creasing the temperature or replacing oxygen with nitrogen or argon gave **2a,b**, as determined by ^{31}P NMR spectroscopy. The formation of the η^1-O_2 adduct was found to be reversible, and the oxygenation-deoxygenation cycle could be repeated several times.

Reaction of 5a,b with SO_2. SO_2 was bubbled for 15 min through a yellow CH_2Cl_2 (20 mL) solution of **5a,b** (0.2 mmol) prepared as above and maintained under oxygen at −15 °C. The reaction mixture was allowed to reach room temperature, and then ethanol was added. On concentration, yellow crystals of $[(triphos)Rh(SO_4)]Y$ (Y = BPh_4, **6a**; PF_6 = **6b**) precipitated in 80–85% yield. They were collected by filtration, and the filtrate was evaporated to dryness. The residue was extracted twice with diethyl ether. The ethereal solution was evaporated at reduced pressure to give 3,5-DBQ. Anal. Calcd for $C_{65}H_{59}BO_4P_3RhS$ (**6a**): C, 83.31; H, 5.20; Rh, 9.00. Found: C, 68.12; H, 5.09; Rh, 8.91. $\Lambda_M = 52\ \Omega^{-1}\ cm^2\ mol^{-1}$. Anal. Calcd for $C_{41}H_{39}F_6O_4P_4RhS$ (**6b**): C, 50.84; H, 4.06; Rh, 10.62. Found: C, 50.67; H, 4.07; Rh, 10.48. $\Lambda_M = 81\ \Omega^{-1}\ cm^2\ mol^{-1}$.

Catalytic Reaction of 5a,b with PPh_3. A 30-fold excess of PPh_3 (0.31 g, 1.2 mmol) was added to a yellow CH_2Cl_2 (10 mL) solution of **5a,b** (0.04 mmol) prepared as above and maintained under oxygen at −15 °C for 5 h. After that time, nitrogen was bubbled throughout the yellow solution at room temperature until it became green. The solution was then concentrated to 2 mL and analyzed by ^{31}P NMR spectroscopy. Only the resonances due to $OPPh_3$ (δ 29.86 ppm) and **2a,b** were observed.

Catalytic Reaction of 5a,b with 3,5-BDCat. A 30-fold excess of 3,5-BDCat (0.27 g, 1.2 mmol) was added to a yellow CH_2Cl_2 (10 mL) solution of **5a,b** (0.04 mmol) prepared as above and maintained under oxygen at −15 °C for 24 h. The reaction mixture, after being quenched with nitrogen to stop further oxidation, was extracted with water, and the aqueous layer was analyzed by the usual method of iodometry.[21] The amount of H_2O_2 accumulated during the reaction was found to be nearly correspondent to that of 3,5-DBQ. The CH_2Cl_2 layer was evaporated at reduced pressure and the residue extracted twice with *n*-pentane. The undissolved solid was authenticated as **2a,b** by ^{31}P NMR spectroscopy (CD_2Cl_2, 298 K). The liquid phase was concentrated to dryness to give a solid that was chromatographed on a silica gel column by using chloroform as eluant. Over six different reactions, a 66 (2)% conversion was found for 3,5-di-*tert*-butylcatechol with the following product distributions: 3,5-DBQ [92 (1)%], 3,5-di-*tert*-butyl-1-oxacyclohepta-3,5-diene-2,7-dione [5 (1)%], and 2,4-di-*tert*-butyl-2*H*-pyran-2-one [3 (0.5)%] (numbers in parentheses are estimated standard deviations). The products were characterized by comparison of their ^1H NMR and mass spectra with those of authentic specimens.

Acknowledgment. Part of this work was supported by Progetto Finalizzato "Chimica Fine e Secondaria", CNR, Rome, Italy.

