

Synthesis, Characterization, and Reactivity of Catecholato Adducts of Iron(III) Triaza- and Tetraazamacrocyclic Complexes: Chemical Evidence of the Role of the Metal Ion in the Oxidative Cleavage

Andrea Dei,* Dante Gatteschi, and Luca Pardi

Department of Chemistry, University of Florence, Florence, Italy

Received December 2, 1991

Iron(III)–catecholato complexes of formulas $[\text{Fe}(\text{SS-CTH})(\text{Cat})]\text{Y}$, $[\text{Fe}(\text{Cyclam})(\text{Cat})]\text{Y}$, and $[\text{Fe}(\text{TACN})(\text{Cat})\text{Cl}]$ (SS-CTH = (SS)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; Cyclam = 1,4,8,11-tetraazacyclotetradecane; TACN = 1,4,7-triazacyclononane; Cat = DTBCat = 3,5-di-*tert*-butylcatechol; TCCat = tetrachlorocatechol; Y = PF_6 , ClO_4) have been synthesized. Magnetic measurements and EPR spectra indicate that all these complexes have to be formulated as high-spin iron(III) derivatives. Cyclic voltammetry experiments show that all of these complexes undergo electron transfer reactions involving either the metal ion (iron(III)–iron(II) couple) or the coordinated dioxolene ligand (catecholato to semiquinonato for all the derivatives and semiquinonato to quinone for DTBCat complexes). The electronic spectra of these complexes are dominated by LMCT transitions which were assigned with the help of the CD spectra obtained with the (–)SS-CTH derivatives. A striking correlation between the energy of the first LMCT electronic transitions and the free energy changes of the process $\text{Fe}^{\text{III}}(\text{Cat})\text{–Fe}^{\text{II}}(\text{SQ})$ (SQ = semiquinonato), calculated from electrochemical data, is observed. The tetraazamacrocyclic derivatives of DTBCat are inert toward dioxygen, whereas the triazamacrocyclic one shows an enhanced reactivity in polar solvents yielding either quinone and extradiol cleavage reaction products. The different chemical behavior of these complexes strongly supports the suggestion that the catechol cleavage reaction first requires the coordination of the dioxygen molecule to a coordinatively unsaturated iron(II) center. This result is believed to be relevant in order to understand the enzymatic reaction mechanism of dioxygenases.

Introduction

The catechol dioxygenases are metalloproteins catalyzing the oxidative cleavage of catechol or its derivatives with the incorporation of molecular dioxygen, yielding two different products, i.e. muconic acids and muconic semialdehydes.^{1–5} The enzymes catalyzing reactions giving rise to muconic acids are called intradiol dioxygenases, whereas those yielding muconic semialdehydes are extradioldioxygenases. The former are known to contain high-spin iron(III), whereas in the latter the metal center is in general high-spin iron(II). This seems one of the distinguishing features of the two families of metalloenzymes. In both cases evidence exists that the enzyme–substrate interaction occurs through the coordination of the bidentate dioxolene, thus yielding five-coordinate adducts.^{6–12} These findings represent a significant contribution for elucidating the nature of these enzymes, but important questions concerning the intimate mechanism of the catalytic degradation of the substrate remain open.¹³

As a general expectation, the different behavior of the two enzymes has to be related to the different oxidation state of the metal ion. Indeed it is believed that dioxygen binds iron(II) in

the extradioldioxygenases,^{10,11} whereas it is proposed to attack on the substrate rather than on the metal ion in the intradioldioxygenases.^{7,8,14,15} The proposals in practice are consistent with the well-known chemical affinity of dioxygen toward iron(II) and iron(III). However it is rather unclear why an extradiol cleavage mechanism should be determined by the formation of an iron–dioxygen adduct. On the other hand it seems obvious that the electronic properties of the iron(III) ion have a determining role in the substrate activation mechanism. If the role of the metal is limited, as often reported, to facilitate the ketonization of the coordinate catechol, it should be quite reasonable to expect that many other metal ions characterized by similar Lewis acidities could behave in an analogous fashion.

Significant progress for understanding the chemistry of these systems has been obtained by the use of simple model complexes.^{15–22} The discovery that several iron(III) complexes may act as models for mimicking enzyme reactions stimulated several efforts for determining the factors affecting reactivity. On the basis of a systematic investigation on a series of catechol adducts of several iron(III) complexes with tripodal ligands, Que and co-workers^{15,21,22} were able to successfully model the enzymatic intradiol cleavage reaction. Indeed they found a clear relationship between the reactivity of the adducts and the Lewis acidity of the iron(III) acceptors, monitored by the frequencies of the two catecholato-to-iron(III) charge-transfer absorptions

- (1) Que, L., Jr. *Adv. Inorg. Biochem.* **1983**, *5*, 167.
- (2) Que, L., Jr. *Coord. Chem. Rev.* **1983**, *50*, 73.
- (3) Que, L., Jr. In *Iron Carriers and Iron Proteins*; Loher, T. M., Ed.; VCH Publishers: New York, 1989; p 467.
- (4) Nozaki, M. *Top. Curr. Chem.* **1979**, *78*, 145.
- (5) Lipscomb, J. D.; Whittaker, J. W.; Arciero, D. M. In *Oxygenases and oxygen metabolism*; Nozaki, M., Yamamoto, S., Coon, M. J., Ernster, L., Estabrook, R. W., Eds.; Academic Press: New York, 1982; p 27.
- (6) Lauffer, R. B.; Que, L., Jr. *J. Am. Chem. Soc.* **1982**, *104*, 7324.
- (7) Whittaker, J. W.; Lipscomb, J. D. *J. Biol. Chem.* **1984**, *259*, 4487.
- (8) Orville, A. M.; Lipscomb, J. D. *J. Biol. Chem.* **1989**, *264*, 8791.
- (9) True, A. E.; Orville, A. M.; Pearce, L. L.; Lipscomb, J. D.; Que, L., Jr. *Biochemistry* **1990**, *29*, 10847.
- (10) Arciero, D. M.; Orville, A. M.; Lipscomb, J. D. *J. Biol. Chem.* **1985**, *260*, 14035.
- (11) Arciero, D. M.; Lipscomb, J. D. *J. Biol. Chem.* **1986**, *261*, 2170.
- (12) Mabrouk, P. A.; Orville, A. M.; Lipscomb, J. D.; Solomon, E. I. *J. Am. Chem. Soc.* **1991**, *113*, 4053.
- (13) Broderick, J. B.; O'Halloran, T. V. *Biochemistry* **1991**, *30*, 7349.

