

## Approaches to the aqueous chemistry of chromium(IV) and chromium(V) in macrocyclic and Schiff base complexes

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**Abstract.** The stabilization of chromium(IV) and chromium(V) in aqueous systems has now been made through designed alterations in Franck–Condon barriers for the interconversion of various oxidation states of chromium. Equatorially coordinated macrocyclic and Schiff base ligands influence the reorganizational barriers for the conversion of Cr(III)–Cr(IV)–Cr(V)–Cr(VI) couples such that Cr(IV) and Cr(V) transients of sufficiently long life time can be generated. A series of macrocyclic and Schiff base complexes of Cr(III) has been synthesised and subjected to non-complementary redox reaction with Ce(IV) or electrochemical oxidation. A Cr(IV) macrocyclic complex,  $\text{Cr}(\text{Me}_4[14]\text{tetraene})(\text{H}_2\text{O})_2^{4+}$ ,  $\frac{1}{2}$  has been generated in aqueous acidic medium, through electrochemical oxidation. The Ce(IV) oxidation of Cr(III) Schiff base complexes, diaqua[N,N'-ethylenebis(salicylideneiminato)chromium(III)], and diaqua[N,N'-propylenebis(salicylideneiminato)chromium(III)] proceed in two stages with 1 Cr:1 Ce(IV) redox stoichiometry. Sufficiently long-lived Cr(IV) intermediates and Cr(V) Schiff base products have been generated. ESR evidence for the formation of Cr(V) Schiff base products and the mechanistic outcome of the oxidation of Cr(III) Schiff bases are discussed.

**Keywords.** Cr(III) macrocycle; Cr(III) Schiff-bases; chromium(IV); chromium(V); stabilization; unusual oxidation states.

### 1. Introduction

Although the carcinogenicity of hexavalent chromium has been much discussed, the biochemical mechanism is not yet fully understood (Dessi *et al* 1989; De Flora *et al* 1990). The incubation of chromate with isolated rat tail tendon liver mitochondria is associated with the reduction of Cr(VI) and the formation of some Cr(V) species. Similar formation of chromium(V) complexes have also been detected in the reduction of chromium(VI) by other cellular systems (Berardi *et al* 1990). The aqueous chemistry of chromium(IV) and chromium(V) has, therefore, gained importance and questions have been raised with respect to their possible involvement in various processes leading to the damage of living cells. The reduction of Cr(VI) by a variety of inorganic and organic reducing agents has been extensively investigated (Espenson 1969; Krumpolc and Rocek 1979). The evidence for the formation of Cr(IV) and Cr(V) transient intermediates in the non-complementary reactions of Cr(VI) has remained mostly indirect (Beattie and Haight 1972). It is believed that in the interconversion of Cr(III) and Cr(VI), Cr(IV) to Cr(V) conversion is the rate-limiting step. The need for changes in coordination number and geometry is assumed to be the probable cause of the relatively slow interconversion of Cr(V) and Cr(IV). This assumption

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arises directly from the importance of Franck–Condon or nuclear reorganizational factors in electron-transfer processes (Marcus 1982; Endicott *et al* 1983). On the basis of the known importance of the Franck–Condon factors, equatorially coordinated macrocyclic and Schiff base ligands will further increase the reorganizational barriers for the conversion of Cr(IV) octahedral to tetrahedral Cr(V) structures. By the choice of suitable ligands, interconversion of Cr(IV) and Cr(V) can be expected to be rendered so slow that the stabilisation of Cr(IV) and Cr(V) intermediates is likely to occur. It can be postulated that the compelling kinetic evidence for such stabilisation of Cr(IV) has been obtained in the Ce(IV) oxidation of a series of Cr(III) macrocycles (Nair *et al* 1987). The reaction was found to be of second order with respect to cerium(IV) when [Cr(III)] was in large excess over [Ce(IV)]. Treatment of the kinetic data showed that as ring puckering became more difficult due to the increase in the unsaturation in the macrocyclic ring and increase in the number of methyl substituents in the ring, the rate of Ce(IV) oxidation to Cr(VI) decreased. The importance of Franck–Condon factors arising from nuclear reorganizational changes in the oxidation of Cr(III) macrocycles by Ce(IV) have been discussed (Nair *et al* 1987). However, in previous work, the Cr(IV) and Cr(V) species formed could not be directly observed using physical methods (Nair *et al* 1987). This communication presents the direct electrochemical and kinetic evidence for the formation of Cr(IV) complexes, and of Cr(V) products in the case of two selected Schiff base complexes of chromium.