Contribution from the Department of Chemistry,
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Electronic Structure and Reactivity of Dioxolene Adducts of Nickel(II) and Copper(II) Triazamacrocyclic Complexes

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Received January 5, 1989

Five-coordinate $[M(Me_3[12]N_3)(DTBSQ)]ClO_4$ and $M(Me_3[12]N_3)(TCCat)$ complexes (M = Ni, Cu; $Me_3[12]N_3$ = 2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene; DTBSQ = 3,5-di-*tert*-butyl-*o*-semiquinonate; TCCat = 3,4,5,6-tetrachlorocatecholate) were obtained from reaction of $[M(Me_3[12]N_3)OH]_2(ClO_4)_2$ with the appropriate catechol. The magnetic interaction in the nickel(II)-semiquinonate complex is antiferromagnetic ($\mu = 1.89\ \mu_B$), and it is ferromagnetic in the corresponding copper(II) derivative ($\mu = 2.80\ \mu_B$). All the isolated complexes have been found to undergo to one-electron redox processes, and the reaction products have been characterized by electronic and EPR spectroscopy. Evidence is presented that oxidation of the dioxolene ligand originates the redox chain M(II)-Cat, M(II)-SQ, M(II)-Q (Cat = 3,5-di-*tert*-butylcatecholate, M = Ni, Cu; Cat = tetrachlorocatecholate, M = Ni; SQ = semiquinoate; Q = quinone), but it is apparent that the species Cu(I)-TCQ (TCQ = tetrachloro-*o*-benzoquinone) results from one-electron oxidation of the Cu(II)-TCCat complex. The electronic spectra of all the stable species are reported and assigned. The role of the electronic structure of the adducts in determining the physical properties and the reactivity is discussed.

Introduction

Adducts between paramagnetic metal ions and organic radicals provide stimulating examples for understanding the interactions between separate paramagnetic centers.[1-29] Among the most intensively studied systems are those formed by nitroxides[2,4-15] and semiquinones.[1,3,17-29] Since the latter are much stronger ligands than the former, any interaction may be predicted to be more intense for semiquinones than for nitroxides.

Most semiquinone complexes so far investigated have been found to exhibit a strong antiferromagnetic coupling,[1,3,17-23] a feature that often has caused ambiguities about the proper formulation of the correct formal oxidation state of the metal ions

