24-methylenecholesterol (**6N**). In other words, this sponge is capable of de novo biosynthesis,[2] side-chain dealkylation (at C-24), and C-24 side-chain alkylation.

Experiments are under way to examine more precisely the course and scope of these dealkylations among sponge sterols.

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Internal Electron Transfer in a Quinone Adduct of a Nickel(II)–Catecholate Complex

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Quinoid molecules are known to form charge-transfer complexes where they behave either as donors or acceptors toward many organic molecules and to easily undergo redox processes.[1] In addition, they act as good ligands toward transition-metal ions.[2,3] Since the π electron levels of these molecules have energies comparable to 3d metal orbitals, transition-metal–quinoid adducts provide simulating perspectives for designing redox reagents characterized by peculiar reactivity properties. Recent studies aim at the elucidation of the role of quinoid molecules in naturally occurring reaction processes as well as in the synthesis of electron-transfer catalysts.[4-9]

Redox processes involving quinoid molecules and substrates often occur via formation of charge-transfer adducts, followed by electron transfer between the reactants. One may expect that a similar mechanism is operative when the quinoid molecule is coordinated to a metal ion, even if in this case the electron transfer may involve an electronic rearrangement within the metal quinoid adduct. Evidence exists that this mechanism is often operative, but an alternative reaction pathway must be considered, as the following results clearly show.

The Ni(TCCat) complex (L = 2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene; TCCat = tetrachlorocatecholate) was synthesized from the reaction between the five-coordinate $[NiL(OH)]_2(ClO_4)_2$[10] and tetrachlorocatechol. On the basis of the electronic spectra[11] and of magnetic measurements ($\mu_{eff} = 3.22$ μ_B) this compound may be formulated as a high spin five-coordinate nickel(II) catecholate adduct. We found that this compound reacts reversibly with tetrachloro-1,2-benzoquinone (TCQ) yielding a compound of formula "NiL(TCCat)(TCQ)". The reaction can be followed by the appearance in the electronic spectrum of an intense absorption band at 12 700 cm^{-1} (ϵ = 2000 l cm^{-1} mol^{-1}). "NiL(TCCat)(TCQ)" can be isolated as a solid owing to its insolubility.

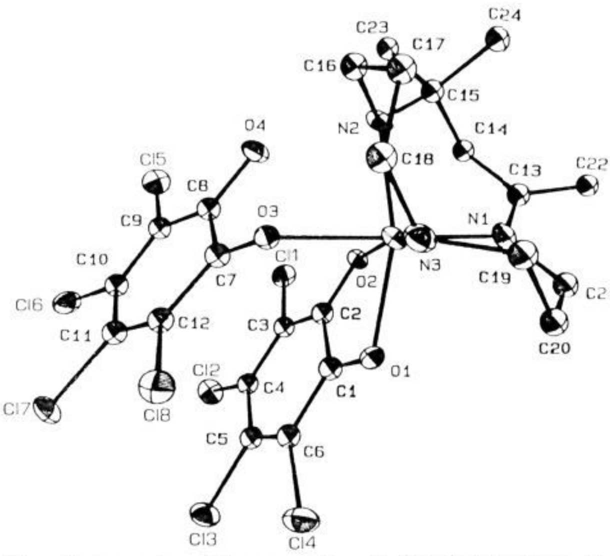

Figure 1. ORTEP view of the asymmetric unit of NiL(TCSQ)TCQ. Selected bond distances (pm) and angles (deg). Distances: Ni–O1 = 212 (1), Ni–O2 = 210 (1), Ni–O3 = 221 (1), Ni–N1 = 206 (2), Ni–N2 = 211 (1), Ni–N3 = 208 (2), C1–O1 = 125 (1), C2–O2 = 128 (1), C7–O3 = 123 (1), C8–O4 = 123 (1), C1–C2 = 147 (2), C2–C3 = 143 (2), C3–C4 = 142 (2), C4–C5 = 140 (2), C5–C6 = 134 (2), C1–C6 = 147 (2), C7–C8 = 151 (2), C8–C9, 142 (2); C9–C10, 139 (2), C10–C11 = 144 (2), C11–C12 = 131 (2). Angles: O1–Ni–O2 = 78.6 (0.4), O1–Ni–O3 = 79.1 (0.3), O1–Ni–N1 = 102.1 (0.4), O1–Ni–N2 = 162.3 (0.4), O2–Ni–O3 = 87.5 (0.3), O2–Ni–N1 = 95.7 (0.4), O2–Ni–N2 = 91.7 (0.4), O2–Ni–N3 = 164.6 (0.3), O3–Ni–N1 = 176.7 (0.4), O3–Ni–N2 = 85.7 (0.4), O3–Ni–N3 = 82.7 (0.4), N2–Ni–N1 = 93.6 (0.4), N1–Ni–N3 = 94.3 (0.5), N2–Ni–N3 = 99.3 (0.4).