- (14) Que, L., Jr.; Lipscomb, J. D.; Munck, E.; Wood, J. M. *Biochim. Biophys. Acta* **1977**, *485*, 60.
- (15) Cox, D. D.; Que, L., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 8085.
- (16) Weller, M. G.; Weser, U. *J. Am. Chem. Soc.* **1982**, *104*, 3752.
- (17) Weller, M. G.; Weser, U. *Inorg. Chim. Acta* **1985**, *107*, 243.
- (18) Funabiki, T.; Mizoguchi, A.; Sugimoto, T.; Tada, S.; Tsuji, M.; Sakamoto, H.; Yoshida, S. *J. Am. Chem. Soc.* **1986**, *108*, 2921.
- (19) Funabiki, T.; Konishi, T.; Kobayashi, S.; Mizoguchi, A.; Takano, M.; Yoshida, S. *Chem. Lett.* **1987**, 719.
- (20) Que, L., Jr.; Kolanczyk, R. C.; White, L. S. *J. Am. Chem. Soc.* **1987**, *109*, 5373.
- (21) Cox, D. D.; Benkovic, S. J.; Bloom, L. M.; Bradley, F. C.; Nelson, M. J.; Que, L., Jr.; Wallick, D. E. *J. Am. Chem. Soc.* **1988**, *110*, 2026.
- (22) Jang, H. G.; Cox, D. D.; Que, L., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 9200.

occurring in the visible region. The authors found that on diminishing the energy gap between the ligand and metal orbitals, an increase of the oxygenation rates as well as an increase of yields and specificity of the cleaved products is observed. These experimental results correlate well with an NMR investigation showing how the increased reactivity of a given iron(III)-catecholato adduct is strictly related to the semiquinonato character of the coordinated ligand.^{15,22}

In this frame we think that the following results may provide new perspectives about this problem. In this paper we wish to report and discuss the synthesis, the characterization and the reactivity of the di-*tert*-butyl-catecholato (DTBCat) monoadducts on an iron(III)-triazamacrocyclic and two iron(III)-tetraazamacrocyclic acceptors. The triazamacrocyclic is 1,4,7-triazacyclononane, and the tetraazamacrocyclics are 1,4,8,11-tetraazacyclotetradecane (cyclam) and (*SS*)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (*SS*-CTH). The optical activity of the latter ligand allowed us to record the circular dichroism spectra in addition to the electronic spectra. In a previous work we have shown how this technique can be useful in order to elucidate the electronic properties of metal-dioxolene moieties.²³ For comparison the tetrachlorocatecholato (TCCat) monoadducts of the same iron(III) macrocycles complexes were synthesized and characterized. The chemical and physical properties of the compounds reported here provide a useful basis of data to be considered in order to elucidate the mechanism of substrate activation in the enzymatic processes according to the model developed by Que and co-workers.^{15,22}

Experimental Section

Materials. 3,4,5,6-Tetrachlorobenzoquinone (TCQ), 3,5-di-*tert*-butyl-*o*-quinone (DTBQ), 3,5-di-*tert*-butylcatechol (DTBCatH₂), 1,4,7-triazacyclononane (TACN), and 1,4,8,11-tetraazacyclotetradecane (cyclam) were used as received (Aldrich). The tetraazamacrocyclic (-)*SS*-CTH^{23,24} and the complexes *cis*-Fe(cyclam)Cl₃²⁵ and Fe(TACN)Cl₃²⁶ were prepared according to literature methods.

Fe(*SS*-CTH)Cl₂. A 5-mmol amount of FeCl₂·4H₂O was gently refluxed for 0.5 h under nitrogen atmosphere in 30 mL of a dimethylformamide-triethyl orthoformate 2/1 mixture. The resulting solution was added to a warm dimethylformamide solution (30 mL) of *SS*-CTH (6 mmol). Light blue-green crystals separated on cooling. The solid product was filtered out on a sintered glass frit and washed with ethanol-diethyl ether mixtures and then with diethyl ether, before being dried in a stream of nitrogen. Because of its extreme sensitivity toward dioxygen, this compound was prepared immediately before the use.

Fe(*SS*-CTH)(TCCat)PF₆. A solution of TCQ (1 mmol) in methanol or ethanol (20 mL) was added under nitrogen atmosphere to a suspension of Fe(*SS*-CTH)Cl₂ (1 mmol) in the same solvent (30 mL). The resulting mixture was gently heated for 0.5 h and then filtered. The addition of a saturated aqueous solution of KPF₆ yielded a microcrystalline product, which was filtered out, washed with a methanol-water mixture and diethyl ether, and then recrystallized from dichloromethane-pentane. Yield: 40–45%. (Anal. Found: C, 36.13; H, 5.14; N, 7.44. Calcd for C₂₂H₃₆Cl₄F₆FeN₄O₂P: C, 36.13; H, 4.96; N, 7.66.)

Fe(*SS*-CTH)(DTBCat)PF₆. This compound was prepared in a similar fashion using DTBQ instead of TCQ. (Yield: 36–40%.) Higher yields were obtained with the following procedure. Fe(*SS*-CTH)Cl₂ (2 mmol) was suspended in a deaerated solution of DTBCatH₂ (2 mmol) in methanol (30 mL), and then 4 mmol of solid NaOH was added. The suspension was gently warmed and stirred for 1 h under nitrogen atmosphere and stirred in the air for 0.5 h. The addition of a saturated aqueous solution of KPF₆ yielded a microcrystalline violet product, which was washed with water and recrystallized from dichloromethane-pentane mixture. Yield: 81–89%. (Anal. Found: C, 51.16; H, 8.08; N, 7.78. Calcd for C₃₀H₅₆F₆FeN₄O₂P: C, 51.06; H, 7.99; N, 7.94.)

[Fe(cyclam)(Cat)]Y (Cat = DTBCat, TCCat; Y = ClO₄, PF₆). *cis*-Fe(cyclam)Cl₃ (1 mmol) was suspended in a deaerated solution of the appropriate catechol (1 mmol) in methanol (30 mL). Sodium hydroxide (2 mmol) was added as solid, and the suspension was stirred under nitrogen for 1 h at 40 °C. The blue solutions were filtered and then mixed with an aqueous solution of NaClO₄ or KPF₆ until cloudiness. Dark microcrystalline materials were collected after 2 h and then recrystallized from dichloromethane/pentane or methanol/water mixtures. Yield: 80–90%. (Anal. (i) Found for the Fe(cyclam)(DTBCat)ClO₄·CH₂Cl₂ derivative: C, 45.28; H, 7.12; N, 8.27. Calcd for C₂₅H₄₆Cl₃FeN₄O₆: C, 45.39; H, 7.02; N, 8.47. (ii) Found for Fe(cyclam)(TCCat)PF₆: C, 30.08; H, 3.82; N, 8.34. Calcd for C₁₆H₂₄Cl₄F₆FeN₄O₂P: C, 29.70; H, 3.74; N, 8.66.)

Fe(TACN)(DTBCat)Cl·H₂O. Fe(TACN)Cl₃ (1 mmol) was suspended in a deaerated solution of 3,5-di-*tert*-butylcatechol in 30 mL of methanol. Triethylamine (0.5 mL) was then added, and the resulting solution was gently warmed for 0.5 h under a stream of nitrogen and then concentrated under vacuum until a microcrystalline material began to appear. It was filtered on a sintered glass funnel, washed with water, and then recrystallized under nitrogen from dichloromethane-pentane mixtures. Yield: 40–45%. (Anal. Found: C, 52.75; H, 8.21; N, 8.91. Calcd for C₂₀H₃₇ClFeN₃O₃: C, 52.35; H, 8.13; N, 9.16.)

Fe(TACN)(TCCat)Cl. Fe(TACN)Cl₃ (1 mmol) was suspended in a solution of H₂TCCat (1 mmol) in ethanol (40 mL). Triethylamine (0.5 mL) was added, and the resulting blue-violet solution was stirred at room temperature for 1 h. A violet microcrystalline material was obtained. It was filtered out, washed with ethanol, and then recrystallized from acetonitrile-ethanol mixtures. Yield: 46%. The same derivative can be obtained in lower yield from Fe(TACN)Cl₂ and TCQ in ethanol under inert atmosphere. (Anal. Found: C, 30.91; H, 3.33; N, 8.82. Calcd for C₁₂H₁₅Cl₅FeN₃O₂: C, 30.90; H, 3.24; N, 9.01.)

