

# A Pulse Radiolysis Study of the Reaction of Hydroxyl Radicals with *trans*-Dihydroxo(1,4,8,11-tetraazacyclotetradecane)chromium(III)

O. Mønsted,<sup>a</sup> Gwyneth Nord<sup>a,\*</sup> and P. Pagsberg<sup>b</sup>

<sup>a</sup>Department of Inorganic Chemistry, H. C. Ørsted Institute, University of Copenhagen, DK-2100 Copenhagen Ø and <sup>b</sup>Chemistry Department, Risø National Laboratory, DK-4000 Roskilde, Denmark

Mønsted, O., Nord, G. and Pagsberg, P., 1987. A Pulse Radiolysis Study of the Reaction of Hydroxyl Radicals with *trans*-Dihydroxo(1,4,8,11-tetraazacyclotetradecane)chromium(III). – Acta Chem. Scand., Ser. A 41: 104-109.

Hydroxyl radicals react rapidly with the title chromium(III) complex. In weakly alkaline solution, around pH  $\approx$  9, the product rearranges by a first-order process followed by a second-order process. This sequence is interpreted as the formation of a chromium(IV) complex which then forms a  $\mu$ -peroxochromium(III) dimer. The dimer decomposes by a two-electron oxidation of the macrocyclic ligand with the concomitant formation of a double bond. In more strongly basic solution and also in dilute acid, the decay kinetics are more complicated.

Supplementary measurements using *trans*-difluoro(1,4,8,11-tetraazacyclotetradecane)chromium(III), which does not contain coordinated hydroxide, and *cis*-dihydroxo(*rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)chromium(III), for which dimerization is sterically hindered, support the above interpretation of the consecutive reactions for the title complex.

The title chromium(III) complex, *trans*-[Cr(cyclam)(OH)<sub>2</sub>]<sup>3+</sup>, is an effective substrate for the one-electron reduction of permanganate in basic solution.<sup>1</sup> This can be explained by the consecutive formation and oxidation of  $\mu$ -peroxo complexes containing one manganese and one chromium atom. The present study of the reaction of the chromium(III) complex and other related chromium(III) complexes with the highly oxidising hydroxyl radical was made in an attempt to obtain additional evidence for the interaction of the chromium centre with peroxide in analogous dimers.

## Results

The diprotonated form of the title complex is an acid for which  $-\log(K_{A1}/M) \approx 3.048 \pm 0.011$  and  $-\log(K_{A2}/M) \approx 7.39 \pm 0.02$  at 25 °C in 1 M NaClO<sub>4</sub>.<sup>2</sup> At the lower ionic strengths of the solutions used in the present work these values are

\*To whom correspondence should be addressed.

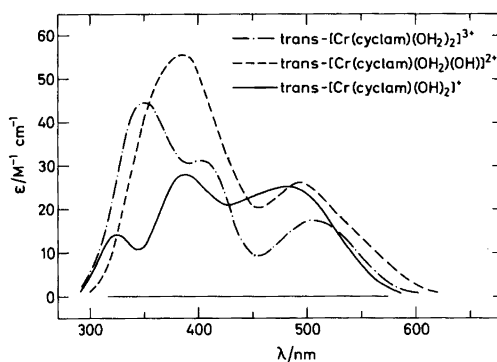


Fig. 1. Absorption spectra of the title complex and of its protonated forms.

not valid, but the degree of protonation of the complexes was determined using the absorption spectra of the diaqua, aquahydroxo and dihydroxo complexes (Fig. 1). The reaction with hydroxyl radicals was studied at pH  $\approx$  3, where approximately equal concentrations of the diaqua-

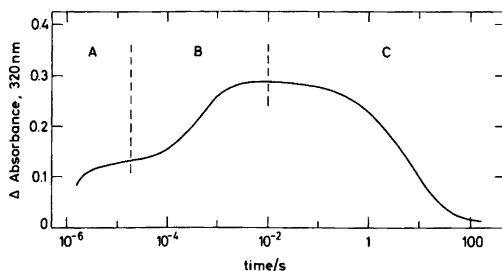


Fig. 2. Absorbance change measured in a 5 cm cell during the reaction between 1.00 mM *trans*-[Cr(cyclam)(OH)<sub>2</sub>]<sup>+</sup> and 0.080 mM ·OH at pH 9.2.

and aquahydroxo forms are present, at pH ≈ 4, where the main species is the aquahydroxo complex, and at pH ≈ 9 and ≈ 11, where only *trans*-[Cr(cyclam)(OH)<sub>2</sub>]<sup>+</sup> is present and where further deprotonation could be kinetically significant at the higher pH.

