Oxidation-State Determination

X-ray Absorption Spectroscopic and Electrochemical Studies of Tris(catecholato(2−))chromate(V/IV/III) Complexes**

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Complexes of transition-metal ions with redox-active catecholato ligands have been studied extensively as potential conductive or magnetic molecular materials[1] and as biologically active substances.[2] In particular, chromium–catecholato complexes have been considered among the possible reactive species in Cr^{VI}-induced genotoxicity.[3] There has been a recent debate[3,4] over the involvement of the Cr center in the redox reactions of such complexes. Pierpont[1,4] has suggested, on the basis of X-ray crystallographic and magnetic studies, that these reactions are exclusively ligand-centered and lead to interconversions of catecholato, *o*-semiquinonato, and *o*-quinone forms of the ligands, while the metal ion remains in the Cr^{III} state. Our research group[3c] has previously assigned the metal oxidation state in $[Cr(3,5\text{-dtbcat})_3]^-$ (dtbcat = di-*tert*-butylcatecholato(2−)) as Cr^V (with a strong electron delocalization between the Cr ion and the ligands), based on X-ray absorption spectroscopic (XAS) and EPR spectroscopic data. Herein, definitive evidence for the

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formation of Cr^{IV}– and Cr^{V}–catecholato complexes by sequential one-electron oxidations of $[Cr^{III}(cat)_3]^{3-}$ (cat = catecholato(2−)) has been obtained by electrochemical XAS studies of a redox series ($[Cr(cat)_3]^{n-}$ ($n = 1$–3)).

Solutions of chromium–catecholato complexes in DMF, used for the electrochemical generation of $[Cr(cat)_3]^{n-}$ ($n = 1$–3), were prepared by aerial oxidation of $K_3[Cr(cat)_3]$ (synthesized by a known method).[5] Three reversible one-electron oxidation/reduction steps (with $E_{1/2} = -296$, −89, and +396 mV versus Ag/AgCl; or −831, −624, and −139 mV versus the ferrocenium/ferrocene couple; $\Delta E_p = 58$–64 mV at 295 K)[6] were observed by cyclic voltammetric analysis of such solutions containing an excess of free ligand and $(nBu_4N)BF_4$ as a supporting electrolyte (Figure 1). To our knowledge, these are the first reported reversible electron-transfer reactions for a Cr^{III} complex with unsubstituted catechol (similar electrochemical behavior has been observed for Cr^{III} complexes of catechol derivatives).[7] Bulk electrolysis of the air-oxidized (dark red, mainly $[Cr(cat)_3]^{2-}$) solution at $E = -600$ mV led to a green air-sensitive solution of $[Cr(cat)_3]^{3-}$. Two sequential one-electron oxidation steps, starting from the green solution, led to a dark-red solution of $[Cr(cat)_3]^{2-}$ ($E = -190$ mV), then to a dark-violet solution of $[Cr(cat)_3]^{-}$ ($E = +200$ mV). One-electron oxidations at −190 and +200 mV were confirmed by coulometric measurements (experimental error ±10%), while the electrolysis at +600 mV was slow and nonstoichiometric, which is indicative of oxidative degradation of $[Cr(cat)_3]^{-}$. Electronic and EPR spectra of the electrogenerated species (see the Supporting Information) were in agreement with nearly quantitative (ca. 90–95%) formation of $[Cr(cat)_3]^{n-}$ complexes with $n = 3$, 2, or 1 at −600, −190, and +200 mV, respectively, and with the oxidative degradation at +600 mV (by comparison with the published data for Cr complexes of substituted catechols).[3,7,8] EPR spectroscopic analysis also revealed a significant decomposition of the electrochemically generated $[Cr(cat)_3]^{-}$ ($E = +200$ mV) in the absence of added free ligand (see the Supporting Information). Solutions of the $[Cr(cat)_3]^{n-}$ complexes ($n = 1$–3) for XAS studies contained excess ligand, and were either generated directly in the XAS cell (in situ spectroelectrochemistry at 295 K), or frozen in liquid N_2 for the XAS studies at 10 K.

