Pulse radiolytic studies on *cis*-dichlorobis-(2,2′-bipyridine)cobalt(III) and *cis*-dichlorobis-(1,10-phenanthroline)cobalt(III) complexes

Smita Ghosh, Vitthal A Kawade, Avinash V Sapre & Avinash S Kumbhar*

National Centre for Free Radical Research, Department of Chemistry, University of Pune, Pune 411 007, India

Email: askum@chem.unipune.ernet.in

The reactions of hydrated electron (e^-_{aq}) with Co(III) polypyridyl complexes of the type [Co(NN)$_2$Cl$_2$]Cl where NN = 2,2′-bipyridine (bpy), and 1,10-phenanthroline (phen) have been studied by pulse radiolysis. The rate constants for the reactions at 300 K have been evaluated to be $(7.6\pm0.2)\times10^{10}$, and $(6.9\pm0.2)\times10^{10}$ dm^3 mol^{-1} s^{-1}, respectively. Time resolved transient absorption spectra show two broad peaks at 360 and 610 nm for the bpy complex and a single broad peak at 420 nm for the phen complex at 1 μs. Comparison with reported transient spectra of the anion radicals of ligands indicates that the electron is located on the complex as a whole. The anion radicals of both the complexes initially produced, decay in the time scale of ~80 μs. Steady state absorption spectra on irradiation point out to breakdown of the phen complex, and the bpy-Co(III) complex is reduced to Co(II) complex. Conductance of the solution substantially increases on irradiation for both the complexes and can be attributed to aquation/de-ligation of the phen complex. The phen complex anion radical undergoes aquation/de-ligation by intramolecular electron transfer leading to dissociation of the complex. For bpy complex the conductance increases due to the release of chloride ions and reduction to Co(II) complex species is observed.

IPC Code: Int. Cl.[8] C07F15/06

The redox chemistry of metal-polypyridyl complexes has been studied due to their potential applications as anticancer agents for probing structural changes in DNA and in solar energy conversion[1-3]. Such studies have been restricted to tris-polypyridyl complexes[1-5] of the type [Ru(phen)$_3$]$^{2+}$, [Co(bpy)$_3$]$^{3+}$ and [Co(phen)$_3$]$^{3+}$. The precursors to these tris-polypyridyl complexes, the bis-polypyridyl complexes of the type [Co(NN)$_2$Cl$_2$]Cl where NN denotes polypyridyl ligands, have been synthesized, characterized and their interactions with DNA reported[6]. As it would be interesting to study the radiation chemical behavior of complexes having more than one ligand, we report herein the reaction of e^-_{aq} with [Co(III)(2,2′-bipyridine)$_2$Cl$_2$]Cl and [Co(III)(1,10-phenanthroline)$_2$Cl$_2$]Cl complexes and the spectral and kinetic properties of the transients produced. The structure of the ligand and complex is depicted in Scheme 1. One interest in such molecules is how the electron initially located migrates in the complex, which contains more than one site of electron attack. Earlier studies[7] on *tris* acetylacetonato Co(III) showed that all the three radical products of water radiolysis, viz. e^-_{aq}, $^\bullet$OH and H$^\bullet$ result in reduction of Co(III) to Co(II). It is interesting to see in complex containing multiple ligands what is the fate of electron adduct species formed by electron addition.

Experimental

The cobalt (III) complexes with 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen) were synthesized by chlorine oxidation method[8]. These complexes were characterized using standard techniques like UV-vis, IR, NMR and elemental analysis[6]. Both the complexes are stable towards hydrolysis at least for 8 h as checked by its UV-vis spectra. Optical absorption spectra were recorded using Shimazdu (model 1601) UV-vis spectrophotometer. Conductivities were measured using Equip-Tronics model: EQ-664 conductivity meter.

Millipore Milli-Q filtered water was used throughout this work. IOLAR grade N$_2$ (99.99% pure) was used for deaerating solutions. *t*-Butanol (reagent grade) and benzophenone (Fluka) were used as received. Complex solutions containing 0.5 mol dm^{-3} of *t*-butanol were saturated with N$_2$ before carrying out irradiations[9].