Physical Measurements. Polycrystalline powder EPR spectra were recorded with a Bruker ER200 spectrometer working at X-band frequency. Electronic spectra were recorded in the range 5000–40 000 cm⁻¹ on a Perkin-Elmer Lambda 6 spectrophotometer. The circular dichroism spectra were carried out by using a Jasco J-500 C spectropolarimeter in the range 10 000–40 000 cm⁻¹. The infrared spectra were recorded on a Perkin-Elmer 283 spectrophotometer. Proton NMR spectra were recorded on a Varian VXR 300 spectrometer operating at 299.945 MHz. Chemical shifts are relative to tetramethylsilane as an external reference or calibrated against the solvent as reference signal. The electrochemical analysis by cyclic voltammetry was carried out by using an electrochemical unit (Amel Model 553 potentiostat equipped with Amel 863, 560/A, and 568 elements and an Amel 731 integrator) and a classical three-electrode cell. The working electrode was a platinum microsphere, the reference electrode was a platinum disk, and the reference electrode was a calomel electrode in aqueous saturated KCl (SCE). Before each experiment the solution was carefully deaerated with a nitrogen flow. All potentials here reported are referenced against ferrocenium/ferrocene (Fc⁺/Fc). Under our experimental conditions the couple Fc⁺/Fc lies at +0.345 V vs SCE in acetonitrile with 0.1 M NBu₄PF₆.

Variable magnetic susceptibility measurements data were measured by using a fully automatized Aztec DSM5 susceptometer equipped with an Oxford CF1200S continuous flow cryostat and a Bruker B-E15 electromagnet. The apparatus was calibrated by measuring the magnetic susceptibilities of a pure sample of manganese Tutton salt at several temperatures between 4.2 and 300 K. Diamagnetic corrections were estimated from Pascal's constants.

Results

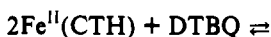
Synthesis and Characterization. Iron(III) complexes containing a single chelated catecholato dianion, according to the general formulas Fe(L)(Cat)Y (L = *SS*-CTH, cyclam; Cat = DTBCat, TCCat; Y = ClO₄, PF₆) and Fe(TACN)(Cat)Cl, were obtained in three different ways: (i) by the reaction of the iron(III)-macrocyclic derivative with the appropriate catechol in basic medium; (ii) by the aerial oxidation of a previously formed catecholato adduct of an iron(II)-macrocyclic species; (iii) by the oxidative addition of the appropriate quinone to the iron(II)-macrocyclic complex.

The choice of the two tetraazamacrocyclics as coligands was suggested by the ability of the ligands to adopt a folded

- (23) Benelli, C.; Dei, A.; Gatteschi, D.; Pardi, L. *Inorg. Chem.* **1989**, *28*, 1476.
 (24) Ito, H.; Fujita, J.; Toriumi, K.; Ito, T. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 298.
 (25) Chan, P.-K.; Poon, C.-K. *J. Chem. Soc., Dalton Trans.* **1976**, 858.
 (26) Wiegardt, K.; Pohl, K.; Gebert, W. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 727.

configuration in a pseudooctahedral coordination polyhedron²⁷ as well by the expected inertness of the iron-macrocycle complexes toward dissociation. The former expectation was verified as observed for other 3d metal ions,²⁸⁻³¹ but not the latter. Indeed macrocycle displacement reactions were observed using dioxolene/iron ratios larger than 1 and this was found a significant complication for isolating pure reaction products. Methods i and ii were found to be very efficient provided that stoichiometric amounts of catechol were used. It is particularly important to point out that the $[\text{Fe}(\text{L})(\text{DTBCat})]^+$ species are stable toward aerial oxidation whereas $\text{Fe}(\text{TACN})(\text{DTBCat})\text{Cl}$ is not. As it will be discussed below, this experimental aspect is believed to be relevant in order to formulate an hypothesis on the reaction mechanism of iron(III)-catecholato adducts with molecular dioxygen.

Method iii was attempted with the purpose of obtaining iron(III)-semiquinonato derivatives. The oxidative addition of the quinone to the iron(II)-macrocycle derivatives moiety should in principle yield an iron(III)-semiquinonato adduct as a result of a metal to ligand one electron transfer process. Since we obtained a catecholato derivative, it is apparent that further reduction processes occur. This second reduction process of the dioxolene ligand may occur by reaction with the alcoholic medium, and it may be justified by the strong oxidizing power of the iron(III)-semiquinonato species. The possibility that the stoichiometry for the formation of the catecholato complex from the oxidative addition might be



should be also considered. The observed reaction yields seem consistent with this mechanism. However it should be pointed out that semiquinonato and not catecholato adducts are obtained when DTBQ reacts with chromium(II)- or cobalt(II)-tetraazamacrocyclic moieties.^{29,30} In addition Schiff base iron(III)-semiquinonato complexes have been obtained following the same procedure.^{32,33} On the other hand we found that when the oxidative addition involves the $\text{Fe}(\text{TACN})^{2+}$ moiety, only catecholato derivatives are obtained in very low yield. Electrochemical experiments (see below) indicate that the $\text{Fe}(\text{TACN})(\text{DTBSQ})\text{Cl}^+$ species is not stable.

In a similar way solid compounds containing $[\text{Fe}(\text{CTH})(\text{TCCat})]^+$ or $\text{Fe}(\text{TACN})(\text{TCCat})\text{Cl}$ are obtained when TCQ is allowed to react with iron(II)-macrocycle substrate. In this case the failure to isolate semiquinonato complexes can be explained with the very strong oxidizing properties of these complexes, as well as their high reactivity toward nucleophilic agents.

The formulation of these derivatives as iron(III)-catecholato adducts follows from magnetic susceptibility measurements. All these complexes are characterized by effective magnetic moments in the range 5.95–6.1 μ_B (Table I), which are independent of temperature in the range 297–77 K. The observed values are in agreement with a $S = 5/2$ ground state, consistent with the presence of iron(III)-catecholato derivatives. On the basis of charge and stoichiometry considerations, an alternative formulation of the products as iron(II)-semiquinonato derivatives could also be possible. However the observed magnetic moments would require a strong ferromagnetic coupling between the two para-

Table I. Magnetic Data for $\text{FeL}(\text{Cat})\text{PF}_6$ (L = SS-CTH, Cyclam) and $\text{Fe}(\text{TACN})(\text{Cat})\text{Cl}$

compd	$\mu_{\text{eff}} (\mu_B)^a$	compd	$\mu_{\text{eff}} (\mu_B)^a$
$\text{Fe}(\text{SS-CTH})(\text{DTBCat})\text{PF}_6$	6.01	$\text{Fe}(\text{cyclam})(\text{TCCat})\text{PF}_6$	5.95
$\text{Fe}(\text{SS-CTH})(\text{TCCat})\text{PF}_6$	5.91	$\text{Fe}(\text{TACN})(\text{DTBCat})\text{Cl}$	5.94
$\text{Fe}(\text{cyclam})(\text{DTBCat})\text{PF}_6$	5.91	$\text{Fe}(\text{TACN})(\text{TCCat})\text{Cl}$	6.02

^a $T = 295$ K.