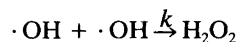
Only in alkaline solution was the system simple, in that the variation of the absorbance with time from successive pulses was identical and there was a linear increase in the initial absorbance profile with radiation dose. Also, the change of absorbance with time was unaffected by small concentrations (≈ 8 μM) of dioxygen and of hydrogen peroxide under these conditions. Fig. 2 displays a typical reaction profile. There are three well-separated consecutive reactions reflected by

- (A) a rapid increase in absorbance giving a plateau in less than 5 μs;
- (B) a first-order increase in absorbance within a time span of less than 100 μs to about 1 ms;
- (C) a slow second-order decay.

The initial rate of increase of absorbance was very high and reproducible as a function of increase in radiation dose and with successive doses over the entire pH range which was investigated. For all the hydroxo and aqua complexes, the first plateau was easily measurable; in acidic solutions the absorbance was less than that in alkaline, but a detailed study of this region was confined to the conditions under which the system as a whole was most simple, i.e. pH ≈ 9, and is described below.

(A) *μs kinetics and stoichiometry at pH 9.2.* In order to establish the stoichiometry, 50 ns pulses were used for solutions of complexes less concen-

trated than 30 μM and with doses of less than 4.0 krad. This ensured that the reaction:



with  $k = 1.03 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ,<sup>3</sup> could compete with the ·OH + Cr(III) reaction. The fast increase in absorbance to the first plateau as well as the concentration of hydrogen peroxide produced after complete decay were measured. It was found that both the stoichiometry and the absorbance profiles could be reproduced using a value of  $2.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  for the rate constant for the 1:1 reaction between Cr(III) and ·OH.

(B) *Decay of the first intermediate: k<sub>1</sub>-path.* This is a first-order process over the entire pH range (cf.  $k_1$  in Table 1). The reaction involves spectral changes which would accord with change in the oxidation state of the metal centre (see Fig. 3). The intensities and also the values of  $k_1$  change with pH. The origins of these changes and the probable structures of the two intermediates are discussed in the last section.

(C) *The decay kinetics of the second intermediate: k<sub>2</sub>-path.* As stated above, only for pH ≥ 9 were the kinetics simple second-order and independent of the order of successive pulses. The second-order rate constants measured at 320 nm, where no residual absorption was detected, are given in Table 1. For the pH range 9.2–9.6, the molar absorption coefficient for the second intermediate is constant ( $\epsilon_{II}$  in Table 1) but increases at pH ≈ 11. An interpretation of this path is given in the discussion section, together with the evidence for the formulation of the second intermediate as a chromium(IV) complex.

At pH ≈ 4.3 and 3.1 the absorption change was less than that in the alkaline solutions. Two other main features observed during this last stage differed also from the behaviour of the complexes in alkaline solution. Firstly, the decay rate increased with successive pulses and secondly, an extra absorbance was observed when 2–8 μM concentrations of dioxygen and/or hydrogen peroxide were added. Although, as stated above, the first two stages in the absorption profile were analogous in the pH range which was investigated, the “slow” final decay at pH ≈ 4.3 was different from that at pH ≈ 3.1. At pH ≈ 4.3 the decay rate was second-order but with increased rate

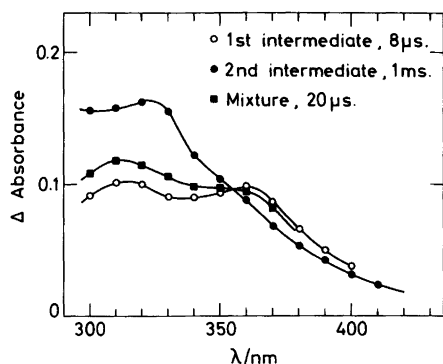


Fig. 3. Absorption spectra of intermediates and of mixture at pH 3.2 for the reaction of the protonated chromium(III) title complex with hydroxyl radicals.

for successive pulses; at pH  $\approx$  3.1 the decay for first pulses was first-order but approached second-order for successive pulses. Small decreases in pH were found on successive pulsing of the acidic solutions, but these are difficult to interpret since they would be accompanied by considerable buffering of the solutions.