Pulse radiolysis studies were carried out using the facility at National Center for Free Radical Research, University of Pune. The facility is based on 7 MeV linear accelerator (AS&E, HESD, USA) giving

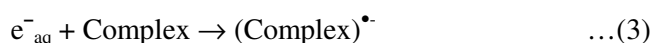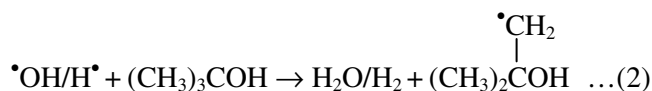[Co(NN)$_2$Cl$_2$]Cl   2,2'-bipyridine(bpy)   1,10-Phenanthroline(phen)
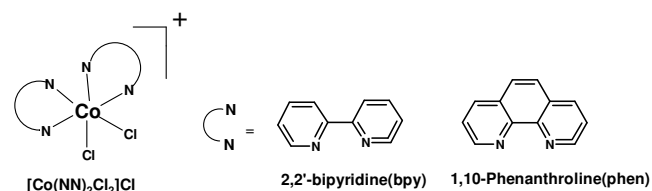
Scheme 1

electron pulses of 10, 20, 50, 100, 200, 400 and 3000 ns duration. Optical absorption detection system (Luzchem Canada), consists of 175 W Xe lamp (Cermax parallel lamp), 1/8 M monochromator (CVI CM 110), photomultiplier (Hamammatsu 7400U-04) and digital oscilloscope (Tektronix TDS 3032 B, 300 MHz, 2.5 GS/s). Acquisition of kinetic and spectral data was achieved by mLFP and superspec software (LUZCHEM) based on Labview platform. Details of pulse radiolysis system are reported elsewhere[10,11]. The present work was carried using 50 ns electron pulses at a dose range of 10-15 Gy per pulse. Radiation dose was measured using air saturated KCNS dosimeter taking $G\varepsilon$ for $(SCN)_2^{\bullet-}$ to be 21,522 $dm^3 \, mol^{-1} \, cm^{-1}$ at 480 nm[12], G being the number of molecules produced per 100 eV energy absorbed. Substituting the values of molar extinction coefficients of the complex (ε_c), the absorption values in the transient absorption spectra were corrected using Eq. (A), where ε_R and ε_c are the molar extinction coefficients of the transient radical species and the complex respectively at a particular wavelength, ΔOD_D is the optical density of $(SCN)_2^{\bullet-}$ at 480 nm (obtained from KSCN dosimeter solution) and ΔOD_R is the optical density of transient at particular wavelength.

$$\varepsilon_R = \varepsilon_c + 21,522 \times \Delta OD_R / [\Delta OD_D \times G \, (e^-_{aq})] \quad \ldots(A)$$

Results and discussion

Radiolysis of water generates hydrated electrons (e^-_{aq}), $^\bullet OH$ and $H^\bullet$ atoms as primary transient radical species. To selectively study reactions of e^-_{aq}, in N_2 saturated aqueous solutions of the complex, t-butanol (0.5 mol dm^{-3}) is added as scavenger to remove $^\bullet OH$ and $H^\bullet$ atoms[13]. The reaction of e^-_{aq} with both the complexes was studied and absorption spectra before and after radiolysis were compared. Typical reactions are depicted by Eqs (1)-(4).

$$H_2O \text{ -}/\text{\textbackslash}/\text{\textbackslash}/\text{\textbackslash}\text{-> } e^-_{aq}, \, ^\bullet OH, \, ^\bullet H \quad \ldots(1)$$

$$^\bullet OH/H^\bullet + (CH_3)_3 COH \rightarrow H_2O/H_2 + (CH_3)_2 \overset{\overset{\textstyle ^\bullet CH_2}{|}}{C}OH \quad \ldots(2)$$

$$e^-_{aq} + Complex \rightarrow (Complex)^{\bullet-} \quad \ldots(3)$$

$$(Complex)^{\bullet-} \rightarrow Products \quad \ldots(4)$$

Figures 1 and 2 show, the time resolved transient absorption spectra of the complex anion formed on reaction with e^-_{aq} which also decays in the time region of ~100 μs for both bpy and phen complexes. The rate constants of the reaction of e^-_{aq} with the complexes determined by decay of e^-_{aq} at 700 nm are given in Table 1. These rates are diffusion controlled and comparable with the tris cobalt (III) complexes with phen and bpy[14].