Chart I

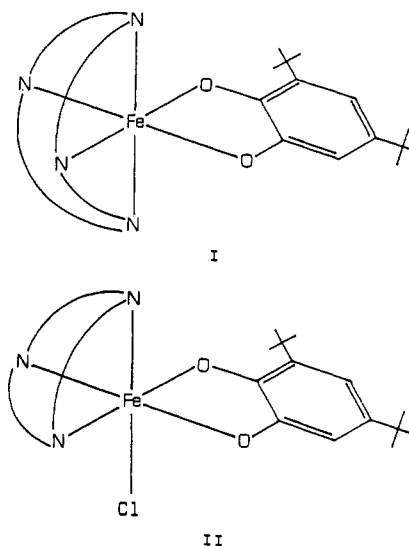


Table II. Electrochemical Potentials (V) of the $\text{Fe}(\text{L})(\text{Cat})^{n+}$ Complexes in Acetonitrile with 0.1 M $\text{NBu}_4\text{PF}_6^{a-c}$

compd	+1/0	+2/+1	+3/+2
$\text{Fe}(\text{SS-CTH})(\text{DTBCat})\text{PF}_6$	-1.21 (80)	0.07 (75)	0.95 i
$\text{Fe}(\text{cyclam})(\text{DTBCat})\text{PF}_6$	-1.33 (92)	-0.11 (71)	0.90 i
$\text{Fe}(\text{TACN})(\text{DTBCat})\text{Cl}$	-1.23 ^d	-0.10 i	
$\text{Fe}(\text{SS-CTH})(\text{TCCat})\text{PF}_6$	-0.81 (86)	0.62 i	
$\text{Fe}(\text{cyclam})(\text{TCCat})\text{PF}_6$	-0.90 (88)	0.47 i	
$\text{Fe}(\text{TACN})(\text{TCCat})\text{Cl}$	-0.91 (93)	0.49 i	

^a All potentials are referenced to the ferrocenium/ferrocene couple. The potentials are the average anodic and cathodic peak potentials in cyclic voltammograms recorded at 100 mV s^{-1} . i = irreversible process. ^b At 25 °C for ca. 10^{-3} M solutions. ^c E (mV) in parentheses. ^d $E_{\text{ox}} = -1.05$, $E_{\text{red}} = -1.40$.

magnetic centers, determined by the orthogonality of the magnetic orbitals.³⁴ This is highly improbable given the $t_{2g}^4e_g^2$ electronic configuration of the iron(II) ion in pseudooctahedral symmetry, which on the contrary leads to the expectation that an iron(II)-semiquinonato adduct should be characterized by a quartet ground state. Therefore this alternative should be discarded.

The infrared spectra of $\text{Fe}(\text{SS-CTH})(\text{cat})\text{PF}_6$ are virtually superimposable with those of the chromium(III), cobalt(III), and rhodium(III) analogues.^{29,30,35} Throughout this work we assume that all the $[\text{Fe}(\text{L})\text{Cat}]^+$ complexes contain six-coordinate iron(III) complexes, the tetradentate macrocycle occupying four nonconsecutive coordination sites and the catecholato dianion acting as a bidentate ligand according to structure I in Chart I, whereas the $[\text{Fe}(\text{TACN})(\text{Cat})\text{Cl}]$ complexes are assumed to exhibit the coordination geometry shown in structure II of Chart I.

Electrochemistry. The cyclic voltammograms of deaerated acetonitrile solutions of $[\text{Fe}(\text{SS-CTH})(\text{DTBCat})]\text{PF}_6$ display one redox process at -1.21 V and two subsequent oxidation processes at +0.07 and +0.95 V vs ferrocenium/ferrocene reference (Fc^+/Fc) (Table II). The first two couples exhibit the features of reversible electron transfer processes, the peak to peak separation

(27) Curtis, N. F.; Swann, D. N.; Waters, D. N. *J. Chem. Soc., Dalton Trans.* 1973, 1963.

(28) Benelli, C.; Dei, A.; Gatteschi, D.; Pardi, L. *Inorg. Chem.* 1988, 27, 2831.

(29) Benelli, C.; Dei, A.; Gatteschi, D.; Pardi, L. *Inorg. Chim. Acta* 1989, 163, 99.

(30) Benelli, C.; Dei, A.; Gatteschi, D.; Gudel, H.; Pardi, L. *Inorg. Chem.* 1989, 28, 3089.

(31) Unpublished results of this laboratory.

(32) Kessel, S. L.; Emberson, R. M.; Debrunner, P. G.; Hendrickson, D. N. *Inorg. Chem.* 1980, 19, 1170.

(33) Tuchagues, J. P. M.; Hendrickson, D. N. *Inorg. Chem.* 1983, 21, 2545.

(34) Dei, A.; Gatteschi, D. *Inorg. Chim. Acta* 1992, 200, 813.

(35) Dei, A.; Pardi, L. *Inorg. Chim. Acta* 1991, 181, 3.

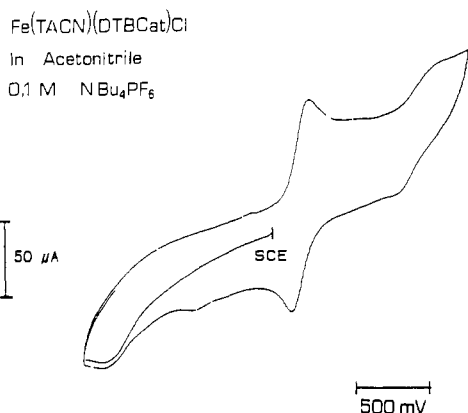
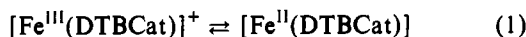


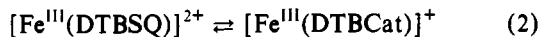
Figure 1. Cyclic voltammogram of a deaerated acetonitrile solution of Fe(TACN)(DTBCat)Cl. Scan rate: 0.2 V s⁻¹.

approaching the value of 60 mV at low scan rates. Coulometric experiments indicate that these reactions are mono-electronic. The most positive couple is not reversible and the cyclic voltammogram of the solution after electrolysis at +1.1 V vs Fc⁺/Fc shows the wave features characteristic of the free quinone ligand.

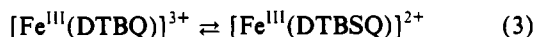
The electrochemical behavior of this complex is quite similar to that observed for other catecholato adducts of transition metal ions and in particular to those observed for the chromium(III) and cobalt(III) M(CTH)(DTBCat)⁺ analogues.^{22,23} On this basis we assign the couple occurring at -1.21 V to the metal-centered electron transfer process



(the macrocyclic ligand is omitted for sake of simplicity), whereas the couples occurring at positive potentials are associated with electron transfer processes involving the dioxolene ligand, i.e.



and



involving the formation of a thermodynamically stable semiquinonato adduct and an unstable quinone adduct. It should be mentioned that the redox potential characterizing the process (2) is about 0.2 V more positive than those observed for cobalt(III) and chromium(III) derivatives.

The cyclic voltammograms of solutions containing the [Fe(cyclam)(DTBCat)]⁺ species are very similar, showing two reversible one-electron processes at -1.33 and -0.11 V vs Fc⁺/Fc and a nonreversible one at ca +0.9 V. The assignment of these redox processes is the same as discussed above.

