Inorganica Chimica Acta, *86* (1984) L59–L60

Synthesis and Characterization of a Novel Periodatobis(1,10-phenanthroline)chromium(V) Complex

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Received January 10, 1984

Chromium(V) is often proposed as an intermediate in mechanisms of chromium(VI) oxidations [1]. Kon [2] was the first to report the formation of chromium(V) in the oxidation of several organic acids by chromium(VI) in glacial acetic acid. Relatively more stable chromium(V) complexes were also recognized in the reduction of chromium(VI) by other organic substrates [3–8]. Few compounds of chromium(V), mostly derivatives of CrO_4^{3-}, $Cr(O_2)_4^{3-}$ and CrO^{3+}, have been isolated [9]. Recently a number of chelated chromium(V) complexes of tertiary α-hydroxy acids were synthesized by the reduction of chromium(VI) by these acids [10]. These are stable, water-soluble complexes.

In the course of the oxidation of the complex, *cis*-diaquabis(1,10-phenanthroline)chromium(III), $[Cr^{III}(phen)_2(H_2O)_2]^{3+}$, by IO_4^- it was observed that a long-lived intermediate was formed, as shown in Fig. 1. The relatively high absorption in the 550–650 nm region exhibited by this intermediate is uncharacteristic of chromium(VI). Chromium(V) complexes of tertiary α-hydroxy acids exhibited similar absorption behaviour in this wavelength region.

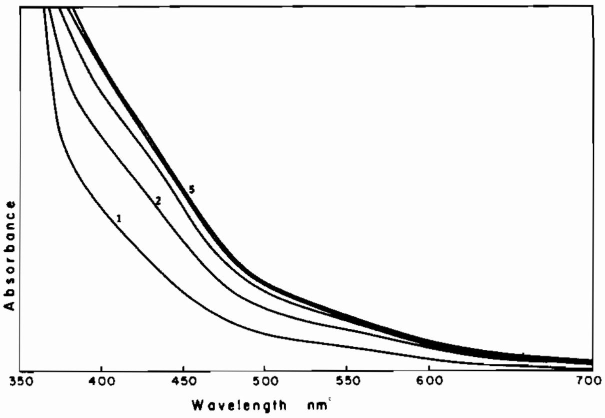

Fig. 1. UV–visible absorption spectrum of the primary product of the oxidation of $[Cr^{III}(phen)_2(H_2O)_2]^{3+}$ by IO_4^- as a function of time, (1) 1 min, (2) 10 min, (3) 20 min, (4) 30 min, (5) 40 min. $[Cr^{III}]_T = 8.2 \times 10^{-4}$ *M*, $[IO_4^-]$ = 0.01 *M*, pH = 1.46, I = 0.20 *M* and T = 25 °C (1 cm path length).

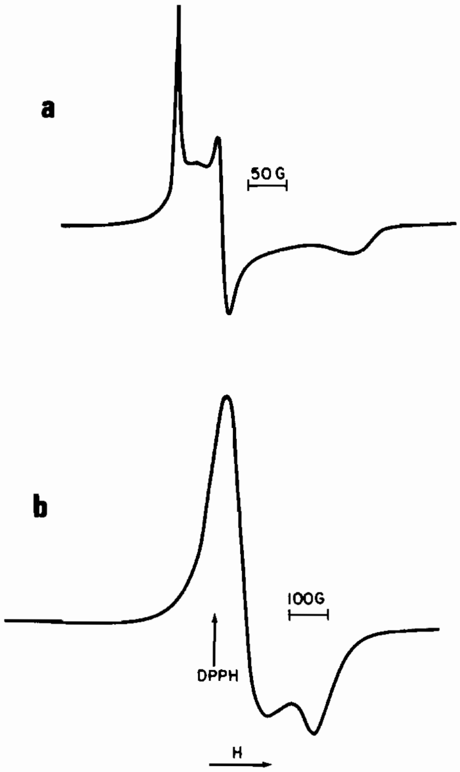

Fig. 2. a) EPR spectra of frozen solution of the primary product of oxidation of $[Cr^{III}(phen)_2(H_2O)_2]^{3+}$ by IO_4^-, $[Cr^{III}]_T = 2.0 \times 10^{-3}$ *M*, $[IO_4^-]$ = 0.03 *M*, pH = 2.73 and T = –150 °C. b) EPR spectra of the isolated Cr(V) complex $[Cr(phen)_2IO_6]$.