Transient absorption spectra of [Co(III)(bpy)₂Cl₂]Cl complex

The time resolved transient absorption spectra of the anion radical of the bpy complex shows two broad peaks at 360 and 610 nm at 1 μs. The former peak decays and shows progressive shift to blue region; at 80 μs, the spectrum shows peak at 290 nm. The latter
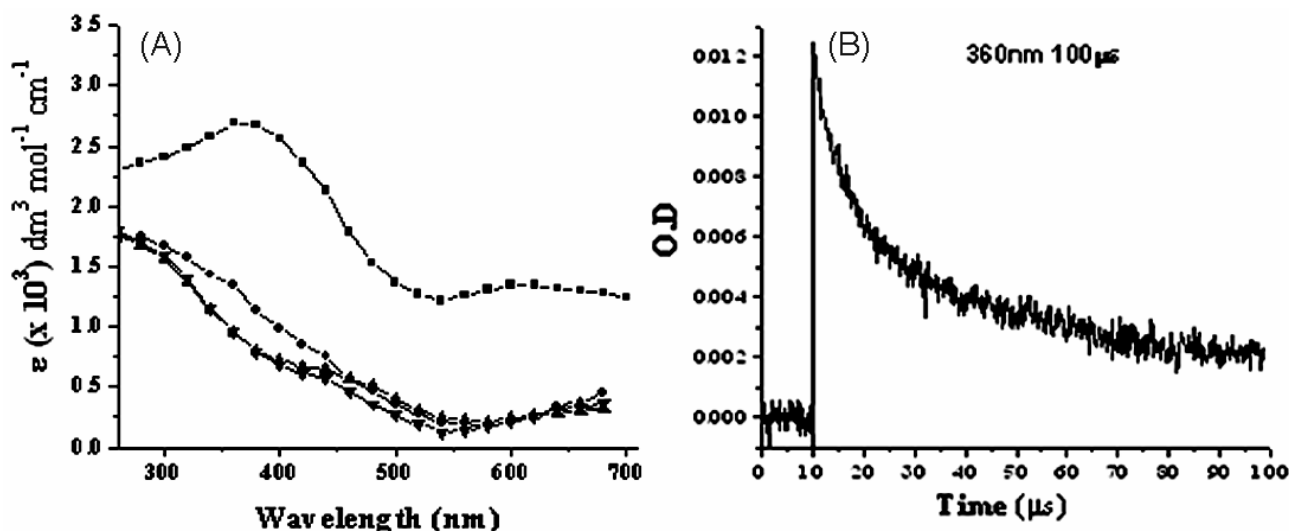

Fig. 1 — (A) Time resolved absorption spectra observed in the reaction of e^-_{aq} with [Co(bpy)₂Cl₂]Cl 1(■), 20(●), 40(▲), and 80(▼) μs after the pulse; (B) decay at 360 nm [Complex] = 2×10^{-4} mol dm^{-3}, dose per pulse 10 ~ Gy.

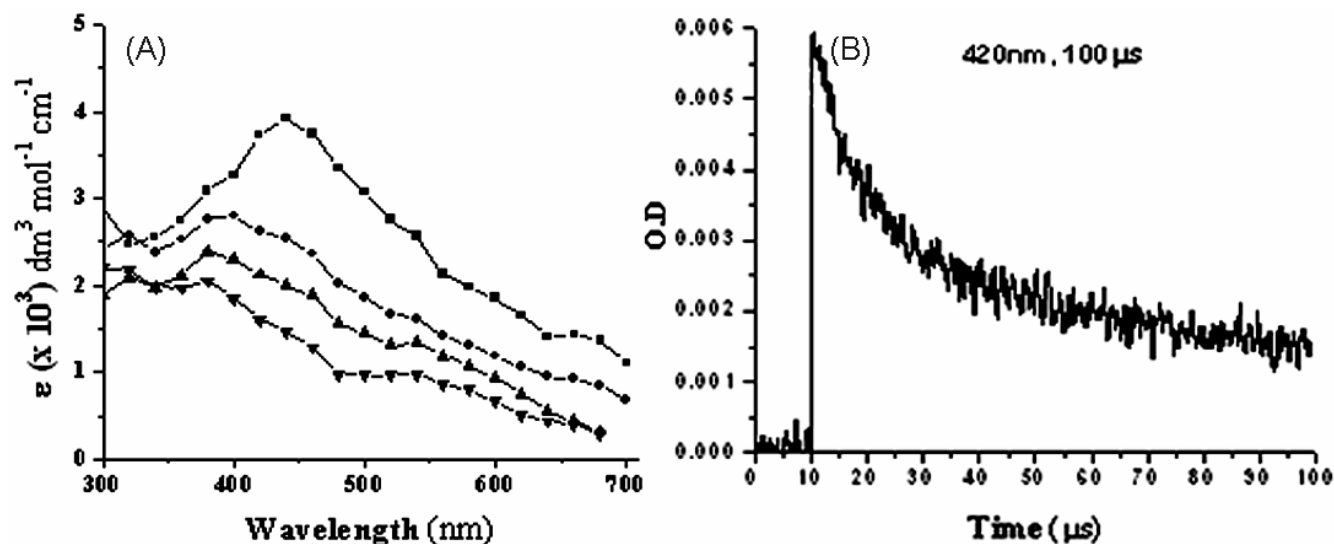Fig. 2 — (A) Time resolved absorption spectra observed in the reaction of e^-_{aq} with [Co(phen)$_2$Cl$_2$]Cl 2(■), 20(●), 40(▲), and 80(▼) μs after the pulse; (B) decay at 420 nm [Complex] = 2×10^{-4} mol dm^{-3}, dose per pulse 10 ~ Gy.