*Measurements in argon-saturated solutions.* It seemed possible that in acid, not only the acid-base properties of the second intermediate, formulated as a chromium(IV) complex, but also competition between the chromium(III) complex and nitrous oxide for electrons could be a complicating factor. By analogy with pulse radiolysis

studies<sup>4</sup> of (5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)nickel(II) under nitrous oxide and under dinitrogen, the direct reaction of electrons with the chromium(III) complex should lead to chromium(II) which would react with the chromium(IV) intermediate. It is generally accepted that in aqueous solutions saturated with argon or with dinitrogen, the primary yield of hydroxyl radicals, which is equal to that of electrons, is one-half of the yield of hydroxyl radicals in solutions saturated with nitrous oxide. Measurements were therefore made with solutions saturated with argon at pH 4.2.

In contrast to the nickel system no evidence for reduction of the chromium(III) complex was found, since not only was the absorbance change for the argon-saturated solutions half of that in those saturated with nitrous oxide but also the rate constants were the same.

In agreement with the above, the second plateau absorbances for two different chromium(III) complex concentrations at pH = 3.1 lead to the same calculated value of  $\epsilon_{II}$ . Also, since the second-order rate constant for the  $N_2O + e^-$  reaction is  $5.6 \times 10^9 M^{-1} s^{-1}$ <sup>3</sup> and the solubility of nitrous oxide is 25 mM at 1 atm pressure, a rate constant significantly higher than  $8 \times 10^{10} M^{-1} s^{-1}$ , which seems to be the upper limit for reductions of metal complexes by electrons,<sup>5,6</sup> would be required. Similarly, direct reduction of the complex by hydrogen atoms can be eliminated as a competing path.<sup>7</sup> A probable general mechanism for the decay of the second intermediate in acidic solution is given in the discussion section.

Table 1. Data for pulse radiolysis of *trans*-dihydroxo-, *trans*-aqua-hydroxo-, and *trans*-diaqua(1,4,8,11-tetraazacyclotetradecane)chromium(III).

| pH                 | dose/krad | $\epsilon_I^a/M^{-1} cm^{-1}$ | $10^{-3} k_1^b/s^{-1}$ | $\epsilon_{II}^a/M^{-1} cm^{-1}$ | $10^{-3} k_2^c/M^{-1} s^{-1}$ |
|--------------------|-----------|-------------------------------|------------------------|----------------------------------|-------------------------------|
| 10.9               | 8.2–14.5  | 404 ± 20                      | 10.7 ± 0.6             | 755 ± 30                         | 4.3 ± 0.2                     |
| 9.6 <sup>d</sup>   | 7.0–30.8  | 360 ± 18                      | 2.92 ± 0.10            | 723 ± 20                         | 2.19 ± 0.11                   |
| 9.5 <sup>e</sup>   | 8.5–13.7  | 377 ± 18                      | 2.94 ± 0.10            | 724 ± 20                         | 2.16 ± 0.11                   |
| 9.2                | 10.2–12.6 |                               |                        | 725 ± 25                         | 1.65 ± 0.09                   |
| 4.3 <sup>e,f</sup> | 7.2–20.5  | 280 ± 14                      | 11.0 ± 0.5             | 459 ± 15                         | 2.6 ± 0.3                     |
| 3.1 <sup>e,f</sup> | 7.9–14.3  | 185 ± 9                       | 5.3 ± 0.2              | 354 ± 13                         | <sup>d</sup>                  |

<sup>a</sup> $\epsilon_I$  and  $\epsilon_{II}$  are the molar absorbances of the first and second intermediates at 320 nm, respectively, calculated from the appropriate plateau absorbances (Fig. 2) and the hydroxyl radical concentrations:  $[OH] = G \cdot \text{dose}$  with  $G \approx 5.8 \mu M \text{ krad}^{-1}$ . <sup>b</sup> $k_1$  is the first-order rate constant for the decay of the first intermediate. <sup>c</sup> $k_2$  is the second-order rate constant for the decay of the second intermediate. <sup>d</sup>The decay is first-order with  $k \approx 0.140 \pm 0.007 s^{-1}$  (see text). <sup>e</sup>Concentration of *trans*-[Cr(cyclam)(OH)<sub>2</sub>]<sup>+</sup> varied between 1.0 mM and 0.5 mM; others 1.00 mM. <sup>f</sup>Data for first pulses only.

*Product analysis.* There was no measurable di-oxygen in the product solutions about thirty minutes after pulsing or later. The hydrogen peroxide level detected a few minutes after pulsing, or later, never exceeded that which could accord with primary dose product, and was usually much less than one per cent of that corresponding to total conversion of  $\cdot\text{OH}$  to  $\text{H}_2\text{O}_2$ .