The X-ray crystal structure[12] of the adduct indicates that both dioxolene ligands are coordinated to the nickel ion in a highly distorted pseudooctahedral coordination geometry (Figure 1). One of the dioxolene ligands acts as bidentate and the other as monodentate. The Ni–O distances are significantly different for the two molecules, being 210 pm for the chelate and 221 pm for the monodentate ligands, respectively. The three nitrogen donors of the cyclic ligand occupy the remaining facial coordination sites.

The structural parameters of the coordinated dioxolene molecule have been taken as the main evidence for determining the nature of the ligand, i.e., quinone, semiquinone, or catecholate.[2] In the present case the structural parameters of the chelate dioxolene are consistent with the anionic semiquinone nature of this moiety, as shown by the average values of the C–O (127 pm) and of the C(1)–C(2) distances (147 pm). The structural parameters of the monodentate dioxolene on the other hand are close to those expected for the quinonic form of the molecule, the C–O distances being 123 pm longer than those observed in the free molecule (120.8 pm),[13] but are significantly shorter than those expected for a reduced form of the dioxolene ligand. Moreover the other C–C distances within the ring are very close to those observed in the free quinone.

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[11] Its electronic spectrum shows bands at 7000 (ϵ = 55 l cm^{-1} mol^{-1}), 12 500 (ϵ = 20 l cm^{-1} mol^{-1}), and 17 400 (ϵ = 60 l cm^{-1} mol^{-1}) cm^{-1}, respectively, supporting the formulation of five-coordinate nickel(II)–cathecolate adduct. More intense bands occurring at 23 400 (ϵ = 1800 l cm^{-1} mol^{-1}) and 25 700 (ϵ = 1900 l cm^{-1} mol^{-1}) are assigned to LMCT transitions.

[12] Crystal and experimental data for the title compound: $C_{24}H_{25}N_3O_4Cl_8Ni$, monoclinic, $P2_1/c$, $a = 1450.2$ (5), $b = 874.1$ (2), $c = 2316.4$ (8), $\beta = 98.92$ (3), $V = 2.9008$ (1) $\times 10^9$ pm^3, $Z = 4$, $D_{calcd} = 1.744$ g cm^{-3}, $\mu = 13.64$ cm^{-1}. A well-shaped crystal of dimension 0.35 × 0.30 × 0.15 was used for data collection (CAD4 Enraf Nonius diffractometer, Mo Kα λ = 71.069 pm, scan mode: ω–2θ, scan range: $2.5 \le \theta \le 22.5$, measured reflections: $-15 \le h \le 15$, $0 \le k \le 9$, $0 \le l \le 25$, total number 4200, $F \ge 6\sigma(F)$ 1938). Refinement of structure: Patterson map localized in Ni atom. The final refinement with hydrogen atoms in fixed idealized position converged with $R = 0.060$, $R_w = 0.056$. Computer programs used in the structure solution are reported in the following: Sheldrick, G. SHELX76 *System of Computing Programs*; University of Cambridge, England, 1976. Johnson, C. K. ORTEP, Report ORNL 3.794; Oak Ridge National Laboratory: Oak Ridge, TN, 1965.