peak shows decay and progressive red shift and at 80 μs the absorption still shows red shift beyond 680 nm. The decay profile at 360 nm shows absorption beyond 100 μs. The initial portion of the decay curve gives second order rate constant of (8.2 ± 0.2) × 10^6 dm^3 mol^{-1} s^{-1}. The transient absorption at 360 nm decays completely in ~200 μs time.

The complex radical anion can decay by: (1) aquation, (2) de-ligation, and (3) reduction to give Co(II). Reduction to Co(II) has been observed in the case of *tris*(acetylacetonato)Co(III)[7] complex. De-ligation has been observed in the case of mixed ligand Co(II) complexes and takes place in millisecond time scale[15]. Three sites of electron localization exist in both the complexes studied, viz. metal ion, ligands (phen/bpy) and chloride. UV-vis spectra of the complex after irradiation indicate that the complex breaks and de-ligation/aquation occurs.

Table 1 — Rate constants of hydrated electron (e^-_{aq}) with [Co(III)(2,2'-bipyridine)$_2$Cl$_2$]Cl and [Co(III)(1,10-phenan-throline)$_2$Cl$_2$]Cl complexes (temperature = 300 K)

Complex	Rate constant (dm^3 mol^{-1} s^{-1})
[Co(2,2'-bipyridine)$_2$Cl$_2$]Cl *p*H= 6.2	7.6(±0.2)×10^{10}
[Co(1,10-phenanthroline)$_2$Cl$_2$]Cl *p*H= 6.2	6.9(±0.2)×10^{10}
*[Co(2,2'-bipyridine)$_3$]$^{3+}$	8.8×10^{10}
*[Co(1,10-phenanthroline)$_3$]$^{3+}$	7.5×10^{10}
#2,2'-Bipyridine	2.5×10^{10}
#1,10-Phenanthroline	2.5×10^{10}

*Values from ref. 14; #Values from ref. 16

Transient absorption spectra of [Co(III)(phen)$_2$Cl$_2$]Cl complex

The time resolved transient absorption spectra of the anion radical of the phen complex shows one broad peak at 420 nm at 1 μs, which decays and shows progressive blue shift; and at 80 μs shows peak at 300 nm. The decay profile at 420 nm shows absorption beyond 100 μs. The initial portion of the decay curve gives second order rate constant of (8.1 ± 0.2) × 10^6 dm^3 mol^{-1} s^{-1}. The transient absorption decays at 450 nm completely in ~200 μs time.

Reaction of e^-_{aq} with the ligands

The ligands phen and bpy also react with e^-_{aq} (Ref. 16):

$$e^-_{aq} + bpy/phen \rightarrow (bpy/phen)^{•-} \qquad …(5)$$

The rate constants of e^-_{aq} with ligands are obtained by Mulazzani *et al.*[16] and are 2.5×10^{10} dm^3 mol^{-1} s^{-1} for both phen and bpy. The anion radical of phen has a sharp transient absorption peak at 330 and a broad one at 520 nm, at ~1 μs time window. The radical anion then protonates at *p*H 6.2 where experiments have been carried out and the absorption peaks shifts to 360 and 680 nm, respectively.