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(1) Kaim, W. *Coord. Chem. Rev.* **1987**, *76*, 187 and references therein.
(2) Delhaes, P., Drillon, M., Eds. *Organic and Inorganic Low Dimensional Crystalline Materials*; Plenum Press: New York, 1987.
(3) Pierpont, C. G.; Buchanan, R. M. *Coord. Chem. Rev.* **1981**, *38*, 45 and references therein.
(4) Eaton, S. S.; Eaton, G. R. *Coord. Chem. Rev.* **1978**, *26*, 207.
(5) Lim, Y. Y.; Drago, R. S. *J. Am. Chem. Soc.* **1971**, *93*, 891.
(6) Dickman, M. M.; Doedens, R. J. *Inorg. Chem.* **1981**, *20*, 2677.
(7) Dickman, M. M.; Doedens, R. J. *Inorg. Chem.* **1983**, *22*, 591.
(8) Grand, A.; Rey, P.; Subra, R. *Inorg. Chem.* **1983**, *22*, 391.
(9) Porter, L. C.; Doedens, R. J. *Inorg. Chem.* **1985**, *24*, 1006.
(10) Caneschi, A.; Gatteschi, D.; Laugier, J.; Rey, P. *J. Am. Chem. Soc.* **1987**, *109*, 2191.
(11) Benelli, C.; Caneschi, A.; Gatteschi, D.; Laugier, J.; Rey, P. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 913.
(12) Caneschi, A.; Gatteschi, D.; Hoffmann, S. K.; Laugier, J.; Rey, P.; Sessoli, R. *Inorg. Chem.* **1988**, *27*, 2390.
(13) Caneschi, A.; Gatteschi, D.; Laugier, J.; Rey, P.; Sessoli, R.; Zanchini, C. *J. Am. Chem. Soc.* **1988**, *110*, 2795.
(14) Caneschi, A.; Gatteschi, D.; Laugier, J.; Pardi, L.; Rey, P.; Zanchini, C. *Inorg. Chem.* **1988**, *27*, 2027.
(15) Caneschi, A.; Gatteschi, D.; Grand, A.; Laugier, J.; Pardi, L.; Rey, P. *Inorg. Chem.* **1988**, *27*, 1031.
(16) Erler, B. S.; Scholz, W. F.; Lee, Y. J.; Scheidt, W. R.; Reed, C. A. *J. Am. Chem. Soc.* **1987**, *109*, 2644.
(17) Buchanan, R. M.; Downs, H. H.; Shortill, W. B.; Pierpont, C. G.; Kessel, S. L.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1978**, *100*, 4318.
(18) Sofen, S. R.; Ware, D. C.; Cooper, S. R.; Raymond, K. N. *Inorg. Chem.* **1979**, *18*, 234.
(19) Kessel, S. L.; Emerson, R. H.; Debrunner, P. G.; Hendrickson, D. N. *Inorg. Chem.* **1980**, *19*, 1170.
(20) Lynch, M. W.; Valentine, M.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1982**, *104*, 6982.
(21) Cass, M. E.; Greene, D. L.; Buchanan, R. M.; Pierpont, C. G. *J. Am. Chem. Soc.* **1983**, *105*, 2680.
(22) Tuchagues, J. M.; Hendrickson, D. N. *Inorg. Chem.* **1983**, *22*, 2545.
(23) Lynch, M. W.; Hendrickson, D. N.; Fitzgerald, B. J.; Pierpont, C. G. *J. Am. Chem. Soc.* **1984**, *106*, 2041.
(24) Kahn, O.; Prins, R.; Reedijk, J.; Thompson, J. S. *Inorg. Chem.* **1987**, *26*, 3557.
(25) Benelli, C.; Dei, A.; Gatteschi, D.; Pardi, L. *Inorg. Chem.* **1988**, *27*, 2831.
(26) Benelli, C.; Dei, A.; Gatteschi, D.; Pardi, L. *J. Am. Chem. Soc.* **1988**, *110*, 6771.
(27) Benelli, C.; Dei, A.; Gatteschi, D.; Pardi, L. *Inorg. Chem.* **1989**, *28*, 1476.
(28) Benelli, C.; Dei, A.; Gatteschi, D.; Pardi, L. *Inorg. Chim. Acta* **1989**, *163*, 99.
(29) Benelli, C.; Dei, A.; Gatteschi, D.; Gudel, H.; Pardi, L. *Inorg. Chem.* **1989**, *28*, 3089.

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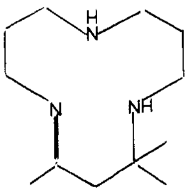
and of the ligand(s). On the other hand, strong ferromagnetic coupling has been recently observed in a square-planar copper(II)-semiquinonate adduct[24] and in pseudooctahedral nickel(II)-semiquinonate adducts.[25,27] In the latter the energy separation between the ground-state quartet and the excited doublet was found to be so high that J was estimated to be larger than 400 cm^{-1}.

The nature of the coupling in these systems is easily rationalized by taking into account the symmetry of the magnetic orbitals of the metal ions and of the ligands. When the condition of orthogonality holds, a ferromagnetic interaction occurs, while in the opposite case an antiferromagnetic interaction is operative. The situation is similar to that observed for exchange-coupled pairs of metal ions,[30-32] but the overlap of the magnetic orbitals can be followed more easily in the case of metal-radical interactions.