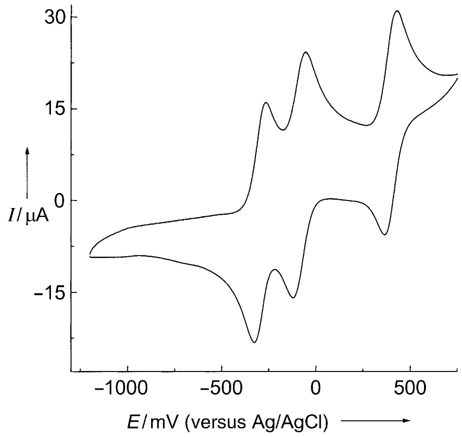


Figure 1. A typical cyclic voltammogram of the air-oxidized (saturated with Ar after oxidation) solution of $K_3[Cr(cat)_3]$ (10 mM) in DMF in the presence of $catH_2$ (20 mM) and $(nBu_4N)BF_4$ (0.10 M) at a glassy carbon electrode: scan rate 100 mVs^{-1}; 100% internal resistance compensation.

Typical changes in X-ray absorption near-edge structure (XANES) in the spectra of the $[Cr(cat)_3]^{n-}$ complexes ($n = 1$–3) during the in situ electrochemical XAS (295 K) are shown in Figure 2. Small, but significant, increases in the edge energies (6002.9 versus 6002.4 eV) and in the intensities of pre-edge peaks for $[Cr(cat)_3]^{2-/1-}$ (relative to $[Cr(cat)_3]^{3-}$) point to an increase in the Cr oxidation state in the former complexes to greater than Cr^{III}.[3c] A shift in the edge position by about 0.5 eV is similar to that observed for related Cr^{III}/Cr^{IV} couples,[3c] and is consistent with the redox chemistry being predominantly metal-centered. The changes in the XANES spectra were fully reversible, as shown by bulk electrolysis at −600 mV, followed by oxidation at +200 mV, and re-reduction at −600 mV (Figure 2). Very similar changes in the XANES spectra were observed for a series of frozen solutions of $[Cr(cat)_3]^{n-}$ ($n = 1$–3) at 10 K (see the Supporting Information).

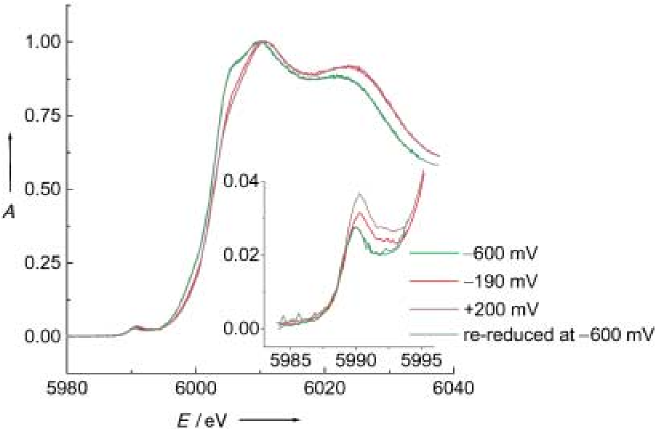


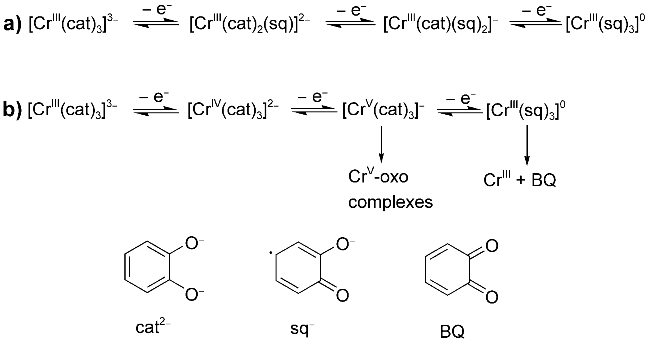
Figure 2. XANES spectra of the $[Cr(cat)_3]^{n-}$ ($n = 1$–3) solutions, generated in situ (295 K) by bulk electrolysis of a solution of $[Cr(cat)_3]^{n-}$ (10 mM), $catH_2$ (20 mM), and $(nBu_4N)BF_4$ (0.10 M) in DMF.