At wavelength greater than  $\approx 300$  nm, the absorbance changes after one dose (ca. 12 krad) decayed to zero; however, at shorter wavelengths there was a gradual increase in the final absorbance of the solutions with decreasing wavelength.

*trans-[Cr(cyclam)F<sub>2</sub>]<sup>+</sup> +  $\cdot\text{OH}$ .* This reaction was studied at pH = 9.2 with doses and complex concentrations similar to those used for the title complex; the absorbance changes at 320 nm were, however, very different. An initial absorbance change was complete in less than 2  $\mu\text{s}$  and gradually decayed. For a first pulse of 10.1 krad, this *initial maximum absorbance* was about one-third of that found for the dihydroxo complex and was not linearly dependent upon the dose. At all doses, the absorbance change *decreased* with successive pulsing at 30 s intervals. This would accord with a change in stoichiometry of the system with successive doses. Since the rate of fluoride ligand hydrolysis of the chromium(III) complex<sup>8</sup> is too slow to account for the observed change in absorbance with dose interval, it is concluded that a product which is very rapidly oxidised by hydroxyl radicals builds up in the solution.

*cis-[Cr(cycb)(OH)<sub>2</sub>]<sup>+</sup> and  $\cdot\text{OH}$ .* *cycb* is *rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, and steric hindrance from the methyl groups of this ligand effectively prevents dimerization of the complex (see Fig. 2 in Ref. 9). The first two stages in the absorbance vs. time profile were analogous to those for the title complex and furthermore, there was no change in absorbance with successive pulses at pH  $\approx 9.2$  within the investigated time scales, ( $\epsilon_1 = 350 \text{ M}^{-1} \text{ cm}^{-1}$  at 320 nm and  $k_1 = 250 \text{ s}^{-1}$ ). The "slow" decay of the complex was measured at pH = 9.2 and also at pH = 4.5, and in both cases was strictly *first-order*, though faster at pH = 4.5 than at pH = 9.2; the second plateau absorbance increased linearly with dose and was independent of pH within experimental error ( $\epsilon_{11} = 480 \text{ M}^{-1}$

$\text{cm}^{-1}$ ,  $k = 0.030 \text{ s}^{-1}$  at pH = 9.2;  $\epsilon_{11} = 520 \text{ M}^{-1} \text{ cm}^{-1}$ ,  $k = 0.28 \text{ s}^{-1}$  at pH = 4.5).

## Discussion

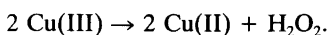
The use of chromium(III) complexes in pulse radiolysis studies has the advantage over the much-studied nickel(II) systems that the coordination shells of the inert reactants are known, but the "cyclam"-type chromium(III) complexes used in the present work have the disadvantage that the changes in absorbance occurring on oxidation by hydroxyl radicals are small. This not only limited the present studies to the use of large doses but also meant that it was not feasible to attempt to interpret measurements at wavelengths greater than about 400 nm.

Of the three stages in the absorbance-time profile illustrated in Fig. 2, only the first was found with  $[\text{Cr}(\text{cyclam})\text{F}_2]^+$  as reactant, and absorbance changes for this system were particularly small. It was, however, clear that reaction with hydroxyl radicals is very fast, which meant that attempts to unambiguously ascertain the site of attack of  $\cdot\text{OH}$  on the title complex by comparison with the difluoro complex were abortive. For the difluoro complex, only attack at the "cyclam" ligand seems reasonable, which accords with the literature mechanisms for oxidative ligand dehydrogenation based on the rapid reaction of hydroxyl radicals both with uncomplexed 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene<sup>11</sup> and also with the nickel(II) complex of 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-1,4,8,11-tetraene.<sup>4</sup> This latter complex resembles the complex *trans*- $[\text{Cr}(\text{cyclam})\text{F}_2]^+$  in that no transformation of the initial spectrum other than a uniform decay process was observed. The nickel(II) complexes of the more saturated ligands give nickel(III) complexes, but attempts to interpret consecutive absorbance changes in detail are complicated by the effect of coordination of anions.<sup>4,12</sup>