The electrochemical behavior of Fe(TACN)(DTBCat)Cl is rather different from that exhibited by the tetraazamacrocyclic derivatives. The metal-centered redox process is not reversible ($E_{\text{red}} = -1.40$, $E_{\text{ox}} = -1.05$ V vs Fc⁺/Fc), and the semiquinonato species, which can be electrogenerated at potentials higher than -0.10 V by oxidation of the catecholato derivative, is not stable and rapidly decomposes. This is evidenced by the presence of the reduction waves associated to the free DTBQ in the reverse scan of the cyclic voltammogram (Figure 1).

The electrochemical behavior of the TCCat derivatives is quite different from that of the DTBCat ones. The Fe(SS-CTH)(TCCat)⁺ complex shows a reversible one electron transfer process at -0.81 V vs Fc⁺/Fc, which can be reasonably attributed to the metal-centered redox process Fe^{III}(TCCat)⁺/Fe^{II}(TCCat). A further oxidation process occurs at ca. +0.6 V with apparent decomposition of the reacting species. The cyclam and the TACN derivatives show in a similar fashion a reversible process at -0.90 and -0.91 V and irreversible processes at +0.47 and +0.49 V vs

Table III. Electronic Spectral Data for FeL(diox)²⁺ (L = SS-CTH, Cyclam) and Fe(TACN)(Cat)Cl in Acetonitrile^a

Fe(SS-CTH)(DTBCat)PF ₆	12 000 (3.41), 18 900 (3.24), 29 800 sh, 34 700 (3.83) (CD spectrum: ^b 12 300 sh, 18 600 (-1.98) 29 500 sh, 31 500 (3.9), 33 400 sh, 38 500 (1.74))
Fe(cyclam)(DTBCat)PF ₆	13 000 (3.43), 20 000 (3.28), 30 000 (3.30), 34 700 (3.83)
Fe(SS-CTH)(TCCat)PF ₆	14 100 (3.42), 20 200 (3.22), 27 500 sh, 32 900 (3.78) (CD spectrum: ^b 14 800 (-0.95), 21 000 (-1.06), 31 500 (3.9), 36 300 (4.24))
Fe(Cyclam)(TCCat)PF ₆	14 950 (3.64), 20 600 (3.29), 27 500 sh, 32 900 32 900 (3.68), 34 100 sh
Fe(TACN)(DTBCat)Cl	14 400 (3.38), 22 500 (3.21), 29 000 sh, 34 300 (3.76)
Fe(TACN)(TCCat)Cl	14 900 (3.48), 22 600 (3.34), 27 400 sh, 32 800 (3.69)

^a log ε in parentheses; sh = shoulder. ^b Δε in parentheses.

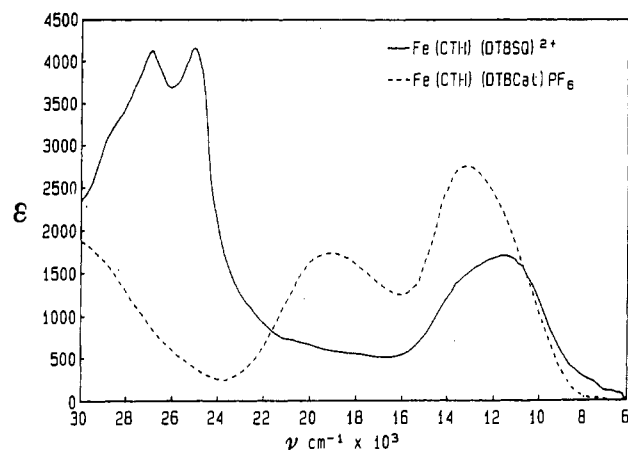


Figure 2. Electronic spectra of Fe(SS-CTH)(DTBCat)²⁺ (---) and Fe(CTH)(DTBSQ)²⁺ (—) in acetonitrile solution with 0.1 M NBu₄PF₆.

Fc⁺/Fc, respectively. The cyclic voltammograms after exhaustive electrolysis of the solutions of these compounds at +0.8 and +0.65 V vs Fc⁺/Fc, respectively, evidence the decomposition of the electrogenerated species. Electronic spectroscopy and TLC on alumina provide evidence that the oxidation products are TCQ and hexachloro-2,3-oxanthrenequinone, resulting from the nucleophilic reaction between two dioxolene ligands.^{32,36} This behavior is quite different from those we reported for the chromium(III) and cobalt(III) tetrachlorocatecholato analogues.^{29,30} Both these derivatives show reversible one electron transfer processes at +0.47 V vs Fc⁺/Fc, which on the basis of spectral evidence has to be assigned to the tetrachlorosemiquinonato/tetrachlorocatecholato couple. The full reversibility and stability of the electrogenerated species can probably be attributed to the inertness toward metal-ligand dissociation characterizing the complexes of these metal ions.

Electronic Spectra and CD Spectra. The spectral parameters of the catecholato complexes, as well as those of the one-electron exhaustively oxidized acetonitrile solutions of the DTBCat derivatives, are reported in Table III. The electronic and CD spectra of the chromophores [Fe(SS-CTH)(Cat)]⁺ (Cat = DTBCat, TCCat) are shown in Figures 2 and 3, respectively.

Catecholato Complexes. The spectra of the six catecholato derivatives are strictly similar to each other. They are characterized by two intense absorption bands in the range 12 000–15 300 cm⁻¹ and 18 900–22 600 cm⁻¹, respectively, and by a pattern of more intense absorptions in the UV region. As shown by comparison with the spectra of the [Zn(SS-CTH)(Cat)]

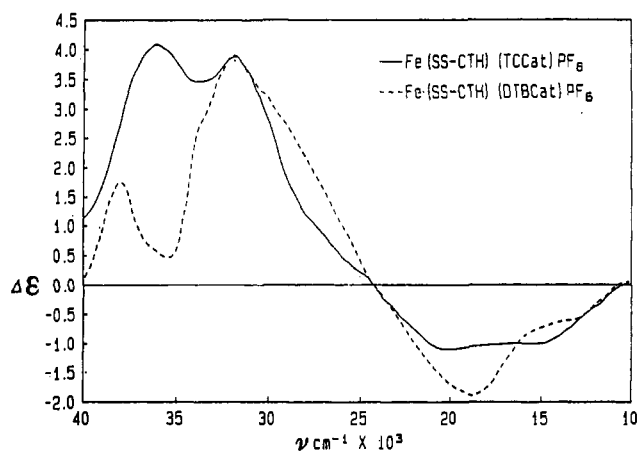


Figure 3. CD spectra of $\text{Fe}(\text{SS-CTH})(\text{DTBCat})^+$ (---) and $\text{Fe}(\text{SS-CTH})(\text{TCCat})^+$ (—) chromophores in acetonitrile.

derivatives, which show bands only in the UV region (assigned to the internal transition of the dioxolene ligand),²³ the bands appearing in the visible region of these iron(III)-catecholato complexes must be charge transfer in nature. On the basis of the relative reducing power of the two catecholato ligands, the observed spectral shifts are consistent with a LMCT character of the transitions, as previously suggested.^{21,37,38}

As a further support to this assignment these complexes exhibit a significant negative solvatochromism, i.e. the CT bands are blue shifted in polar solvents with respect to nonpolar ones. This means that the moment of the electronic transition lies antiparallel to the ground state dipole moment of the chromophore.³⁹⁻⁴²