Changes in the Cr–O bond lengths in the $[Cr(cat)_3]^{n-}$ complexes ($n = 1$–3) were determined by multiple scattering (MS) analyses of X-ray absorption fine structure (XAFS) spectra (Table 1; full details of MS XAFS analyses are given in the Supporting Information). The MS XAFS models included all the non-H atoms in $[Cr(cat)_3]^{n-}$ and led to excellent fits (goodness-of-fit parameter, $R = 14$–16%; fits with $R < 20\%$ are considered acceptable)[9] for both frozen solutions and the solutions obtained by electrolysis in situ (see the Supporting Information). The optimized bond lengths and angles from the MS XAFS calculations for $[Cr(cat)_3]^{3-}$ agreed, within the experimental errors, to those determined from the crystal structure of $K_3[Cr(cat)_3]$ (see the Supporting Information).[5b] Analyses of systematic errors of MS XAFS calculations (see the Supporting Information) have shown that significant increases in the R value ($\geq 0.5\,\%$) were caused by small deviations from the optimum (≤ 0.005 Å) in the Cr–O bond lengths, or by much larger deviations (0.02–0.04 Å) in the bond lengths within the ligands. Errors in the bond lengths, which arise from the noise in the data (determined by Monte–Carlo analysis),[9] did not exceed 0.002 Å for the Cr–O bonds and 0.01 Å for the bonds within the ligands. No significant changes were detected in the bond lengths within the ligands or in the bond angles of $[Cr(cat)_3]^{n-}$ ($n = 1$–3; see the Supporting Information). In addition, good single-scattering (SS) XAFS fits of the first coordination shells (six equal Cr–O bonds) were obtained for all samples (see the Supporting Information), and the calculated average Cr–O bond lengths were the same (within 0.001–0.006 Å), as the corresponding values obtained by MS calculations (see Table 1 and the Supporting Information).

Table 1: Average Cr–O bond lengths in $[Cr(cat)_3]^{n-}$ complexes.[a]

n	T [K]	Cr–O [Å][b]
3[c]	295[e]	1.980[f]
2[c]	295[e]	1.943
1[c]	295[e]	1.937
3[d]	10	1.986
2[c]	10	1.966
1[c]	10	1.952

[a] Determined by MS XAFS analyses (see the Supporting Information). [b] Errors in the determination of the bond lengths did not exceed 0.005 Å (see the Supporting Information). [c] Solutions of $[Cr(cat)_3]^{n-}$ (10 mM), $catH_2$ (20 mM), and $(nBu_4N)BF_4$ (0.10 M) in DMF generated by bulk electrolysis (at −600, −190, and +200 mV for $n = 3$, 2, and 1, respectively). [d] Solution of $K_3[Cr(cat)_3]$ (10 mM) in aqueous NaOH (0.10 M). [e] Determined by in situ spectroelectrochemistry. [f] Values determined by X-ray crystallography: 1.97–2.00 Å.[5b]



Scheme 1. Redox sequences of the electronic isomers formed during the oxidation of $[Cr(cat)_3]^{3-}$: a) as assumed by most authors[1,4] and b) as proposed in the current work.