## 2. Experimental

### 2.1 Materials

The diaquo chromium(III) complexes of the tetraaza macrocyclic ligands 5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradec-4,6,11,13-tetraene was prepared as described earlier (Nair *et al* 1986). The diaquo Cr(III) complexes of the 12- and 13-membered Schiff base ligands N,N'-ethylenebis(salicylideneimine), (salen) and N,N'-propylenebis(salicylideneimine), (salprn) were prepared by literature methods (Coggon *et al* 1970; Kanthimathi *et al* 1993). Iodosyl benzene was prepared by base hydrolysis of iodo benzene diacetate.

### 2.2 Kinetic measurements

The kinetics of the reaction of iodosyl benzene and Ce(IV) with Cr(III) multidentate complexes were studied using an Aminco stopped-flow spectrophotometer. Generally pseudo first-order conditions were maintained for the reaction. The kinetics were carried out in the presence of Ce(III) and sulphate as a function of  $[H^+]$ . The reactions of Cr(III)-Schiff base complexes with iodosyl benzene were investigated at 590 nm as a function of  $[H^+]$  and temperature. The reactions of Ce(IV) with the Schiff base complexes of Cr(III) have been investigated in aqueous acidic media at 25°C.  $I = 1.0$  M ( $LiClO_4$ ) at 560 and 416 nm. Typical concentration ranges employed were [Ce(IV)],  $(0.5-4.0) \times 10^{-3}$  M, [Cr(III)],  $1 \times 10^{-4}$  M, [Ce(III)],  $(1-10) \times 10^{-4}$  M,  $[H^+]$ , 0.1–0.5 M and  $[SO_4^{-2}]$ ,  $(3-12) \times 10^{-2}$  M.

### 2.3 Product analysis

The products formed at the end of the oxidation of Cr(III)-Schiff base complexes with iodosyl benzene, [iodosylbenzene],  $1 \times 10^{-4}$  M and [Cr(III)],  $3 \times 10^{-4}$  M at  $[H^+] = 0.01$  M were analysed. The mixture at the end of reaction was passed through a Dowex 50 W-X2 cation exchange column. No anionic Cr(VI) product was obtained. EPR of the product mixture showed the presence of Cr(V). For the product analysis of the oxidation of Cr(III) Schiff base complexes with Ce(IV), the Cr(III) complexes and Ce(IV) solution were mixed in 1:4 ratio. The reaction product as well as excess Ce(IV) were completely absorbed on a Dowex 50 W-X8 column indicating that the final product formed is not dichromate. Separation of products on a Sephadex LH-20 gave rise to two chromium-containing bands, with one of them being mixed with Ce(IV) and the other free of any Ce(IV). The Ce(IV) free band had an electronic spectrum with absorption maxima at 275 nm and molar absorption coefficients,  $1.5 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ .

