# Flash-photolysis Studies of the Electron-transfer Reactions of Dioxygen Complexes of Cobalt(III) with Tris(2,2′-bipyridyl)ruthenium(III)†

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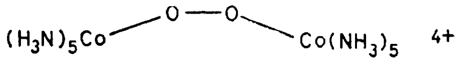
Electron-transfer reactions between the μ-peroxo-cobalt(III) complexes $[(H_3N)_5Co(\mu\text{-}O_2)Co(NH_3)_5]^{4+}$ (1), $[(H_3N)_4Co(\mu\text{-}O_2)(\mu\text{-}NH_2)Co(NH_3)_4]^{3+}$ (2), and $[(L\text{-}L)_2Co(\mu\text{-}O_2)(\mu\text{-}NH_2)Co(L\text{-}L)_2]^{3+}$ [L–L = ethylenediamine (3), 2,2′-bipyridyl (4), or 1,10-phenanthroline (5)] and $[Ru(bipy)_3]^{3+}$ (bipy = 2,2′-bipyridyl) have been investigated. The reactants have been generated by the electron-transfer quenching of the excited state of $[Ru(bipy)_3]^{2+}$ by the corresponding μ-superoxo-complexes using flash photolysis. The half-wave potentials measured by polarography for complexes (3), (4), and (5) are 1.00 ± 0.05, 1.04 ± 0.05, and 1.04 ± 0.05 V respectively. The observed rate constants are used to calculate the self-exchange electron-transfer rate constants for the bridged cobalt(III) complexes. The Marcus cross relationship has been used to predict the rate constants determined earlier for the electron-transfer reaction between (3) and the superoxo-forms of complexes (1), (4), and (5).

MOLECULAR oxygen co-ordinates to metal ions forming complexes of different structural types and in different oxidation states.[1] Dioxygen complexes of transition metals are used as model systems for the investigation of biological oxygenation and oxidation reactions,[2,3] and in recent years there have been several studies on the structure and function of dioxygen complexes.[4,5] The existence of binuclear cobalt complexes co-ordinated to oxygen has been known for a long time [6] and in recent years mononuclear oxygen complexes of cobalt have also been synthesized.[7] In the binuclear cobalt(III) complexes bridged by oxygen the bridge is found to be either in the superoxide or peroxide form. Electron-transfer reactions of these superoxo- and peroxo-complexes have been investigated by Sykes and co-workers [8] with reducing agents such as $Fe^{II}$, $Cr^{II}$, $[Ru(NH_3)_6]^{2+}$, and $V^{II}$, and more recently by McLenden and Mooney [9] using cobalt(II) bipyridyl and phenanthroline complexes. These studies indicate that the redox reactions of the cobalt(III) dioxygen complexes occur at the oxygen bridge with no reduction of the metal centre. Recently it has been observed [10] that unstable metal ions $Zn^I$ and $Cd^I$ reduce the superoxo-complexes of cobalt(III) by an inner-sphere pathway. It is also known [11] that the excited state of tris(2,2′-bipyridyl)ruthenium(II) reduces binuclear superoxo-complexes of cobalt(III) at nearly diffusion-controlled rates. Even with strong reducing agents it appears that the redox reaction occurs at the oxygen centre and the cobalt(III) centre is not involved.[11b]



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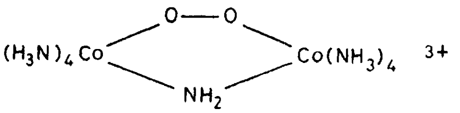

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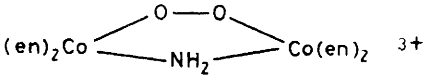

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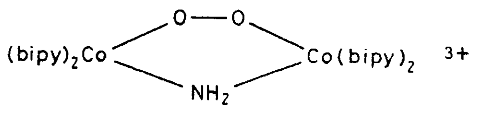

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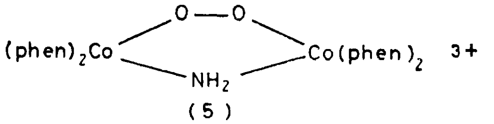

