{-3}	9.15	21.0	3.1
1×10^{-3}	9.35	20.0	2.5
2×10^{-3}	9.25	21.0	3.3
1.5×10^{-4}	9.25	14.5	1.2
1.5×10^{-4}	9.45	20.0	2.1
1.5×10^{-4}	9.25	25.0	3.3
1.5×10^{-4}	9.25	30.0	3.8
1.5×10^{-4}	9.25	35.0	5.6
1.5×10^{-4}	9.25	40.0	8.4

The process under study, as in the case of the oxygenated histidinate complex of cobalt, may be stipulated by the redox reaction of oxygenated and nonoxygenated forms of the complex, (*4*).

$$[\mu O_2Co_2(Mc)_2]^{4+} + 2Co(Mc)^{2+} + 2H_2O \longrightarrow 4Co(Mc)OH^{2+} \qquad (4)$$

The mechanism of this process is still open to discussion. Inner-sphere electron transfer between the oxygenated and nonoxygenated forms of the complex with bulky ligands is unlikely. Outer-sphere electron transfer is more probable as in the case of the reaction of μ-superoxide binuclear cobalt(III)-ammonia with cobalt(II)-bipyridyl or phenanthroline complexes.[21] The rate of this reaction increases on decreasing $E°Co^{(3+/2+)}$ of the reductant.

A Co-hist$_2$ complex is a high-spin compound containing three unpaired electrons, whereas a $[Co(Mc)(H_2O)]^{2+}$ species is a low-spin complex involving one unpaired electron. The corresponding oxygenated binuclear complexes in both cases are diamagnetic. Such a difference in the spin states of the reactants may be the cause of appreciable differences in the redox process rate.[22] However, the effective rate constant for the irreversible oxidation of an oxygenated tetraazamacrocyclic complex is higher only by a factor of 2–3 than a histidinate complex.[13] The rate of electron transfer reacton is presumably unlikely to make an appreciable contribution to the rate-determining step.

It is quite possible that oxygen–oxygen or cobalt–oxygen bond dissociation under the polarizing action of a reductant (Co(II) complex) may be a slow step. A stronger polarizing effect would be expected if the complex ion (reductant) has a positive charge. Thus there are more favourable conditions for homolytic O–O bond rupture and heterolytic Co–O bond rupture in a symmetric binuclear oxygenated complex of cobalt with a tetraazamacrocyclic ligand than with histidinate ion. The complex ion of the former has a positive charge and the latter is electroneutral. This suggestion is confirmed by the slowing of irreversible oxidation at pH = 12 (Fig. 1), when the hydroxo complex formed has a lower positive charge.

Skurlatov, who has developed the concept of partial charge transfer complexes, reports that such reactions as

$$M^{n+1}\,(O\text{–}O)^{2-}\,M^{n+1} \rightleftharpoons 2M^{n+1}\,O^{-},\quad M^{n+1}\,(O\text{–}O)\,M^{n+1} \overset{2H^{+}}{\rightleftharpoons} 2\,M^{n+1} + H_2O_2$$

are possible.[23] The possibility of a homolytic bond dissociation to yield $Fe(II)O^{\cdot}$, transforming to a ferryl ion, $Fe(IV)O^{2-}$, has been admitted by Collman[24] in the irreversible oxidation of oxygenated iron complexes.

Heterocyclic cobalt-molecular oxygen bond dissociation is less probable for the process under study, occurring in weakly alkaline solutions. At the same time, such bond dissociation was observed in acidic solutions as a result of the protonation of a dioxygen bridge.[25] Thus one may suggest that the slow step for the process under study is a homolytic oxygen–oxygen bond dissociation under the polarizing effect of the reductant species, (*5*); charges are omitted.

$$(Mc)Co\text{–}O_2\text{–}Co(Mc) \rightleftharpoons 2(Mc)CoO \qquad (5)$$

The resultant, highly reactive $(Mc)Co(III)O^{\cdot}$ or $(Mc)Co(IV)O^{2-}$ species* rapidly recombine or react with the reductant, (*6*).

$$(Mc)CoO + (Mc)Co(II) + H_2O \longrightarrow 2(Mc)Co(III)OH \qquad (6)$$

Using the steady-state method, we obtain the kinetic equation below.

$$-\frac{d[\mu O_2Co_2(Mc)_2]}{dt} = \frac{k_5k_6[\mu O_2Co_2(Mc)_2][(Mc)Co(II)]}{k_{-5}[(Mc)CoO] + k_6[(Mc)Co(II)]}$$

It is quite probable that $k_6[(Mc)Co(II)] \gg k_{-5}[(Mc)CoO]$, since the concentration of species is small, and k_{-5} is reasonably small. For this case,

$$d[\mu O_2Co_2(Mc)_2]/dt = k_5[\mu O_2Co_2(Mc)_2] \qquad (7)$$

This equation coincides with the experimental law (*3*) in form.

The proposed approach to analysis of the mechanism applies to irreversible oxidation of oxygenated transition metal complexes in weakly alkaline aqueous solution if there is considerable electronic density transfer from the central ion.

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