The transition moments of the two LMCT bands of these iron(III)-catecholato chromophores are similar, the higher energy one being broader than the other one. This rules out the possibility that the transitions involve the HOMO of the dioxolene ligand and both the t_{2g} and e_g orbitals of the metal ion, since they should be characterized by different transition moments. A similar conclusion was reached by Cox et al.²¹ from resonance Raman studies of iron(III)-catecholato complexes. In fact we observed that for the $\text{M}(\text{CTH})(\text{cat})^+$ chromophores ($\text{M} = \text{Co}(\text{III}), \text{Rh}(\text{III})$) the LMCT transitions, which involve the HOMO of the catecholato and the e_g orbitals of the metal ions, are characterized by small intensities ($\epsilon = 200$).^{29,35}

The CD spectra of the two SS-CTH derivatives indicate that the two bands are characterized by different dissymmetry factors ($\Delta\epsilon/\epsilon$). The band at ca. $18\,900\text{ cm}^{-1}$ in the spectrum of the $[\text{Fe}(\text{SS-CTH})(\text{DTBCat})]^+$ is characterized by a dissymmetry factor five times larger than the band at $12\,000\text{ cm}^{-1}$, thus indicating a different dipole allowedness for the two transitions.

Molecular orbital calculations (CNDO/2) show that the highest occupied molecular orbital of the catecholato dianion has π^* character $3b_1$ in C_{2v} symmetry. The nearest occupied molecular orbitals behave as $2a_2, 9a_1,$ and $7b_2$, the first being π^* in character and the others being orbitals lying in the dioxolene plane which may act as σ donors. The metal d orbitals span $a_1(x^2 - y^2), a_1(z^2), a_2(xy), b_1(xz),$ and $b_2(yz)$ representations in C_{2v} (the yz plane is assumed to contain the plane of the dioxolene). The $9a_1$ and $7b_2$ orbitals of the dioxolene ligand overlap σ with the z^2 and yz metal orbitals whereas $3b_1$ and $2a_2$ orbitals overlap π with the xz orbital. Therefore two intense CT transitions involving the two $\pi^* 3b_1$ and $2a_2$ and the xz metal orbital are expected, since

they involve in plane orbitals and are electric dipole allowed, but one of them, namely the $3b_1(\pi^*)-b_1(xz)$, is magnetic dipole forbidden and therefore is expected to be weak in the CD spectrum. Furthermore four transitions involving the $9a_1$ and $7b_2$ ligand orbitals and the z^2 and yz metal orbitals are expected, two of them being magnetic dipole forbidden. All the other possible transitions are expected to be weak since they involve in-plane and out-of-plane pairs of orbitals.

The problem is to determine the energy pattern of the electronic levels of the dioxolene ligand. CNDO/2 calculations on the free ligand suggest the following order: $3b_1(\pi^*)(\text{HOMO}) > 9a_1(\sigma) > 2a_2(\pi^*) > 7b_2(\sigma)$, but the electronic and CD spectra of $\text{Zn}(\text{SS-CTH})(\text{SQ})^+$ ($\text{SQ} = \text{DTBSQ}, \text{TCSQ}$) can be interpreted with a different energy order, i.e. $3b_1 > 9a_1 > 7b_2 > 2a_2$.²³

On the basis of these considerations, the first allowed LMCT transition should be the $3b_1(\pi^*)-b_1(xz)$, which is electric dipole allowed and magnetic dipole forbidden. This prediction is consistent with the behavior of the lower energy transition in the electronic and CD spectra of the $\text{Fe}(\text{SS-CTH})(\text{Cat})^+$ chromophores and, furthermore, is consistent also with the negative solvatochromism characterizing this transition.

The LMCT transitions at $18\,900$ and $20\,200\text{ cm}^{-1}$ in the spectra of DTBCat and TCCat derivatives, respectively, cannot be assigned to charge transfer from the $3b_1(\pi^*)$ to the yz or z^2 orbitals, since these transitions are expected to be weak because of overlap orthogonality. On the other hand it cannot be assigned as well to $9a_1(\sigma)-b_1(xz)$ for the same reason or $9a_1(\sigma)-a_1(z^2)$, which is magnetic dipole forbidden, and $9a_1(\sigma)-b_2(yz)$ since this transition is expected to occur to higher energy. Therefore, it is suggested that in the coordinated catecholato the $2a_2(\pi^*)$ follows immediately the $3b_1(\text{HOMO})$, the $9a_1(\sigma)$ and the $7b_2(\sigma)$ orbitals being strongly stabilized by interaction with the metal ion. In this hypothesis this LMCT transition should be attributed to $2a_2(\pi^*)-b_1(xz)$, which is both electric and magnetic dipole allowed in agreement with the spectral data. Support for this assignment comes from the spectra of the $\text{Co}(\text{CTH})(\text{Cat})^+$ analogues, which show two subsequent weak LMCT bands in the visible region of the electronic spectrum.²⁹ Since the t_{2g} orbitals are fully occupied in the cobalt chromophores, the LMCT transitions involve ligand orbitals and the yz metal orbital and, as mentioned above, their low intensities indicate that the orbitals involved in the charge-transfer process are probably orthogonal.

Transitions involving the σ^* orbitals occur at higher energies but are more difficult to be assigned since they overlap with internal transitions of the catecholato ligand. The LMCT transition appearing as a shoulder at $27\,800\text{ cm}^{-1}$, but decreasing in intensity in the CD spectrum, could be consistent with the $9a_1(\sigma)-a_1(z^2)$ transition.

As a final remark, we wish to point out the different order of the energies of the ligand orbitals on passing from the catecholato dianion to the semiquinonato monoanion. This is probably due to the increasing $\pi^* \text{C}=\text{O}$ antibonding character of the HOMO which follows the removal of one electron from the catecholato dianion.

Semiquinonato Complexes. The electronic spectrum of the $\text{Fe}(\text{SS-CTH})(\text{DTBSQ})^{2+}$ chromophore is shown in Figure 2.

The intense absorption at $11\,400\text{ cm}^{-1}$ falls in the range expected for the $9a_1-3b_1$ transition of the semiquinonato ligand ($n-\pi^*$ in character).^{23,28,30} However its molar absorption coefficient is larger than those previously observed for this transition and therefore we suggest that it is due to the overlap of the above transition with a CT transition. The lack of comparison with the spectra of other iron(III)-semiquinonato chromophores does not allow us to determine the MLCT or LMCT character of this band.

The bands appearing in the range $25\,000-28\,000\text{ cm}^{-1}$, by comparison with the spectrum of the $\text{Zn}(\text{SS-CTH})(\text{DTBSQ})^+$,²³ are also assigned to the overlap of an internal ligand transition

(37) Salama, S.; Stong, J. D.; Neilands, J. B.; Spiro, T. G. *Biochemistry* **1978**, *17*, 3781.

(38) Karpishin, T. B.; Gebhard, M. S.; Solomon, E. I.; Raymond, K. N. *J. Am. Chem. Soc.* **1991**, *113*, 2977.

(39) Lever, A. B. P. *Inorganic Electronic Spectroscopy*; Elsevier: Amsterdam, 1984; p 208.

(40) Dodsworth, E. S.; Lever, A. B. P. *Chem. Phys. Lett.* **1984**, *112*, 567.

(41) Saito, M.; Fujita, J.; Saito, K. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 863.

(42) Dodsworth, E. S.; Lever, A. B. P. *Inorg. Chem.* **1990**, *29*, 499.