## 3. Results and discussion

### 3.1 Cr(III)-macrocyclic complexes

Since the results of Ce(IV) oxidation of Cr(III) macrocycles showed that oxidation of Cr(III) became more difficult as the ring unsaturation increased, the Cr(III) complex of the tetraaza macrocycle,  $\text{Me}_4[14]$  tetraene has been oxidized electrochemically. The cyclic voltammogram of *trans*-Cr( $\text{Me}_4[14]$  tetraene)( $\text{H}_2\text{O}$ ) $_2^{3+}$  in both aqueous acidic and acetonitrile medium showed a quasi-reversible wave with cathodic-anodic separation of 59–80 mV (figure 1). Cyclic voltammogram of the Cr(III) complex of

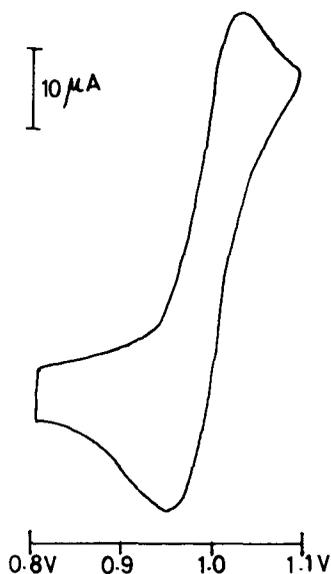
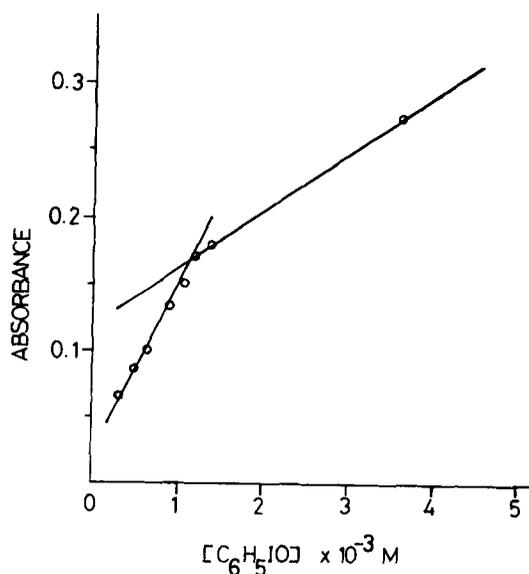


Figure 1. The cyclic voltammogram of  $\text{Cr}(\text{Me}_4[14]\text{tetraene})(\text{H}_2\text{O})_2^{3+}$  at  $[H^+] = 2.0$  M,  $I = 3.0$  M, scan rate 200 mV/s  $[\text{Cr(III)}] = 2.5 \times 10^{-3}$  M.

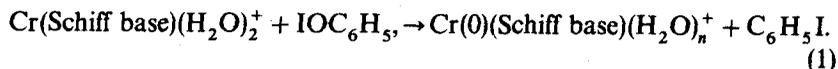


**Figure 2.** The spectrophotometric titration curve for the reactivity of  $\text{Cr}(\text{salen})(\text{H}_2\text{O})_2^+$  and iodosal benzene.

other saturated macrocycles did not show any redox wave in this region, which may in part be explained as due to relatively easy conversion of Cr(IV) to other higher valent oxidation states.

### 3.2 Oxidation of Cr(III)–Schiff base complexes

The stoichiometry for the reaction of  $\text{Cr}(\text{salen})(\text{H}_2\text{O})_2^+$  and  $\text{Cr}(\text{salprn})(\text{H}_2\text{O})_2^+$  with iodosal benzene was investigated spectrophotometrically. The spectrophotometric titration curve for the reaction of  $\text{Cr}(\text{salen})(\text{H}_2\text{O})_2^+$  and iodosal benzene is shown in figure 2. The value observed for the overall stoichiometry 1 Cr: 1.3 iodosal benzene can be approximated to 1:1 within experimental error.