The most important feature revealed by XAFS analyses was a significant decrease in the Cr–O bond length with decreasing n value (increasing oxidation state of the complex) in the $[Cr(cat)_3]^{n-}$ series ($n = 1$–3) in two independent sets of experiments at either 295 or 10 K, as determined by either MS or SS XAFS analyses (see Table 1 and the Supporting Information). This finding is inconsistent with the dominant opinion[1,4] that the oxidation of Cr^{III}–catecholato complexes is exclusively ligand-based (Scheme 1 a). If this was the case, the decreased donor ability of the *o*-semiquinonato(1−) versus catecholato(2−) ligands would lead to an increase in the Cr–O bond lengths.[3c,10] Decreases in the metal–oxygen bond lengths as the oxidation state of the metal ion increases, similar to those found in the $[Cr(cat)_3]^{n-}$ series ($n = 1$–3, Table 1), were observed in a series of crystallographically characterized catecholato complexes of V^{III}, V^{IV}, and V^{V}.[11] On the other hand, oxidation of $[Cr^{III}(tren)(3,6\text{-dtbcat})]^+$ to $[Cr^{III}(tren)(3,6\text{-dtbsq})]^{2+}$ (tren = tris(2-aminoethyl)amine, 3,6-dtbcat = 3,6-di-*tert*-butylcatecholato(2−), and 3,6-dtbsq = 3,6-di-*tert*-butylsemiquinonato(1−)) was accompanied by an increase in the average Cr–O bond length of 0.015 Å (determined by X-ray crystallography).[12] Thus, the results of MS XAFS analyses, together with the XANES data (see Figure 2 and the Supporting Information), strongly support the suggestion[3c] that the effective oxidation states of Cr in $[Cr(cat)_3]^{2-/1-}$ are higher than in $[Cr(cat)_3]^{3-}$, and that the former species can be considered as Cr^{IV} or Cr^{V} complexes with a significant degree of Cr–O π bonding.

Further oxidation of $[Cr(cat)_3]^-$ at $E = +600$ mV (in situ electrochemical XAS experiments, 295 K) led to an increase in the average Cr–O bond length from 1.939(2) to 1.958(2) Å (as determined by SS XAFS analysis of the first coordination shells, see the Supporting Information). Attempts to apply MS analysis to the XAFS spectrum of the reaction mixture, oxidized at $E = +600$ mV, led to poor fits ($R =$ ca. 25 %) and to unreasonably high Debye–Waller factor values (> 0.02 Å^2) for the second and further coordination shells. These features are in agreement with the oxidative degradation of $[Cr^{V}(cat)_3]^-$ at $E = +600$ mV, probably via unstable $[Cr^{III}(sq)_3]^0$ (sq = semiquinonato (1−)), since Cr^{VI} is too strong an oxidant to be stabilized by three catecholato(2−) ligands. Fast ligand exchange of $[Cr^{V}(cat)_3]^-$ with trace amounts of water in DMF at $E = +200$ mV in the absence of excess ligand leads to Cr^{V}–oxo complexes (as shown by EPR spectroscopy; see the Supporting Information). This observation is in agreement with the kinetically labile nature of all d^1 complexes of the first transition series with bidentate ligands (including Cr^{V}),[13] and contradicts the assignment of the former species as d^3 $[Cr^{III}(cat)(sq)_2]^-$ (Scheme 1 a),[1,4] which would be kinetically inert.[13] These observations are consistent with a sequence of redox reactions of Cr–catecholato complexes in Scheme 1 b.

The Cr^{V} complex $[Cr(cat)_3]^-$ is a rare example of a structurally characterized (by MS XAFS modeling, see the Supporting Information) Cr^{V} species without an oxo or nitrido ligand, and the Cr^{IV} complex $[Cr(cat)_3]^{2-}$ is a very rare example of a moderately stable and structurally characterized Cr^{IV} complex.[13] This is also the first example of the structural characterization of all three oxidation states (Cr^{III}–Cr^{V}) in complexes with the same coordination environment, and the first application of electrochemical XAS to the studies of redox reactions in metal complexes with non-innocent ligands. Such studies are not only of fundamental importance in assigning the oxidation states of the metal and the ligand, but are also essential in understanding the reactivities of these complexes, which has wide applications in bioinorganic chemistry and in the design of magnetic materials.[1–3]

Experimental Section

Full details of the used reagents, preparation of reaction solutions, instrumental techniques, and XAS data collection and analysis are given in the Supporting Information.