Another important point to be realized is that the magnetic orbitals are also frontier orbitals, and as such, their overlap is relevant also to redox processes involving metals and radicals. These systems therefore appear to be ideal to test the relationships between magnetic interactions and electron-transfer processes. In order to study these phenomena, it is useful to work on simple 1:1 adducts of metals and radicals in various geometries, in such a way that the magnetic orbitals of the metal ions are changed. For octahedral coordination we found appropriate[25,27-29,34] to use as acceptors metal complexes formed by the tetradentate macrocycle 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (*dl* isomer), while for five-coordination we choose the tridentate macrocycle 2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene ($Me_3[12]N_3$ (I)), which is well-known to yield stable five-coordinate derivatives.[35]



I

In this paper we wish to report the synthesis and the physical properties of 3,5-di-*tert*-butyl-1,2-semiquinonate (DTBSQ) and tetrachlorocatecholate (TCCat) adducts of formula $[M(Me_3[12]N_3)(DTBSQ)]ClO_4$ and $[Ni(Me_3[12]N_3)(TCCat)]$ (M = Ni(II), Cu(II)), trying to correlate the magnetic properties of the metal-semiquinonate derivatives with the electronic spectra and the redox properties and to discuss the catalytic role of the metal ions in the oxidative processes of aromatic substrates.[36-44]

Experimental Section

Materials. The complexes $[M(Me_3[12]N_3)OH]_2(ClO_4)_2$ were synthesized by following a previously reported procedure.[35] 3,5-Di-*tert*-butyl-catechol (Aldrich) was used as received. 3,4,5,6-Tetrachlorocatecol was prepared as the triphenylphosphine adduct by using literature methods.[45]

Synthesis of $[M(Me_3[12]N_3)(DTBSQ)]ClO_4 \cdot H_2O$ (M = Ni, Cu). A 2-mmol amount of $[M(Me_3[12]N_3)(OH)]_2(ClO_4)_2$ was suspended in 30-mL of warm methanol containing the stoichiometric amount of 3,5-di-*tert*-butylcatechol. While the suspension was gently warmed under stirring, 2 mmol of NaOH in the same solvent was added. Upon concentration crystalline compounds were obtained. They were filtered out, washed with methanol, and recrystallized under nitrogen from dichloromethane-pentane mixtures. Yields: Ni, 64%; Cu, 58%. (Anal. Calcd for $C_{26}H_{47}ClN_3NiO_7$: C, 51.37; H, 7.79; N, 6.91. Found C, 51.85; H, 7.82; N, 6.94. Calcd for $C_{26}H_{47}ClCuN_3O_7$: C, 50.82; H, 7.71; N, 6.84. Found: C, 50.88; H, 7.63; N, 6.76.) Attempts to obtain crystals suitable for X-ray analysis by slow evaporation of solutions of the copper derivative were unsuccessful, also operating under inert atmosphere.

Synthesis of $M(Me_3[12]N_3)(TCCat) \cdot H_2O$. These complexes were obtained in a similar way by using tetrachlorocatechol as ligand. They were recrystallized from acetone-methanol mixtures. Yields: Ni, 94%; Cu, 88%. (Anal. Calcd for $C_{18}H_{27}Cl_4N_3NiO_3$: C, 40.48; H, 5.10; N, 7.87. Found: C, 40.32; H, 5.11; N, 7.66. Calcd for $C_{18}H_{27}Cl_4CuN_3O_3$: C, 39.98; H, 5.04; N, 7.77. Found: C, 39.65; H, 5.01; N, 7.58.)

Physical Measurements. Polycrystalline powder and solution EPR spectra were recorded with a Bruker ER200 spectrometer working at X-band frequency. Variable-temperature magnetic susceptibility 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 pure samples of $(NH_4)_2Mn(SO_4)_2 \cdot 6H_2O$ at several temperatures between 4.2 and 300 K. The susceptometer was operated at magnetic field strength of 1.35 T. Diamagnetic corrections were estimated from Pascal's constants and subtracted from the experimental susceptibility data. They were 363.8×10^{-6} and 309.2×10^{-6} emu mol^{-1} for the $[M(Me_3[12]N_3)(DTBSQ)]ClO_4$ and $M(Me_3[12]N_3)(TCCat)$ derivatives, respectively. Electronic spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer. IR spectra were recorded on a Perkin-Elmer 283 infrared spectrometer. Electrochemical data were obtained with an electrochemical unit formed by an Amel 553 potentiostat equipped with Amel 863, 560/A, 568, and 731 electrodes and a classical three-electrode cell. For cyclic voltammetry experiments the working electrode was a platinum microsphere, the auxiliary electrode was a platinum disk, and the reference electrode was a standard calomel electrode (SCE). Under these conditions the couple Fc^+/Fc lies at +0.345 V vs SCE in acetonitrile 0.1 M NBu_4PF_6 at 25 °C. For coulometric experiments a platinum foil was used as a working electrode, whereas a platinum wire served as auxiliary electrode. Before each experiment the solution was carefully deaerated with a nitrogen flow. All the potentials reported here are referenced against SCE, and they were not corrected for junction potential and/or iR potential drops due to the internal resistance of the system.