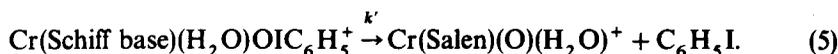
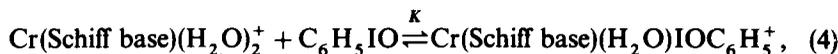


The kinetics of the reaction was investigated under pseudo first-order excess of [iodosal benzene] over [Cr(III)]. The pseudo first-order plots were linear to at least 3 half-lives. The plots of  $k_{\text{obs}}$  against [iodosal benzene] at various  $[\text{H}^+]$  were linear with zero intercept indicating that the reaction is irreversible. From the slopes of linear plots of  $k_{\text{obs}}$  against [iodosal benzene], bimolecular rate constants,  $k_{\text{sec}}$ , could be obtained. The second-order rate constant,  $k_{\text{sec}}$ , exhibits an inverse dependence on  $[\text{H}^+]$ . The rate data can be fitted to the rate law

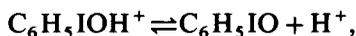
$$k_{\text{sec}} = k_2 K_a / ([\text{H}^+] + K_a) \quad (2)$$

A nonlinear least square fit of  $k_{\text{sec}}$  data to (2) gave the values of  $k_2 K_a$ ,  $K_a$  and  $k_2$  to be  $5 \times 10^{-2} \text{ s}^{-1}$ ,  $1.03 \times 10^{-3} \text{ M}$  and  $48.54 \text{ M}^{-1} \text{ s}^{-1}$  respectively for  $\text{Cr}(\text{salen})(\text{H}_2\text{O})_2^+$ .

The observed rate law can be fitted to the following reaction scheme



Iodosyl benzene seems to exhibit acid–base protonation behaviour within the pH range 1–4 as evident from the changes of UV spectrum depending on  $[\text{H}^+]$ . Previous studies have shown that iodosyl benzene functions as an inner-sphere oxidant or oxygen-transfer agent (Di Sipio *et al* 1972). It has also been shown that  $\text{Cr}(\text{salen})(\text{H}_2\text{O})_2^+$  undergoes ready aquo ligand substitution (Prasad *et al* 1980). Therefore, the formation of an inner-sphere intermediate  $\text{Cr}(\text{III})(\text{salen})(\text{H}_2\text{O})\text{IOC}_6\text{H}_5^+$  seems quite probable. The  $K_a$  value obtained for



the equilibrium based on the fit of  $k_{\text{sec}}$  data to (2) seems realistic. The value of  $k_2$  needs to be considered a composite quantity of  $Kk'$ , where  $K$  corresponds to the equilibrium constant for the formation of the intermediate  $\text{Cr}(\text{III})(\text{salen})(\text{H}_2\text{O})\text{IOC}_6\text{H}_5^+$  and  $k'$  corresponds to the unimolecular decay rate constant. The iodosyl benzene oxidation of  $\text{Cr}(\text{Schiff base})(\text{H}_2\text{O})_2^+$  does produce a stable Cr(V) intermediate with a finite lifetime as confirmed by EPR.

The kinetics of oxidation of  $\text{Cr}(\text{salen})(\text{H}_2\text{O})_2^+$  and  $\text{Cr}(\text{salprn})(\text{H}_2\text{O})_2^+$  by  $\text{Ce}(\text{IV})$  have been investigated under pseudo first-order excess of  $[\text{Ce}(\text{IV})]$  over  $[\text{Cr}(\text{III})]$ . There are two kinetic stages with increasing followed by decreasing absorbance changes as shown in figure 3. Since the two stages have widely differing half-lives it has been possible to obtain reliable pseudo first-order rate constants  $k_1$  and  $k_2$  for the first and second stages respectively. The rate-constant data are independent of