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Keywords: bioinorganic chemistry · chromium · electrochemistry · redox-active ligands · X-ray spectroscopy

[1] For a recent review, see C. G. Pierpont, *Coord. Chem. Rev.* **2001**, *219–221*, 415–433, and references therein.

[2] a) F. L. Meyskens, Jr., P. Farmer, J. P. Fruehauf, *Pigm. Cell Res.* **2001**, *14*, 148–154; b) W. R. Humphries (Rowett Research Services Ltd., UK), WO 9909050, **1999** [*Chem. Abstr.* **1999**, *130*, 205114].

[3] a) D. I. Pattison, P. A. Lay, M. J. Davies, *Inorg. Chem.* **2000**, *39*, 2729–2739; b) D. I. Pattison, M. J. Davies, A. Levina, N. E. Dixon, P. A. Lay, *Chem. Res. Toxicol.* **2001**, *14*, 500–510; c) D. I. Pattison, A. Levina, M. J. Davies, P. A. Lay, *Inorg. Chem.* **2001**, *40*, 214–217.

[4] C. G. Pierpont, *Inorg. Chem.* **2001**, *40*, 5727–5728.

[5] a) S. S. Isied, G. Kuo, K. N. Raymond, *J. Am. Chem. Soc.* **1976**, *98*, 1763–1767; b) K. N. Raymond, S. S. Isied, L. D. Brown, F. R. Fronczek, J. H. Nibert, *J. Am. Chem. Soc.* **1976**, *98*, 1767–1774.

[6] In the following text, the values of the redox potentials are given versus the Ag/AgCl reference electrode.

[7] a) S. R. Sofen, D. C. Ware, S. R. Cooper, K. N. Raymond, *Inorg. Chem.* **1979**, *18*, 234–239; b) H. H. Downs, R. M. Buchanan, C. G. Pierpont, *Inorg. Chem.* **1979**, *18*, 1736–1740.

[8] a) C. G. Pierpont, H. H. Downs, *J. Am. Chem. Soc.* **1976**, *98*, 4834–4838; b) S. P. Solodovnikov, K. Sarbasov, B. L. Tumansky, A. I. Prokof'ev, V. B. Vol'eva, N. N. Bubnov, M. I. Kabachnik, *Izv. Akad. Nauk SSSR Ser. Khim.* **1984**, *8*, 1789–1794; c) M. Branca, M. Fruianu, S. Sau, M. A. Zoroddu, *J. Inorg. Biochem.* **1996**, *62*, 223–230.

[9] A. M. Rich, R. S. Armstrong, P. J. Ellis, H. C. Freeman, P. A. Lay, *Inorg. Chem.* **1998**, *37*, 5743–5753.

[10] R. M. Wood, K. A. Abboud, R. C. Palenik, G. J. Palenik, *Inorg. Chem.* **2000**, *39*, 2065–2068.

[11] a) S. R. Cooper, Y. B. Koh, K. N. Raymond, *J. Am. Chem. Soc.* **1982**, *104*, 5092–5102; b) M. E. Cass, N. R. Gordon, C. G. Pierpont, *Inorg. Chem.* **1986**, *25*, 3962–3967.

[12] J. H. Rodriguez, D. E. Wheeler, J. K. McCusker, *J. Am. Chem. Soc.* **1998**, *120*, 12051–12068.

[13] For a review, see a) R. P. Farrell, P. A. Lay, *Comments Inorg. Chem.* **1992**, *13*, 133–175; b) R. Codd, C. T. Dillon, A. Levina, P. A. Lay, *Coord. Chem. Rev.* **2001**, *216–217*, 533–577.