(5)

In this report we present the results of studies on the kinetics and mechanism of the oxidation of the peroxo-complexes (1)—(5) (en = ethylenediamine, phen = 1,10-phenanthroline) by tris(2,2′-bipyridyl)ruthenium(III), $[Ru(bipy)_3]^{3+}$, to give the superoxo-complexes and $[Ru(bipy)_3]^{2+}$. Both the reactants were generated by optical pulse irradiation and the reaction was monitored by spectrophotometry.[12]

## EXPERIMENTAL

The salt $[Ru(bipy)_3]Cl_2 \cdot 6H_2O$ was prepared according to the procedure given in the literature.[13] For the stopped-flow studies, $[Ru(bipy)_3]^{3+}$ was generated in solution by oxidizing a solution of $[Ru(bipy)_3]Cl_2$ in 0.2 mol dm$^{-3}$ HCl using $PbO_2$. The ruthenium(III) present in the solution was determined by converting it into the ruthenium(II) complex using an excess of iron(II) sulphate and by measuring the absorbance of $[Ru(bipy)_3]^{2+}$ at 450 nm ($\varepsilon = 1.4 \times 10^4$ dm$^3$ mol$^{-1}$ cm$^{-1}$). Superoxo-bridged dicobalt(III) complexes were prepared as described earlier.[14-17] Since the complexes were not very soluble in solutions of $H_2SO_4$ or $HClO_4$ all the experiments were carried out in 1 mol dm$^{-3}$ HCl unless specified otherwise.

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The solutions were deoxygenated by bubbling oxygen-free nitrogen through them for at least 30 min. Other reagents used in the experiments were of analytical reagent grade.

Flash-photolysis experiments were carried out using a 10-cm Pyrex cell in a Nortech type FPX-1 flash-photolysis apparatus, and the transient was recorded using a 05768 storage oscilloscope (Electronic Corporation of India). The half-width of the flash duration was determined to be 30 μs. The reaction between the μ-peroxo-cobalt(III) complex and $[Ru(bipy)_3]^{3+}$ was monitored by following the growth of absorbance at 450 nm corresponding to formation of $[Ru(bipy)_3]^{2+}$.

Stopped-flow measurements were made in a Durrum apparatus. All the experiments were carried out at 25 ± 1 °C. Polarographic half-wave potentials were determined with a Metrimpex polarograph using a saturated calomel electrode (s.c.e.).

## RESULTS

Flash photolysis of a solution of $[Ru(bipy)_3]^{2+}$ and the superoxo-bridged cobalt(III) complex produces bleaching of the solution at 450 nm corresponding to the formation of $[Ru(bipy)_3]^{3+}$ within the duration of the flash. The absorbance at 450 nm was observed to grow on a slower time scale. Flash photolysis of either $[Ru(bipy)_3]^{2+}$ or the superoxo-complex separately does not lead to the bleaching of absorbance at 450 nm. The bleaching and regrowth of the absorbance of $[Ru(bipy)_3]^{2+}$ was followed at wavelengths between 400 and 550 nm. The growth in absorbance corresponds to a second-order reaction. At each wavelength the second-order rate plots [$1/\Delta$ (absorbance) *vs.* time] were linear with identical slopes within experimental error. Bimolecular rate constants were determined for each of the superoxo-complexes from such plots and the results are given in Table 1.

TABLE 1

Rate constants for the oxidation of μ-peroxo-cobalt(III) complexes by $[Ru(bipy)_3]^{3+}$ in 1 mol dm$^{-3}$ HCl