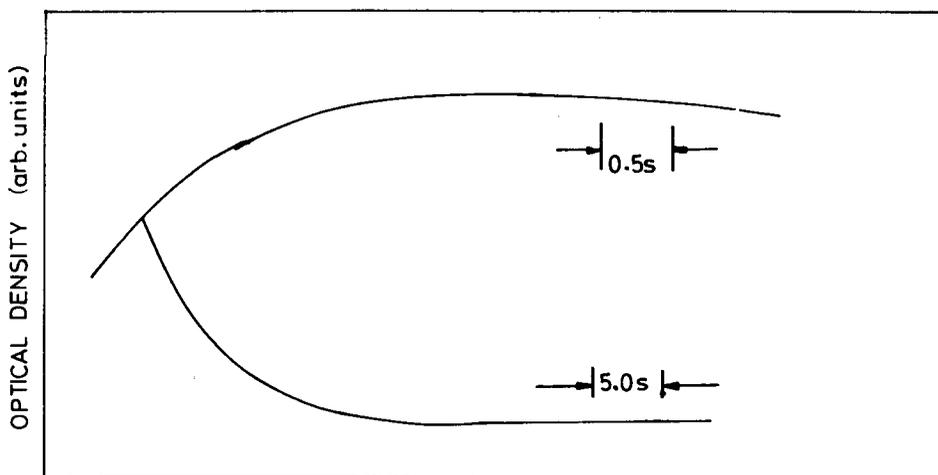


Figure 3. Absorbance changes in the two-stage oxidation of  $\text{Cr}(\text{salprn})(\text{H}_2\text{O})_2^+$  by  $\text{Ce}(\text{IV})$ .

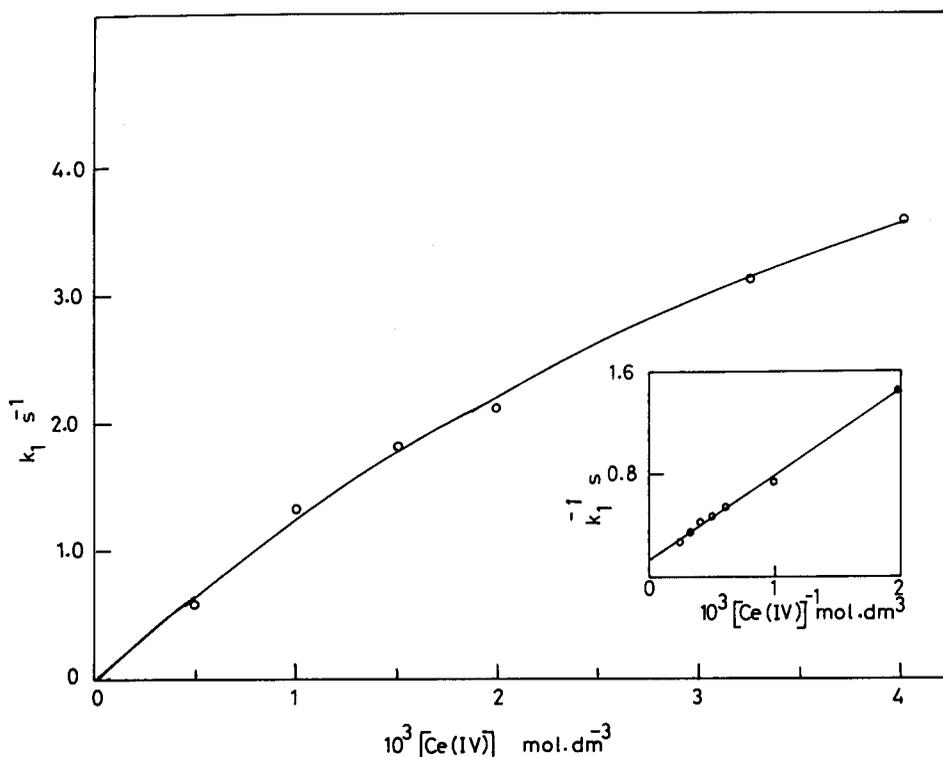
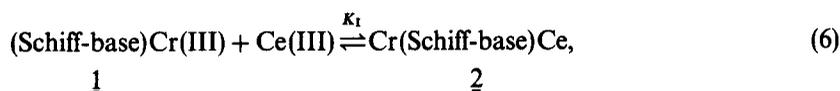