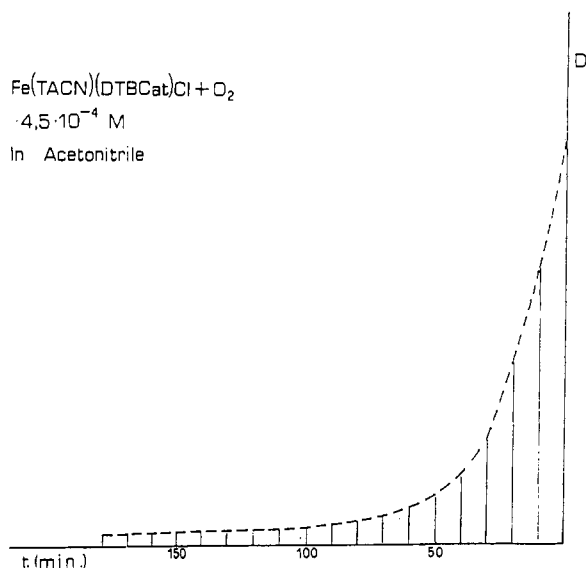


Figure 4. Time dependence of the optical density at 700 nm of an aerated acetonitrile solution of $\text{Fe}(\text{TACN})(\text{DTBCat})\text{Cl}$.

(i.e. $2a_2(\pi^*)-3b_1(\pi^*)(\text{SOMO})$) with CT transitions. A tentative assignment of these transitions cannot be made at this stage.

Reactivity toward Dioxygen. Previous investigations on the reactivity of several iron(III)-3,5-di-*tert*-butylcatecholato complexes have shown that these complexes easily react with aerial molecular dioxygen yielding either *o*-quinone and intradiol or extradiol reaction products as a result of the C–C cleavage of the catecholato ring.^{1–3,15–22} The reaction can be easily followed spectrophotometrically by monitoring the decrease of the intensity of the two LMCT electronic transitions in the visible region. As mentioned above, it has been experimentally found that the reaction rate increases on decreasing the energy of the LMCT transitions^{15,22} and the yield of the cleavage reaction is improved simultaneously.

$[\text{Fe}(\text{SS-CTH})(\text{DTBCat})]^+$ and $[\text{Fe}(\text{Cyclam})(\text{DTBCat})]^+$ are characterized by LMCT bands at very low energy, and therefore an enhanced reactivity was expected. However, as already shown in the description of the synthesis, these complexes can be synthesized and manipulated on the bench and the spectral properties of their solutions in acetonitrile or dimethylformamide are stable for a period of weeks.

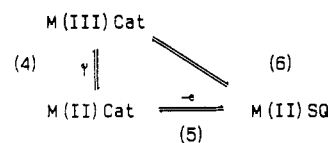
The complex $[\text{Fe}(\text{TACN})(\text{DTBCat})\text{Cl}]$ on the contrary shows an enhanced sensitivity toward aerial dioxygen and must be synthesized and manipulated under inert atmosphere. We found that the reaction in acetonitrile or dimethylformamide is virtually complete within 6 h (Figure 4) but in dichloromethane or chloroform is significantly slower and requires weeks. After workup of the reaction mixture,⁴³ we found that the reaction in acetonitrile yields DTBQ (65%), 3,5-bis(1,1-dimethylethyl)-2*H*-pyranone (30%), and 4,6-bis(1,1-dimethylethyl)-2*H*-pyranone (5%), the last two reaction products being due to the extradiol cleavage of the dioxolene ligand, but only DTBQ from chloroform. The different reactivity behavior in the two solvents is probably due to the different dissociative power of the two solvents. It should be pointed out that reaction products involving the intradiolic cleavage of the dioxolene were not detected.

Discussion

In the following we will first try to justify the observed LMCT transitions, given their relevance to the reactivity toward dioxygen,

(43) The reaction mixture was evaporated to dryness and twice extracted with *n*-pentane which was then removed under vacuum. The components of the obtained solid mixture were identified by following the procedure reported by Bianchini et al. (Bianchini, C.; Frediani, P.; Laschi, F.; Meli, A.; Vizza, F.; Zanello, P. *Inorg. Chem.* **1990**, *29*, 3402).

Scheme I



and also the similarity to biologically important iron siderophores.^{44–46} Second, we will discuss the origin of the reactivity of these complexes and compare it with the interpretation model of Que and co-workers.

One-electron oxidation of a metal(II)–catecholato complex may in principle yield either metal(III)–catecholato or metal(II)–semiquinonato as products, depending on the relative stability of the two different species. The latter quantity is determined by the difference between the redox potentials associated with the two different oxidation processes. Indeed following Scheme I, the sign of the free energy change associated with internal transfer equilibrium 6 will be determined by the difference of the free energy changes values associated to the equilibria 4 and 5.

For the present iron–dioxolene derivatives, iron(III)–catecholato complexes are formed and therefore the free energy change associated with equilibrium 6 is positive. The same result occurs for chromium³⁰ and cobalt,²⁹ whereas the reverse is true for nickel(II)^{23,28,47} and copper(II).⁴⁷ In a forthcoming paper we will show that in the case of manganese both species may be stabilized depending on the nature of the dioxolene ligand.³¹

The ΔG value associated with equilibrium 6 cannot be experimentally determined since only one of the two possible oxidation processes occurs in the practice. However we may estimate it since the experimental data observed for the whole family of $\text{M}(\text{CTH})(\text{diox})$ complexes suggest that the redox potential associated with equilibrium 5 (ligand-centered oxidation process) is roughly constant for metal ions characterized by the same oxidation state.^{23,28–31,35} Indeed it appears that the metal ion provides only an electrostatic potential inducing a positive shift of the semiquinonato–catecholato couple. For divalent metal ions we found that for the couples $\text{M}^{\text{II}}\text{L}(\text{SQ})/\text{M}^{\text{II}}\text{L}(\text{Cat})$ the redox potentials are ca. -0.9 and -0.3 V vs Fc^+/Fc for DTBCat and TCCat, respectively. If these values are combined with those observed for the couples $\text{Fe}^{\text{III}}\text{L}(\text{Cat})/\text{Fe}^{\text{II}}\text{L}(\text{Cat})$, i.e. the metal-centered redox process, we may estimate that the free energy values associated with equilibrium 6 are 0.3 eV for $\text{Fe}(\text{CTH})(\text{DTBCat})$, 0.4 eV for $\text{Fe}(\text{cyclam})(\text{DTBCat})$, 0.5 eV for $\text{Fe}(\text{CTH})(\text{TCCat})$, and 0.6 eV for $\text{Fe}(\text{cyclam})(\text{TCCat})$. The observed optical energies are 1.5 eV for $\text{Fe}(\text{CTH})(\text{DTBCat})$, 1.6 eV for $\text{Fe}(\text{cyclam})(\text{DTBCat})$, 1.8 eV for $\text{Fe}(\text{CTH})(\text{TCCat})$, and 1.9 eV for $\text{Fe}(\text{cyclam})(\text{TCCat})$. The comparison of the quantities calculated from the electrochemical data and those obtained from the electronic spectra stress the direct relationship existing between the energies of the first LMCT band and the free energy associated with equilibrium 6, as suggested by Cox and Que.¹⁵ This is not surprising since equilibrium 6 defines the energy of the transition between the electronic ground state and the first charge-transfer excited state in their respective equilibrium vibrational states (i.e. the $0-0'$ transition) and solvent equilibrium environment. The fact that the observed absorption energies are significantly larger than those calculated (1.2–1.3 eV as an average) can be explained by taking into account that (i) the electronic transitions do not correspond to the $0-0'$ transitions but to highly excited vibronic states of the upper electronic level, since the geometry

(44) Matzanke, B. F.; Miller-Matzanke, G.; Raymond, K. N. In *Iron Carriers and Iron Proteins*; Loehr, T. M., Ed.; Physical Bioinorganic Series; VCH Publishers: New York, 1989; pp 1–121.