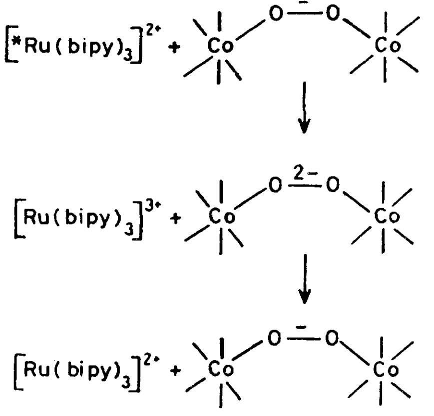
| Complex | $10^{-6}\,k$/dm$^3$ mol$^{-1}$ s$^{-1}$ |
|---|---|
| $[(H_3N)_5Co(\mu\text{-}O_2)Co(NH_3)_5]^{4+}$ | 13.4 ± 0.8 |
| $[(H_3N)_4Co(\mu\text{-}O_2)(\mu\text{-}NH_2)Co(NH_3)_4]^{3+}$ | 0.34 ± 0.03 |
| $[(en)_2Co(\mu\text{-}O_2)(\mu\text{-}NH_2)Co(en)_2]^{3+}$ | 2.45 ± 0.2 |
| $[(bipy)_2Co(\mu\text{-}O_2)(\mu\text{-}NH_2)Co(bipy)_2]^{3+}$ | 303 ± 15 |
| $[(phen)_2Co(\mu\text{-}O_2)(\mu\text{-}NH_2)Co(phen)_2]^{3+}$ | 364 ± 20 |

In the case of complex (3), the reaction with $[Ru(bipy)_3]^{3+}$ was studied in a stopped-flow apparatus with the peroxo-complex in excess. From the observed pseudo-first-order rate constants for three concentrations of the peroxo-complex, second-order rate constants were determined to be (7.6 ± 1.0) × 10$^5$ dm$^3$ mol$^{-1}$ s$^{-1}$ in 0.4 mol dm$^{-3}$ acid solution. Peroxo-complexes (1) and (2) were unstable under the experimental conditions for the stopped-flow studies, and the reaction between $[Ru(bipy)_3]^{3+}$ and peroxo-complexes (4) and (5) were too fast to be followed in the stopped-flow instrument.

Polarographic half-wave potentials measured for complexes (3), (4), and (5) are respectively 1.00 ± 0.05, 1.04 ± 0.05, and 1.04 ± 0.05 V. The polarographic waves obtained for complexes (1) and (2) did not show a clear half-wave potential presumably due to the decomposition of the complexes.

## DISCUSSION

Tris(2,2′-bipyridyl)ruthenium(III), $[Ru(bipy)_3]^{3+}$, is a powerful oxidizing agent with a standard redox potential of 1.26 V.[18] It is generated in solution by the reaction between the excited state of $[Ru(bipy)_3]^{2+}$, *i.e.* $[{}^*Ru(bipy)_3]^{2+}$, and superoxo-complexes of cobalt(III).[19] The reduction potential for the $[{}^*Ru(bipy)_3]^{2+}$–$[Ru(bipy)_3]^{3+}$ couple is −0.78 V,[18] and in the quenching reaction $[Ru(bipy)_3]^{3+}$ is produced along with the peroxo-bridged cobalt(III) in a quantum yield of nearly 1 in a close-to-diffusion-limited quenching process. The production of $[Ru(bipy)_3]^{3+}$ and the peroxo-complex in the photochemical reaction and the subsequent thermal redox reaction can be described by the Scheme. The ion $[Ru(bipy)_3]^{3+}$ does not oxidize the superoxocobalt(III) complex and there is no observable reaction between the superoxo-complexes of cobalt(III) and $[Ru(bipy)_3]^{2+}$ for days in acid solution.



SCHEME

Peroxo-bridged complexes (3)—(5) are stable in acid solution and the reaction between these and $[Ru(bipy)_3]^{3+}$ occurs within the time of mixing the solutions. With the stopped-flow technique we could measure only the rate constants for the oxidation of (3) by $[Ru(bipy)_3]^{3+}$ at low ionic strength. The flash-photolysis technique is thus advantageous to study the reactions between the peroxo-complexes and $[Ru(bipy)_3]^{3+}$. There is very little net change in the absorption spectrum of the flashed solution which suggests that the thermal reaction just reverses the photochemical electron-transfer reaction. It can also be seen that the rate constant for the reaction between the peroxo-complex (3) and $[Ru(bipy)_3]^{3+}$ measured in the stopped-flow apparatus is similar to that determined in the flash experiment. This suggests that our interpretation of the results is indeed correct. Cobalt(III) peroxo-complexes are known to be oxidized by Ce$^{IV}$ and by $[Fe(phen)_3]^{3+}$ to the superoxo-complexes.[20,21] The conditions which are favourable for the flash experiment, namely $[Ru(bipy)_3]^{2+}$ absorbing major portions of the light, make it difficult to monitor the formation of the peroxo-bridged complex directly.