Synthesis and Magnetic Properties of Solid Derivatives

The reaction of dinuclear $[M(Me_3[12]N_3)OH]_2(ClO_4)_2$ (M = Ni, Cu) with DTBCat and TCCat yields compounds of different nature. The tetrachloro-substituted ligand yields the expected catecholate adducts, whereas semiquinonate derivatives are obtained with di-*tert*-butylcatechol. Catecholate derivatives of the latter ligand were obtained by working under inert atmosphere, but owing to their reactivity, they were not characterized.

The different nature, i.e. catecholate or semiquinonate, of the dioxolene ligands is clearly evidenced by the stoichiometry and by the spectral and magnetic properties of the two series of compounds to be described below. In particular, as we have recently shown,[27] electronic spectra provide a sensitive tool for determining the nature of the dioxolene ligand, since the semiquinonate derivatives of 3d metal ions are characterized by an absorption band in the range 9000-13 000 cm^{-1} to be assigned to a $n-\pi^*$ transition. IR spectroscopy does not provide significant information about the nature of these derivatives. Indeed the strong absorptions of the triazamacrocyclic ligand near 1450 cm^{-1} do not allow unambiguous assignments characterizing either catecholates or semiquinonates.[20] However, the intensity of the band at ca. 1250 cm^{-1}, where absorptions due to the C-O stretching mode are expected to occur, is significantly weaker in the sem-

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(30) Kahn, O.; Charlot, M. F. *Nouv. J. Chim.* **1980**, *4*, 567.

(31) Kahn, O.; Galy, J.; Journaux, Y.; Jaud, J.; Morgestern Badarau, I. *J. Am. Chem. Soc.* **1982**, *104*, 2165.

(32) Journaux, Y.; Kahn, O.; Zarembowitch, J.; Galy, J.; Jaud, J. *J. Am. Chem. Soc.* **1983**, *105*, 7585.

(33) Bencini, A.; Benelli, C.; Dei, A.; Gatteschi, D. *Inorg. Chem.* **1985**, *24*, 695.

(34) Benelli, C.; Dei, A.; Gatteschi, D.; Pardi, L. Manuscript in preparation.

(35) Martin, J. W. J.; Johnston, J. H.; Curtis, N. F. *J. Chem. Soc., Dalton Trans.* **1978**, 68.

(36) Karlin, K. D., Zubieta, J., Eds. *Copper Coordination Chemistry: Biochemical and Inorganic Perspectives*; Adenine Press: New York, 1983.

(37) Karlin, K. D.; Gultneth, Y. *Prog. Inorg. Chem.* **1987**, *35*, 219.

(38) Brown, D. G.; Beckmann, L.; Ashby, C. H.; Vogel, G. C.; Reinprecht, J. T. *Tetrahedron Lett.* **1977**, 1363.

(39) Rogic, M. M.; Demmin, T. R. *J. Am. Chem. Soc.* **1978**, *100*, 5472.

(40) Demmin, T. R.; Swerdloff, M. D.; Rogic, M. M. *J. Am. Chem. Soc.* **1981**, *103*, 5795.

(41) Thompson, J. S.; Calabrese, J. C. *Inorg. Chem.* **1985**, *24*, 3167.