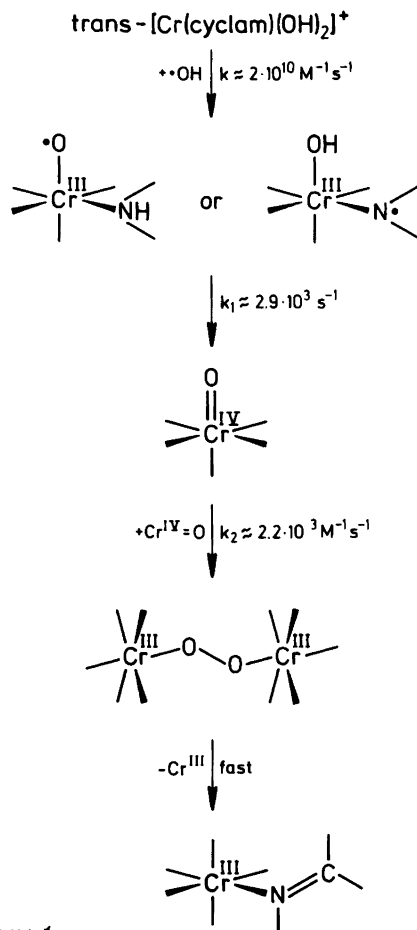
For the present title complex, primary attack by hydroxyl radical either at the hydroxide ligand or at a coordinated nitrogen of the "cyclam" can be envisaged and it is, in fact, only for the complexes which contain either coordinated hydroxide or water that the first-order transformation ( $k_1$  stage; see also B in Fig. 2) occurs. There is no evidence for the presence of organic radicals during stages A and B at any pH value when lack of

change in stoichiometry with increase in dose and absence of effects of added dioxygen<sup>13</sup> and of repeated dose are used as criteria for the absence of such organic radicals. It therefore seems likely that the first intermediate is formed by hydrogen atom transfer from a coordinated hydroxide to a hydroxyl radical, and that the first-order transformation ( $k_1$  path) corresponds to the oxidation of the metal centre. The formulation of the second intermediate as a chromium(IV) complex receives support from the change in the spectra illustrated in Fig. 2, while the pH dependence of  $k_1$  could reflect the acid-base properties of the reactant complex. As stated above in the discussion of the *trans*-[Cr(cyclam)F<sub>2</sub>]<sup>+</sup> system, it cannot, however, be eliminated that the first two stages correspond, either partly or wholly, to an analogous fast hydrogen atom transfer to a hydroxyl radical from the coordinated nitrogen of the "cyclam" ligand, followed by a slower intramolecular hydrogen atom transfer from coordinated hydroxide/water with concomitant oxidation of the metal centre. It is only in the final stage and in acidic solutions that there is a change of rate and rate-order with repeated dose, corresponding to the build-up of relatively long-lived products which are readily oxidised by both dioxygen and by the chromium(IV) complex.

In basic solution the decay of the chromium(IV) complex is second-order and may be compared with that found for the aqua-copper(II) system,<sup>5</sup> for which:



For the present system, no H<sub>2</sub>O<sub>2</sub> is formed; instead, as depicted in Scheme I, a  $\mu$ -peroxo dimer is suggested. It is relevant that for all the alkaline solutions there is an increase of rate constant with increasing pH, reflecting that deprotonation of the hydroxy ligands may be a requirement for dimerization, as would be expected for the formation of such a  $\mu$ -peroxo intermediate. Also, in accord with this, there is a change of rate-law from second-order for the "cyclam" complexes to first-order for "cycb", and this could result from the different steric properties of the ligands, since dimerization of the "cycb" complex through the formation of an O—O bond cannot take place.



Scheme 1.

The lack of evidence in the "cycb" system for ligand intermediates which can be easily oxidised also means that the subsequent reactions of the product complexes of the first-order decay must be fast; these primary products are presumably coordinated ligand-radical complexes.

The fate of the  $\mu$ -peroxo "cyclam" intermediate is of some interest, in that not only the spectral changes accord with the introduction of a double-bond in the ligand but also, from the stoichiometry, this involves a two-electron change. We therefore envisage, as depicted in Scheme 1, intramolecular decomposition of the  $\mu$ -peroxo dimer with dehydrogenation and concomitant formation of the  $>\text{C}=\text{N}-$  moiety. This accords with the results described in Ref. 1.

The new features of the pulse radiolysis studies of the title complex are:

(1) that oxidation of the metal centre in "cyclam" complexes by hydroxyl radicals requires the presence of a proton acid as an additional ligand, and (2) that the initial one-electron oxidation of the metal centre can lead to two-electron oxidation of the organic ligand through what may reasonably be postulated to be a  $\mu$ -peroxo intermediate.