The rate constants for the oxidation of the peroxo-complexes (Table 1) vary by four orders of magnitude, although the reduction potentials of the complexes are similar except in the case of (2) for which a value of 0.75 V is reported.[9] Electron-transfer reactions of tris(2,2′-bipyridyl) complexes of metal ions are expected to be of the outer-sphere type and we have used the Marcus relationship [22] to determine the self-exchange rate constant for the dioxygen complexes of cobalt(III). Marcus theory relates the rate constant for electron-transfer reactions between two reactants by equation (i) where $k_{12}$ is the rate constant for the cross reaction, $k_{11}$

$$k_{12} = (k_{11}k_{22}K_{12}f)^{\frac{1}{2}} \qquad \text{(i)}$$

and $k_{22}$ are the self-exchange rate constants, and $K_{12}$ is the equilibrium constant for the overall reaction; $f$ is a factor given by equation (ii). Using the known self-

$$\log f = (\log^2 k_{12})/4 \log(k_{11}k_{22}/Z^2) \qquad \text{(ii)}$$

exchange rate constant of $2 \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$ for $[Ru(bipy)_3]^{3+}$–$[Ru(bipy)_3]^{2+}$,[18] and the $Z$ value of $10^{11}$, the self-exchange rate constants for the dioxygen complexes were calculated (Table 2).

TABLE 2

Self-exchange electron-transfer rate constants for the superoxo- with the peroxo-complexes

| Complex | $E_{\frac{1}{2}}$/V | $K_{12}$ | $k_{11}$/dm$^3$ mol$^{-1}$ s$^{-1}$ |
|---|---|---|---|
| (1) | 0.95 * | $10^{5.25}$ | 1.8 |
| (2) | 0.75 * | $10^{8.64}$ | $1.3 \times 10^{-7}$ |
| (3) | 1.0 | $10^{4.4}$ | 0.12 |
| (4) | 1.05 | $10^{3.73}$ | $2.2 \times 10^{4}$ |
| (5) | 1.05 | $10^{3.73}$ | $3.2 \times 10^{4}$ |

* Taken from ref. 9.

It may be noted that the calculated self-exchange rate constants for the superoxo-derivatives of (4) and (5) are similar in magnitude to that determined for the free superoxo-ion.[23,24] It is known that the peroxo-complex $[(en)_2Co(\mu\text{-}O_2)(\mu\text{-}NH_2)Co(en)_2]^{3+}$ protonates readily, whereas the corresponding bipy and phen complexes do not protonate in 1 mol dm$^{-3}$ acid solution.[17] The low self-exchange rate constants calculated for complexes (1) and (3) may be partly due to the involvement of protons in the exchange process. In this connection it may be noted that Davies and Sykes [25] have measured the rate constants for the reduction of the superoxo-forms of complexes (1), (2), (4), and (5) using the peroxo-complex (3). The agreement between the calculated values using our self-exchange rate constants and the observed rate constants is fair to good for all the complexes except (2) (Table 3). The discrepancy for (2) is to a great extent traceable to the error in the determination of the redox potential. Closer examination of complexes (2) and (3) with respect to their structural, spectral, and chemical properties [4,6] does suggest that the redox potential for the two complexes cannot differ by as much as 0.3 V. For electron-transfer reactions, the validity of the Marcus model is said to be good even when the calculated and observed rate constants differ by as much as a factor of 25.[22]

TABLE 3

Rate constants for the reduction of the superoxo-forms of cobalt(III) complexes by μ-amido-μ-peroxo-bis[bis-ethylenediamine)cobalt(III)]

| | | $k_{12}$/dm$^3$ mol$^{-1}$ s$^{-1}$ | |
|---|---|---|---|
| Complex | $K_{12}$ | obs.* | calc. |
| (1) | 0.14 | 0.17 | 0.03 |
| (2) | $5.8 \times 10^{-5}$ | 12 | $9.5 \times 10^{-6}$ |
| (4) | $10^{0.67}$ | $2.3 \times 10^{3}$ | 69 |
| (5) | $10^{0.67}$ | $6.7 \times 10^{3}$ | 83 |

* Taken from ref. 25.