(42) Thompson, J. S.; Calabrese, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 1903.

(43) Oishi, N.; Nishida, Y.; Ida, K.; Kida, S. *Bull. Chem. Jpn.* **1980**, *53*, 2847.

(44) Speier, G.; Tycklar, Z. *J. Chem. Soc., Dalton Trans.* **1983**, 1955.

(45) Holmes, R. R.; Day, R. O.; Sau, A. C.; Holmes, J. M. *Inorg. Chem.* **1986**, *25*, 600.

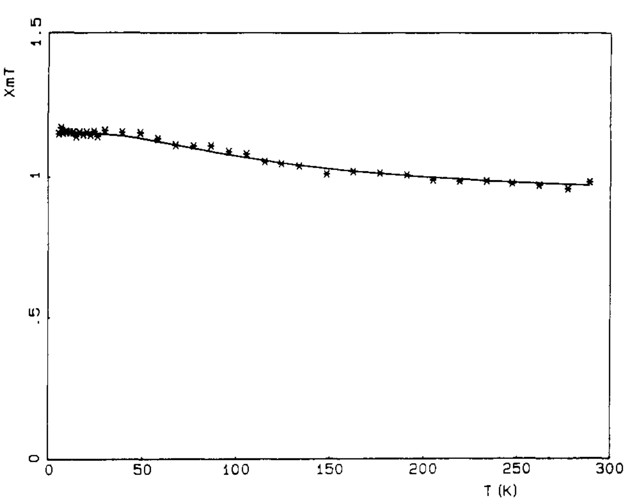

Figure 1. Variation of the χT product with temperature in the range 4–300 K for [Cu(Me$_3$[12]N$_3$)(DBTSQ)]ClO$_4$. The curve represents the best fit (see text).

iquinonate derivatives than in the catecholate ones, thus supporting the assignment.[27,46]

All the isolated complexes are crystalline solids that can be stored for long periods without any significant change of their physical properties and chemical reactivity. The two semiquinone derivatives are stable under nitrogen atmosphere, but their solutions are slowly oxidized by air.

Attempts to synthesize nickel(II) and copper(II) semiquinone derivatives of the tetrachlorodioxolene by using several oxidizing agents (i.e. AgClO$_4$, Br$_2$) were unsuccessful. We found some evidence that the cation Ni(Me$_3$[12]N$_3$)(TCSQ)$^+$ is stable in acetonitrile solution, but any attempt to isolate it led to the precipitation of the insoluble Ni(Me$_3$[12]N$_3$)(TCSQ)(TCQ) complex.[26] For copper we were unable to isolate products having a defined stoichiometry. As supported by TLC on alumina, there exists evidence that the oxidation products are TCQ and, as a minor product, hexachloro-2,3-oxoanthrenequinone, resulting from the nucleophilic reaction between two dioxolene molecules.

All the isolated solid complexes are paramagnetic. The [Ni(Me$_3$[12]N$_3$)(DTBSQ)]ClO$_4$ complex is characterized by μ_{eff} = 1.89 μ_B practically independent of temperature in the range 70–300 K. This shows that the ground state has $S = {}^1/_2$ and no excited multiplet is termally populated. This ground state agrees with a strong antiferromagnetic coupling between the nickel(II) ion (S = 1) and the radical ($S = {}^1/_2$).

The polycrystalline powder EPR spectrum at X-band frequency of this compound shows an isotropic signal with g = 2.26, practically independent of temperature. The g value of the nickel–semiquinonate pair is expected to be given by the relation

$$g = 4/3g_{\text{Ni}} - 1/3g_{\text{SQ}}$$

Assuming g_{SQ} = 2.00, then g_{Ni} is calculated as 2.2, which agrees with a square-pyramidal coordination geometry.[47]

The [Cu(Me$_3$[12]N$_3$)(DTBSQ)]ClO$_4$ complex is characterized by a μ_{eff} = 2.80 μ_B at 288 K. $\chi_M T$ in the range 4–300 K, shown in Figure 1, increases on decreasing temperature reaching a plateau below 40 K with a value of 1.159 emu mol^{-1} K. The experimental data were fitted with the expression valid for two interacting $S = {}^1/_2$ spins yielding g = 2.20 and J = −104.6 cm^{-1}, defined by the spin Hamiltonian $H = -JS_1S_2$, showing that the triplet lies below the singlet state. The compound is EPR silent down to 4.2 K, as still observed for copper(II)– and nickel(I)–semiquinonate derivatives.[24,26] This can be probably attributed to unfavorable electronic relaxation times or large zero-field-splitting effects.