(45) Raymond, K. N.; Carrano, C. J. *Acc. Chem. Res.* **1979**, *12*, 183.

(46) Raymond, K. N.; Miller, G.; Matzanke, B. F. *Top. Curr. Chem.* **1984**, *123*, 49.

(47) Benelli, C.; Dei, A.; Gatteschi, D.; Pardi, L. *Inorg. Chem.* **1990**, *29*, 3409.

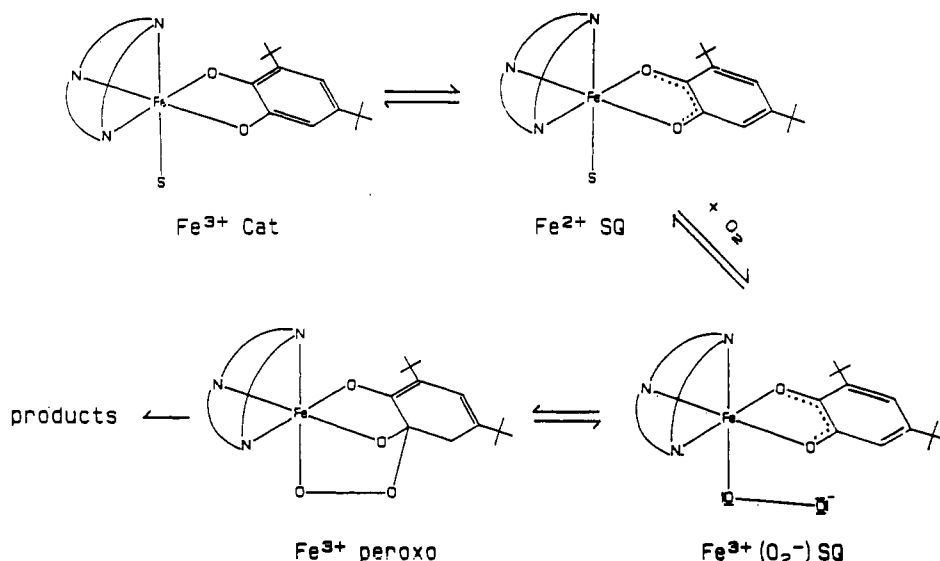


Figure 5. Proposed role of the metal ion in the catechol degradation reaction mechanism.

of the chromophore is expected to change significantly, (ii) the differences of the solvation energies between the ground and excited states are expected to be significant, as indicated by the strong solvatochromism exhibited by these chromophores, and, (iii) the energy separation between the ground sextet of Fe(III)-cat and the corresponding one of Fe(II)-sq is larger than the separation from the quartet state, which is expected to be the ground state of Fe(II)-sq, due to the antiferromagnetic coupling between iron(II) and the semiquinonate ligand.

These data therefore show how the energies characterizing the two electronic isomers Fe(III)-cat and Fe(II)-sq can be very close in some iron-catecholato derivatives, thus emphasizing the noninnocent character of the ligand. This is in full agreement with the suggestions of Que and co-workers:^{15,22} on decrease of the LMCT energy, equilibrium 6 shifts to the left, with a consequent increase of the semiquinonate character of the coordinated dioxolene, as further evidenced by isotropic shift data. This aspect cannot be neglected in suggesting any mechanistic proposal on the enzymatic reactivity.

The second important point deserving discussion concerns the reactivity properties of the iron(III)-catecholato derivatives we have synthesized. The experimental evidence indicates that the di-*tert*-butylcatecholato adducts of the tetraazamacrocycle complexes are in practice inert toward dioxygen, whereas the triazamacrocycle displays a high reactivity in polar solvents, like dimethylformamide or acetonitrile, but reacts very slowly in nonpolar solvents. This different behavior indicates that the reactivity should be presumably associated with the existence of a labile coordination site on the metal center. This is unlikely to occur for tetraazamacrocycle complexes, because of the inertness of the ligand toward dissociation, but it is relatively easy for Fe(TACN)(DTBCat)Cl, which contains a labile monodentate ligand in the coordination sphere. In agreement with this behavior, our results strongly point out the basic role of the metal ion as the center of the dioxygen attack suggesting iron(II)-semiquinonate rather than iron(III)-catecholato as the reacting species. In fact in the former the metal ion may act both as reducing center and as Lewis acid stabilizing the superoxo ligand, which in turn may react with the dioxolene radical. The electron transfer is facilitated by the fact that the energies of the Fe(III)-cat and Fe(II)-sq isomers are very close to each other,

as we showed above. Unfortunately it is quite difficult to provide direct evidence for this process. However the recently reported structures of Ni(L)(TCCat)(TCQ)⁴⁸ (L = 2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene) and Cu(TMEDA)(PhenCat)(PhenQ)⁴⁹ (TMEDA = *N,N,N',N'*-tetramethylethylenediamine; PhenCat = 9,10-phenanthrenediolate; PhenBQ = 9,10-phenanthrenequinone) provide interesting examples of how the charge distribution of a metal-catecholato acceptor is perturbed upon interaction with an electrophile. In both cases, although the catecholato and the quinone have the ideal geometry for a direct electron transfer, it is in practice the metal ion which acts as electron sink. According to this hypothesis, the intramolecular electron transfer could be the determining step of the metal substrate activation and the overall process should follow the mechanism sketched in Figure 5. The transient peroxo species is tentatively formulated in analogy to that recently isolated and characterized by Bianchini and co-workers as a product of the reaction of Ir(p₃)(DTBCat) with dioxygen,⁵⁰ but other formulations are also possible.

A further point worth of discussion concerns the nature of the reaction products. It is important to emphasize that, in addition to the quinone, extradiol cleavage products are observed as a result of the reaction of Fe(TACN)(DTBCat)Cl with dioxygen. This is the first example of a metal complex showing this peculiar reactivity, while all the iron(III)-catecholato derivatives reported so far mimic the enzymes reactions yielding intradiol cleavage products. The present data, therefore, seem to be consistent with the view that the formation of an iron-dioxygen adduct is a prerequisite for the catalytic degradation of the substrate affording extradiol cleavage products.

Acknowledgment. Thanks are expressed to Dr. Claudio Bianchini and Dr. Andrea Meli for helpful discussions. The financial support of the MURST and CNR is gratefully acknowledged.

- (48) Benelli, C.; Dei, A.; Gatteschi, D.; Pardi, L. *J. Am. Chem. Soc.* **1988**, *110*, 6897.
 (49) Speier, G.; Tisza, S.; Rockenbauer, A.; Boone, R. S.; Pierpont, C. G. *Inorg. Chem.* **1992**, *31*, 1017.
 (50) Barbaro, P.; Bianchini, C.; Mealli, C.; Meli, A. *J. Am. Chem. Soc.* **1991**, *113*, 3181.