The self-exchange electron-transfer rate constants shown in Table 2 for the μ-superoxo-complexes and the rate constants in Table 3 for the cross reactions may be considered to belong to same type of reactions in a limited sense. That is, apart from differences in the ligands present in the complexes, the rate constants in Table 3 reflect the electron exchange between the bound dioxygen ligands.

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REFERENCES

[1] R. D. Jones, D. A. Summerville, and F. Basolo, *Chem. Rev.*, 1979, **79**, 139.

[2] G. McLenden and A. E. Martell, *Co-ordination Chem. Rev.*, 1976, **19**, 1.

[3] O. Hayaishi, 'Chemical Models and Mechanisms for Oxygenases in Molecular Mechanisms of Oxygen Activation,' Academic Press, New York, 1975.

[4] A. P. B. Lever and H. B. Gray, *Accounts Chem. Res.*, 1978, **11**, 348.

[5] F. Basolo, B. Hoffman, and J. Ibers, *Accounts Chem. Res.*, 1975, **8**, 384.

[6] A. G. Sykes and J. A. Weil, *Progr. Inorg. Chem.*, 1970, **13**, 1.

[7] S. R. Pickens, A. E. Martell, G. McLenden, A. B. P. Lever, and H. B. Gray, *Inorg. Chem.*, 1978, **17**, 2190.

[8] A. G. Sykes, *Chem. in Britain*, 1974, **10**, 170.

[9] G. McLenden and W. F. Mooney, *Inorg. Chem.*, 1980, **19**, 12.

[10] P. Natarajan and N. V. Raghavan, *J.C.S. Chem. Comm.*, 1980, 268; unpublished work.

[11] (*a*) K. Chandrasekaran and P. Natarajan, *J.C.S. Chem. Comm.*, 1977, 774; (*b*) P. Natarajan and N. V. Raghavan, *J. Amer. Chem. Soc.*, 1980, **102**, 4518.

[12] C. R. Bock, D. G. Whitten, and T. J. Meyer, *J. Amer. Chem. Soc.*, 1974, **96**, 4710.

[13] R. A. Palmer and T. S. Piper, *Inorg. Chem.*, 1966, **5**, 865.

[14] *Inorg. Synth.*, 1972, **12**, 197.

[15] A. Werner, *Annalen*, 1910, **375**, 1.

[16] Y. Sasaki and J. Fujita, *Bull. Chem. Soc. Japan*, 1969, **42**, 2089.

[17] K. M. Davies and A. G. Sykes, *J. Chem. Soc.* (*A*), 1971, 1414.

[18] N. Sutin, *J. Photochem.*, 1979, **10**, 19.

[19] K. Chandrasekaran and P. Natarajan, *Inorg. Chem.*, 1980, **19**, 1714.

[20] M. Mori and J. A. Weil, *J. Amer. Chem. Soc.*, 1967, **89**, 3732.

[21] D. P. Keeton and A. G. Sykes, *J.C.S. Dalton*, 1972, 2530.

[22] M. Chou, C. Creutz, and N. Sutin, *J. Amer. Chem. Soc.*, 1977, **99**, 5615.

[23] D. M. Stanbury, O. Haas, and H. Taube, *Inorg. Chem.*, 1980, **19**, 518.

[24] C.-L. Wong, J. A. Switzer, K. P. Balakrishnan, and J. F. Endicott, *J. Amer. Chem. Soc.*, 1980, **102**, 5511.

[25] K. M. Davies and A. G. Sykes, *J. Chem. Soc.* (*A*), 1971, 1418.