Figure 4. The dependence of  $k_1$  on  $[\text{Ce(IV)}]$ .

the monitoring wavelength. The observed rate constants,  $k_1$ , have been measured as functions of  $[\text{Ce(IV)}]$ ,  $[\text{Ce(III)}]$ ,  $[\text{H}^+]$  and  $[\text{SO}_4^{2-}]$ . The values of  $k_1$  exhibited zero-order dependence on  $[\text{H}^+]$ ,  $[\text{Ce(III)}]$  and  $[\text{SO}_4^{2-}]$ . The dependence of  $k_1$  on  $[\text{Ce(IV)}]$  was as shown in figure 4. The stoichiometry for the formation of the intermediates has been investigated by means of stopped-flow titration at 560 nm, which established the reaction stoichiometry for the first state as  $1:1:1 \pm 0.1$ . The visible spectrum of the intermediate in the spectral range 440–600 nm has been obtained using a stopped-flow spectrophotometer (figure 5). The spectrum of the final product has also been obtained and is shown in figure 5. The overall reaction stoichiometry at the end of the decomposition of the intermediate has also been investigated, which reveals a stoichiometry of  $1:2:1 \pm 0.1$ . The kinetics and stoichiometric data observed for the first stage can be reconciled with the reaction scheme given below



The  $k_1$  data give a satisfactory fit to the rate law below

$$k_1 = K_I k_i [\text{Ce(IV)}] / (1 + K_I [\text{Ce(IV)}]) \quad (8)$$

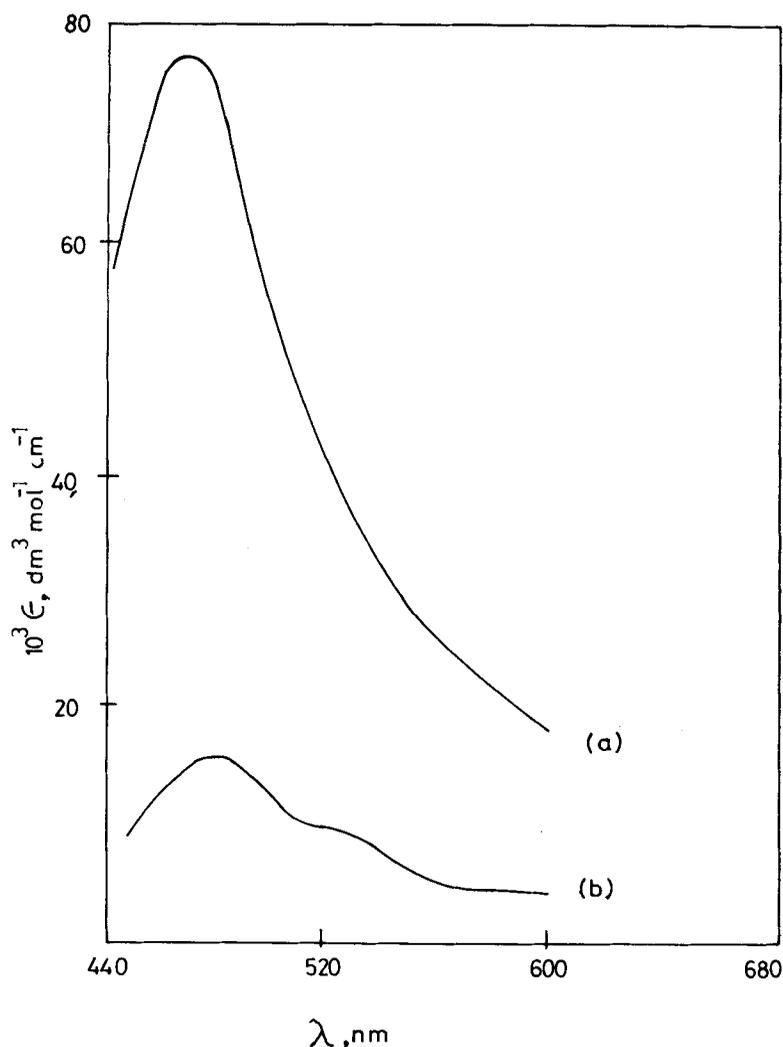
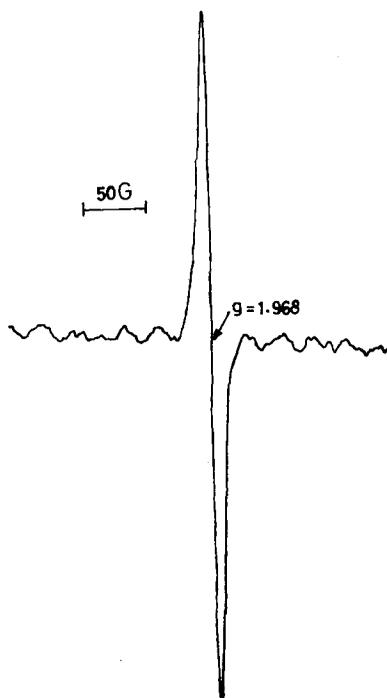