$$(bpy/phen)^{•-} + H^+ \Leftrightarrow (bpyH^•/phenH^•) \qquad …(6)$$

None of these absorption peaks matches with those of phen complex. Hence, the electron is not localized on the ligand (phen) but on the complex as a whole. Similarly for bpy, the transient absorption peak for
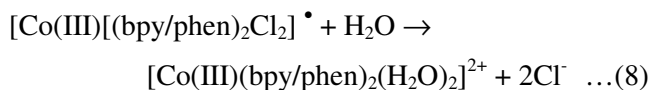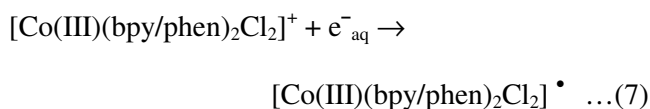
anion radical is seen at 360 nm, which shifts to 320 nm on protonation. For the bpy complex also, the transient absorption peaks do not match with those of the anion radical of bpy. Hence, for bpy complex the electron is located on the complex as a whole.

The phen complex anion decays initially by second order with a rate constant of 8.1×10^6 dm^3 mol^{-1} s^{-1}. For both the complexes, the transient absorption decays in ~200 µs time scale. These observations point to a stable product formation.

However, for $[Co(phen)_3]^{3+}$ and $[Co(bpy)_3]^{3+}$ complexes[16-19], the ligand anion spectra and complex anion spectra match and it is reported that the initially produced transient species on electron reaction are likely to be a Co(III) centre containing coordinated aromatic phen/bpy radical[15]. These species then undergo intramolecular electron transfer to form Co(II) species.
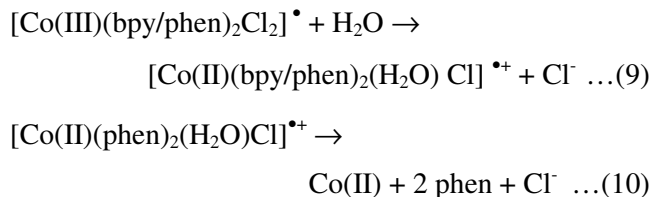
Conductivity measurements

The dichloro complex anions can decay by aquation with release of chloride ions. To ascertain whether such a process occurs on irradiation, conductivity measurements were carried out. The complex solutions were given 3 electron pulses, and conductivities were measured for the unirradiated and irradiated solutions. In case of both the irradiated complexes, the conductivity increases almost three times (Table 2). It points to the replacement of chloride ions in the complexes by the water molecules, i.e. aquation. The following reactions can be put forth to explain both aquation and de-ligation of the complexes on irradiation:

$$[Co(III)(bpy/phen)_2Cl_2]^+ + e^-_{aq} \rightarrow$$
$$[Co(III)(bpy/phen)_2Cl_2]^\bullet \quad …(7)$$

$$[Co(III)[(bpy/phen)_2Cl_2]^\bullet + H_2O \rightarrow$$
$$[Co(III)(bpy/phen)_2(H_2O)_2]^{2+} + 2Cl^- \quad …(8)$$

Release of one chloride ion may also be possible (reaction 9), which might result in reduction of

Table 2 — Conductivity measurements before and after irradiation in milli mhos. (Dose: 15 Gy, pH: 6.2, [Complex] $= 2 \times 10^{-4}$ mol dm^{-3})

Complexes	Before irradiation*	After irradiation
$[Co(bpy)_2Cl_2]Cl$	0.103	0.346
$[Co(phen)_2Cl_2]Cl$	0.162	0.376

*immediately after dissolution

Co(III) to Co(II). The Co(II) species then dissociate to give free ligand and free Co(II) ions.

$$[Co(III)(bpy/phen)_2Cl_2]^\bullet + H_2O \rightarrow$$
$$[Co(II)(bpy/phen)_2(H_2O) Cl]^{\bullet+} + Cl^- \quad …(9)$$

$$[Co(II)(phen)_2(H_2O)Cl]^{\bullet+} \rightarrow$$
$$Co(II) + 2\ phen + Cl^- \quad …(10)$$

Qualitative spot tests carried out using nirtoso-R salt show presence of Co(II) in irradiated solutions for the phen complex.

Such intramolecular electron transfer reactions have been previously observed in Co(III) complexes[9,20].

Steady state optical absorption

Steady state optical absorption spectra show that for phen complex, the OD of the irradiated solution decreases drastically indicating the breakdown of the complex further corroborated by the increase in the conductivity.