This last point is relevant to the previous studies<sup>1</sup> in that evidence has been found for partial charge transfer to a "peroxo" bridge from the chromium(III) centre.

## Experimental

**Pulse radiolysis.** All solutions for pulse radiolysis were prepared with triply-distilled water and were deaerated with nitrous oxide or with argon. The pH was adjusted with perchloric acid or with sodium hydroxide, no attempt being made to adjust ionic strengths by addition of neutral salts. The reaction rates were followed spectrophotometrically at  $22 \pm 1^\circ\text{C}$  in the wavelength range 300 to 500 nm. Most measurements were made at 320 nm with 1.00 mM solutions of complex.

Both an H. R. C. Lineac with 1.0  $\mu\text{s}$  pulses and a Field Emission Corp. Febetron 705 B with 50 ns pulses were used. The pulse-to-pulse variation for single pulses at ten minute intervals was less than  $\pm 5\%$ . Details of the irradiation technique, cell, light source, analysis, monochromator and data processing can be found in Ref. 10. Using the molar absorption coefficients of electrons and hydroxyl radicals and the dimerization rate of hydroxyl radicals given in Ref. 3, we confirmed that in the alkaline solutions saturated with nitrous oxide, the electrons were effectively all converted to hydroxyl radicals and that  $G_{\text{OH}} = \text{radicals}/100 \text{ eV} = 5.8$ .

**Preparation of chromium(III) complexes.** *trans*-[Cr(cyclam)(OH)<sub>2</sub>(OH)](ClO<sub>4</sub>)<sub>2</sub>, *trans*-[Cr(cyclam)F<sub>2</sub>](ClO<sub>4</sub>) and *cis*-[Cr(cycb)(OH)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> · 2 H<sub>2</sub>O were prepared by literature methods or modifications of published procedures.<sup>2,14</sup>

**Analysis.** Hydrogen peroxide was allowed to react with iodide and the triiodide produced was determined spectrophotometrically at 351 nm. A calibration curve was linear in the peroxide concentration range 5  $\mu\text{M}$  to 220  $\mu\text{M}$ .

Dioxygen concentration was measured with a Radiometer Type E 5046 pO<sub>2</sub> electrode together with a PHA 930 module. The system was calibrated with water saturated with air and with O<sub>2</sub> at 1 atm. pressure.

**Acknowledgements.** Thanks are due to Eva Floryan-Løvborg for help with the preliminary studies in acidic solutions and to Anne Bønke Nielsen and Jette Munck for experimental assistance.

## References

1. Mønsted, O. and Nord, G. *Acta Chem. Scand., Ser. A. To be submitted.*
2. Eriksen, J. and Mønsted, O. *Acta Chem. Scand., Ser. A 38* (1984) 775.
3. Pagsberg, P., Christensen, H., Rabini, J., Nilsson, G., Fenger, J. and Nielsen, S. O. *J. Phys. Chem.* 73 (1969) 1029.
4. Maruthamathu, P., Patterson, L. K. and Ferrandi, G. *Inorg. Chem.* 17 (1978) 3157.
5. Meyerstein, D. *Acc. Chem. Res.* 11 (1978) 43.
6. Swartz, H. A., Creutz, C. and Sutin, N. *Inorg. Chem.* 24 (1985) 433.
7. Tait, A. M., Hoffman, M. Z. and Hayon, E. *Inorg. Chem.* 15 (1976) 934.
8. Mønsted, O. *Unpublished work.*
9. Bang, E. and Mønsted, O. *Acta Chem. Scand., Ser. A 38* (1984) 281.
10. Nord, G., Pedersen, B., Floryan-Løvborg, E. and Pagsberg, P. *Inorg. Chem.* 21 (1982) 2327.
11. Whitburn, K. D. and Laurence, G. S. *J. Chem. Soc., Dalton Trans.* (1979) 139.
12. (a) Jaacobi, M., Meyerstein, D. and Lilie, J. *Inorg. Chem.* 18 (1979) 429; (b) Cohen, H., Kirchenbaum, L. J., Zeigerson, E., Jaacobi, M., Fuchs, E., Ginzburg, G. and Meyerstein, D. *Inorg. Chem.* 18 (1979) 2763.
13. Pagsberg, P. *Risø Report No. 256*, Risø National Laboratory, Roskilde, Denmark 1973.
14. Ferguson, I. and Tobe, M. *Inorg. Chim. Acta* 4 (1970) 109.

Received October 17, 1986.