Figure 5. The visible spectra of (a) Cr(IV) intermediate, (b) Cr(V) product.

where  $K_I$  corresponds to an equilibrium constant for the formation of an inner sphere adduct  $\underline{2}$  and  $k_i$  to the first order disproportionation rate. The rate data have been fitted to the rate law using an IBM PC/AT and Los Alamos program. The estimated values of  $K_I$  and  $k_i$  are given in table 1. It can be seen that the disproportionation of the inner sphere adduct of Cr-salen with Ce(IV) is marginally faster compared to the disproportionation of the Ce(IV) Cr-salprn adduct. The analysis of the observed rate constant data,  $k_2$ , in terms of  $[\text{Ce(IV)}]$ ,  $[\text{Ce(III)}]$ ,  $[\text{H}^+]$  and  $[\text{SO}_4^{2-}]$  revealed that  $k_2$  exhibited a dependence only on  $[\text{Ce(IV)}]$ . The bimolecular rate constants are given in table 1. The observed first-order dependence of  $k_2$  on  $[\text{Ce(IV)}]$  and overall reaction stoichiometry of 1:2:1 are consistent with a mechanism involving the further oxidation of the Cr(IV) intermediate to the Cr(V) species. The EPR spectrum of the product (figure 6) further establishes that the final product is Cr(V) ( $g = 1.968$ ).

**Table 1.** Kinetic parameters for the oxidation of Cr(III)-Schiff bases with Ce(IV).

Complexes	$K_1(\text{M}^{-1})$	$k_1(\text{s}^{-1})$	$k_2'(\text{M}^{-1}\text{s}^{-1})$
$\text{Cr}(\text{salen})(\text{H}_2\text{O})_2^+$	$136 \pm 5$	16.6	$460 \pm 12$
$\text{Cr}(\text{salprn})(\text{H}_2\text{O})_2^+$	$150 \pm 7$	$10 \pm 2$	$207 \pm 8$

**Figure 6.** EPR spectrum of the final oxidation product of  $\text{Cr}(\text{salprn})(\text{H}_2\text{O})_2^+$  with Ce(IV). Modulation frequency, 100 kHz; microwave power, 5dB; temperature, 300 K.

#### 4. Conclusion

With a 14-membered macrocyclic ring it was possible to generate a Cr(IV) intermediate by increasing the ring unsaturation and thereby increasing the Franck-Condon barrier to Cr(IV)-Cr(V) conversion. Experimental evidence has now been obtained for the formation of Cr(IV) and Cr(V) products, during the Ce(IV) oxidation of Cr(III)-Schiff base complexes, and of Cr(V) products during the oxidation by iodoso benzene, due to atom-transfer reactions.

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