Extraction of the irradiated complex in chloroform shows the same spectrum as that of phen, and detection of Co(II) by nitroso-R reagent support the conclusion that phen complex dissociates completely. These results confirm the reactions (7)-(10) for the phen complex. On the other hand for bpy complex, the absorption blue shifts on irradiation and may probably be due to the formation of reduced species of the bpy complex. Free bpy was not found in irradiated solutions after extraction in chloroform. This indicates that the $[Co(III)(bpy)_2Cl_2]^+$ complex gets reduced to $[Co(II)(bpy)_2]^{2+}$ complex and the reaction can be expressed by:

$$[Co(III)(bpy)_2Cl_2]^+ + e^-_{aq} + 2H_2O \rightarrow$$
$$[Co(II)(bpy)_2(H_2O)_2]^{2+} + 2Cl \quad …(11)$$
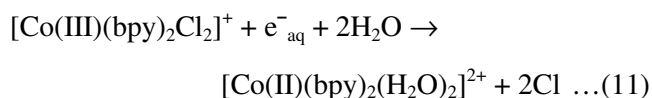
Eq. (11) also explains the increase of conductivity on irradiation for bpy complex.

Thus, during the reactions of e^-_{aq} with two cobalt complexes $[Co(III)(2,2'-bipyridine)_2Cl_2]Cl$ and $[Co(III)(1,10-phenanthroline)_2Cl_2]Cl$, the transient absorption decays in ~200 µs. Steady state absorption spectra on irradiation points out to breakdown of the phen complex to free ligand, free Co(II) and Cl$^-$ ions. On the other hand bpy complex gets reduced and $[Co(II)(bpy)_2(H_2O)_2]^{2+}$ complex is formed and Cl$^-$ ions are released.

Acknowledgement

References

1   Erkkila K E, Odom D T & Barton J K, *Chem Rev,* 99 (1999) 2777.

2   Sigman D S, Mazumder A & Perrin D M, *Chem Rev,* 93 (1993) 2295.

3   Grätzel M, *Inorg Chem,* 44 (2005) 6841.

4   Baxendale J H & Fiti M, *J Chem Soc, Dalton Trans,* (1972) 1995.

5   Hoffman M Z & Simic M, *J Chem Soc Chem Commun*, (1973) 640.

6   Ghosh S, Barve A C, Kumbhar A A, Kumbhar A S, Puranik V G, Datar P A, Sonawane U B & Joshi R R, *J Inorg Biochem*, 100 (2006) 331.

7   Rama Rao K V S, Shastri L V & Shankar J, *Radiation Effects*, 2 (1970) 193.

8   Vlcek A A, *Inorg Chem*, 6 (1967) 1425.

9   Hoffman M Z & Simic M, *J Am Chem Soc*, 94 (1972) 1757.

10   Yadav P, Kulkarni M S, Shridhonkar M & Rao B S M, *Curr Sci*, 92 (2007) 599.

11   Pramod G, Prasanthkumar K P, Mohan H, Manoj V M, Manoj P, Suresh C H & Aravindakumar C T, *J Phys Chem,* A, 110 (2006) 11517.

12   Fielden E M, *The study of Fast Processes and Transient Species by Electron Pulse Radiolysis,* edited by J H Baxendale & F Busi (Riedel Dordrecht, Holland), 1982.

13   Shinohara N, Lilie J & Simic M G, *Inorg Chem*, 16 (1977) 2809.

14   Simic B G, Hoffman M Z, Cheney R P & Mulazzani Q G, *J Phys Chem*, 83 (1979) 439.

15   Funston A M, McFadyen W D & Tregloan P A, *Dalton Trans*, 9 (2002) 2053.

16   Mulazzani Q G, Emmi S, Fuochi P G, Venturi M, Hoffman M Z & Simic M G, *J Phys Chem*, 83 (1979) 1582.

17   Simic M & Ebert M, *Int J Radiat Phys Chem,* 3 (1971) 259.

18   Hoffman M Z, Simic M G, Mulazzani Q G, Emmi S, Fuochi P G & Venturi M, *Radiat Phys Chem*, *12* (1978) 111.

19   Mulazzani Q G, Emmi S, Fuochi P G, Venturi M & Hoffman M Z, *J Am Chem Soc*, 100 (1978) 981.

20   Cohen H & Meyerstein D, *J Chem Soc Dalton Trans*, 23 (1975) 2477.