Table I. Electrochemical Potentials of the [M(Me$_3$[12]N$_3$)(diox)]$^{n+}$ Complexes (M = Ni, Cu; n = 0, 1; diox = Dioxolene)[a,b]

compd	SQ/Cat	Q/SQ[c]
[Ni(Me$_3$[12]N$_3$)(DTBSQ)]$^+$	−0.41	0.38
Ni(Me$_3$[12]N$_3$)(TCCat)	0.25	0.80
[Cu(Me$_3$[12]N$_3$)(DTBSQ)]$^+$	−0.33	0.55
Cu(Me$_3$[12]N$_3$)(TCCat)	0.31[d]	1.00[d]

[a] All potentials are reported with respect to SCE in acetonitrile–0.1 M NBu$_4$PF$_6$. The potentials are the average anodic and cathodic peak potentials for reversible processes and half-height peak anodic potentials for irreversible couples in cyclic voltammograms recorded at 100 mV s^{-1}. [b] At 25 °C for solutions ca. 10^{-3} M. [c] Irreversible. [d] See the text.

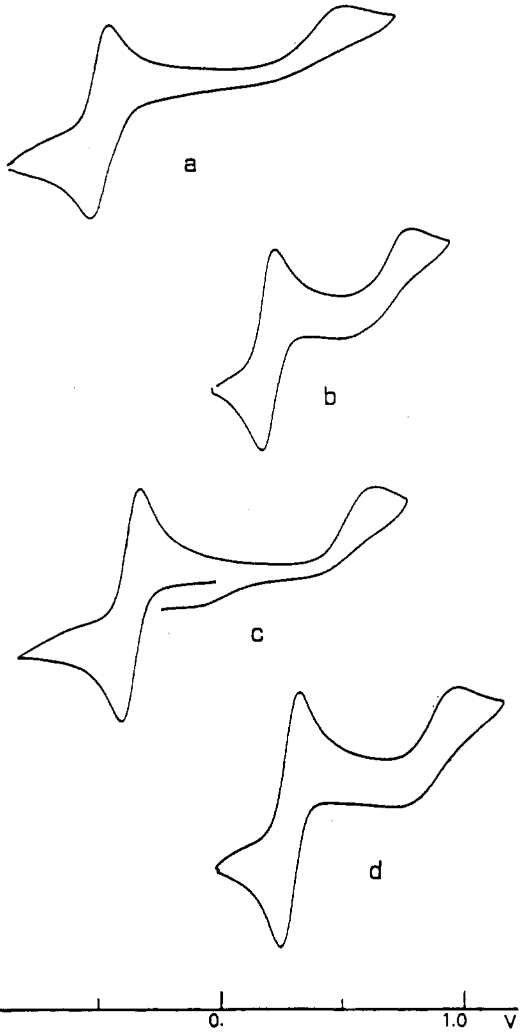

Figure 2. Cyclic voltammograms of [Ni(Me$_3$[12]N$_3$)(DTBSQ)]ClO$_4$ (a), Ni(Me$_3$[12]N$_3$)(TCCat) (b), [Cu(Me$_3$[12]N$_3$)(DTBSQ)]ClO$_4$ (c), and Cu(Me$_3$[12]N$_3$)(TCCat) (d) in acetonitrile–0.1 M NBu$_4$PF$_6$. Scan rates are 0.1 V s^{-1}.