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The structural parameters, therefore, suggest to describe the molecule as containing a semiquinone and a quinone coordinated to the nickel ion, and charge compensation considerations require that the adduct is formulated as Ni^{I}(TCSQ)(TCQ). Whether this ionic description is correct or it simply indicates that one unpaired electron is more delocalized on the metal and the other more on one dioxolene is largely a semantic problem at this stage. The alternative formulation as Ni^{II}(TCCat)(TCQ) could be accepted only if the bond length criterion within the dioxolene ligands were shown to be false. In favor of the Ni(I) formulation are also the Ni–O distances of the chelate ring which are significantly longer than those observed for nickel(II)– or cobalt(II)–semiquinone pseudooctahedral derivatives (205–206 pm).[14–16]

The effective magnetic moment of the complex is 2.97 μ_B, practically independent of temperature in the range 300–20 K. This value is consistent with a nickel(I)–semiquinone strongly ferromagnetically coupled, as observed in analogous copper(II) and nickel(II) complexes.[16,17] The observed value of the effective magnetic moment is low for a nickel(II) complex, while it agrees well with a system in which a nickel(I) is coupled with a radical.[18] By comparison the effective magnetic moment of the parent NiL(TCCat) corresponds to $g = 2.27$.

The two dioxolene moieties interact with each other as shown by the very short distances and the small angle between the planes[19] which are stacked in a pseudoeclipsed configuration. A similar geometry was previously observed in a bis-semiquinone molybdenum complex.[20] The intense absorption band occurring at 12 700 cm^{-1} is tentatively attributed to the transition between the HOMO of the semiquinone and the LUMO of the quinone. A MLCT character of this transition is also possible.

This compound sheds light on the mechanism of electron transfer in dioxolene molecules in the presence of metal ions. Indeed, although in the present case the two quinoid molecules have the ideal geometry for direct electron transfer, it is in fact the metal ion which acts as electron sink. We suggest that this is presumably due to the stabilization of the adduct determined by π back donation from the low valent metal to the quinone. Similar explanations were provided for justifying the stability of ruthenium(II) quinone complexes.[21]

It is tempting to speculate that the redox process in principle might proceed further with the transfer of the electron from nickel(I) to the quinone either via the t_{2g} orbitals or via the semiquinone ligand.

Acknowledgment. The Italian Ministry of Public Education and the CNR are gratefully acknowledged for the financial support.

Supplementary Material Available: Tables of positional parameters and isotropic thermal factors, bond distances and angles, anisotropic thermal factors, and positional parameters of hydrogen atoms (8 pages); listing of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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Modeling the Dinuclear Sites of Iron Biomolecules: Synthesis and Properties of $Fe_2O(OAc)_2Cl_2(bipy)_2$ and Its Use as an Alkane Activation Catalyst

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The study of synthetic models containing the $[Fe_2(\mu\text{-}O)(\mu\text{-}O_2CR)_2]^{2+}$ core established in the oxygen carrier protein hemerythrin (Hr)[2] has received additional impetus and importance with the realization that such units may also be present in other dinuclear iron biomolecules. These include the purple acid phosphatases (PAP),[3] ribonucleotide reductases (RR),[4] and methane monooxygenases (MMO).[5] By using a variety of tridentate N-based ligands (L), synthetic materials of formulation $[Fe_2O(O_2CR)_2L_2]$ have been prepared,[6] establishing the accessibility and stability of this unit outside a polypeptide environment. The tridentate ligands, however, block all terminal binding sites, precluding investigation of native substrate or substrate-analogue binding.[7] Use of bidentate ligands to overcome this problem has led to dimerization of the $[Fe_2O(O_2CR)_2]^{2+}$ unit to yield $[Fe_4O_2(O_2CR)_4]^{4+}$-containing products.[8] However, we herein report a procedure employing 2,2′-bipyridine (bipy) that successfully allows access to a $[Fe_2O(O_2CR)_2]^{2+}$ product and describe the structure, properties, and alkane activation reactivity of $Fe_2O(OAc)_2Cl_2(bipy)_2$ (**1**), possessing Cl$^-$ ligands bound to the now available sixth coordination sites.

To a stirred solution of $[Fe_4O_2(OAc)_7(bipy)_2](ClO_4)$ (**2**) (0.60 g, 0.5 mmol)[9] in MeCN was added bipy (0.69 g, 5.0 mmol) and $NEt_4Cl\cdot H_2O$ (1.48 g, 8.1 mmol). The dark green-brown solution

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