Evidence that the intermediate is indeed a chromium(V) complex was obtained from the EPR spectrum of frozen glasses of this product. The EPR spectrum of the intermediate shown in Fig. 2(a) is similar to the spectra reported for other chromium(V) species [2, 11, 12]. The EPR of a solid sample of the complex is shown in Fig. 2(b). The g-value for the solid chromium(V) complex was calculated as 1.972, and this is in good agreement with the g-values reported for several chromium(V) species [2, 11, 12]. Axial coordination is indicated by the EPR of both the glassy solution and the solid sample.

The intermediate species was isolated from aqueous solution by reacting 0.67 g (0.001 mol) of *cis*-$[Cr^{III}(phen)_2(H_2O)_2](NO_3)_3 \cdot 2H_2O$ with 0.43 g (0.002 mol) of $NaIO_4$ in 25 ml of water at pH ~ 4. On standing a brown precipitate separates. This was filtered off and left to dry in air. *Anal.* Found: C, 45.23; H, 2.64; N, 8.89; I, 19.92; Cr, 8.28. Calcd.

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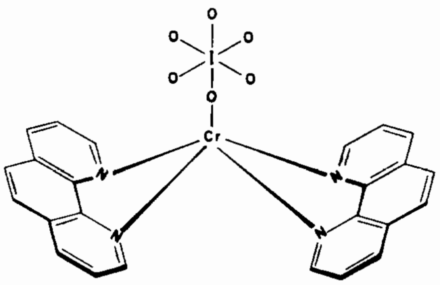

Fig. 3. Proposed structure of the chromium(V) complex, [Cr(phen)$_2$(IO$_6$)].

for [Cr(phen)$_2$IO$_6$]: C, 45.37; H, 2.54; N, 8.81; I, 19.97; Cr, 8.18.

Additional confirmation of the quinquevalent oxidation state of chromium in the isolated complex was obtained from magnetic susceptibility measurements of a solid sample of the complex at 295.3 K. The magnetic susceptibility of this complex was 1.94, comparable to the magnetic susceptibility of other chromium(V) complexes [9, 13]. The value of μ_{eff} = 1.94 confirms the presence of one unpaired electron on the chromium atom (3d^{1}).

The structure of the [Cr^{V}(phen)$_2$IO$_6$] complex has not been determined. It is, however, expected to have a structure that may be represented by Fig. 3. In this structure the two phenanthroline ligands occupy equatorial positions with the completely deprotonated periodate, IO$_6^{6-}$, coordinating axially. This chromium(V) complex differs from the known chromium(V) complexes by the absence of the Cr=O bond, which is characteristic of these complexes. This was confirmed by the absence of any significant absorption in the 900–1050 cm^{-1} region where the Cr=O bond is known to absorb [9, 10]. The absorption of this complex in the visible region may be attributed to a charge transfer from the phenanthroline ligands to chromium(V) (LTM) and/or from chromium(V) to iodine(VII) (MTL). However, absorption due to d–d transitions may also contribute.

The high charge of +5 on the chromium atom is reflected in the complete deprotonation of periodate. Complete deprotonation of periodate to give IO$_6^{5-}$ is reported only when it is coordinated to metal ions in high oxidation states, *e.g.* Cu(III) [13] and Ni(IV) [14].

Acknowledgements

Y. S. would like to thank Mr. W. R. Kennedy, Purdue University, West Lafayette, Ind., U.S.A. for running the EPR spectrum of the glassy solutions, and Purdue University for the facilities offered. Thanks are also due to Professor L. M. Venanzi for the measurement of the magnetic susceptibility, and Professor M. S. El-Ezaby for useful discussion. This work was supported by Grant No. SC 009 offered by the Research Council of the University of Kuwait.

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