Ni(Me$_3$[12]N$_3$)(TCCat) has a μ_{eff} = 3.22 μ_B at room temperature, whereas the copper(II) analogue is characterized by a μ_{eff} = 1.79 μ_B. These values do not change significantly in the range 77–296 K. The EPR spectrum of a polycrystalline powder of the latter complex is broad with $g_\parallel$ = 2.24 and $g_\perp$ = 2.09.

Electrochemical Properties

The electrochemical data of acetonitrile solutions of these complexes are reported in Table I. The cyclic voltammograms of deaerated acetonitrile solutions of [Ni(Me$_3$[12]N$_3$)(DTBSQ)]ClO$_4$ show two redox couples at −0.41 and +0.38 V vs SCE (Figure 2). Controlled-potential coulometric experiments indicate that both redox processes are monoelectronic. The first peak exhibits the usual features of uncomplicated reversible charge-transfer processes (i_c/i_a = 1; $i/v^{1/2}$ = constant, $E_a - E_c$ = 65 mV).[48] The second process is irreversible and gives origin

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(46) Lever, A. B. P.; Auburn, P. R.; Dodsworth, E. S.; Haga, M. A.; Liu, W.; Melnik, M.; Nevin, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 8076.

(47) Gatteschi, D.; Bencini, A. In *Magnetic Structural Correlations in Exchange Coupled Systems*; Willett, R. D., Gatteschi, D., Kahn, O., Eds.; Reidel: Dordrecht, The Netherlands, 1985; p 241.

to a new reduction peak in the reverse scan overlapping with that associated to the first process.

This electrochemical behavior is in agreement with the two ligand-centered one-electron-transfer processes observed for other dioxolene adducts.[25,27-29,49-55] The first process can be reasonably attributed to the catecholate–semiquinonate couple, and the second, to the semiquinonate–quinone one. As previously suggested, the nonreversible character of the latter couple can be ascribed to the instability of the nickel(II)–quinone adduct.[25] Indeed the new reduction peak, which appears at negative potentials, after positive scans, may be attributed to redox processes involving the free quinone.[51] All these suggestions are supported by EPR and electronic spectra of the exhaustively oxidized (at +0.8 V) and reduced (at −0.6 V) solutions of the starting complex. (See also below.)

Similar behavior is observed in the cyclic voltammograms of $Ni(Me_3[12]N_3)(TCCat)$, which show a reversible one-electron process occurring at +0.25 V, followed by a nonreversible one at +0.8 V. The two processes are associated with electron transfers involving only the dioxolene ligand, as supported by spectral data.

The values of the redox potentials associated with the semiquinonate–catecholate couple in the present five-coordinate nickel(II) complexes are more positive by ca. 0.2 V compared to those of the pseudooctahedral nickel(II) adducts.[25,27] Since the differences in solvation energies cannot be expected to play a determining role for these redox couples, this difference should reflect the stronger bonding interaction that occurs in five-coordinate complexes.

The voltammograms of the copper(II)–DTBSQ and –TCCat derivatives are also shown in Figure 2 with two redox processes occurring at −0.325 and +0.55 V for $[Cu(Me_3[12]N_3)(DTBSQ)]ClO_4$ and +0.31 and +1.0 V for $Cu(N_3[12]N_3)(TCCat)$. Again, the features of the voltammograms indicate that the first process is reversible and the second is not, whereas controlled-potential electrolysis experiments show that all the processes are monoelectronic. While the reactivity of the copper–di-*tert*-butyldioxolene derivative is similar to that of the nickel complexes, a different behavior is observed for the copper–tetrachlorocatecholate complex. Indeed the product of one-electron oxidation of $Cu(Me_3[12]N_3)(TCCat)$ is not a copper(II)–semiquinonate adduct but rather it can be described as a copper(I)–quinone adduct, as evidenced by the electronic spectra to be discussed below. In this hypothesis we must assume that a fast internal electron transfer follows the oxidation of the ligand according to the reaction sequence

$$Cu^{II}(Me_3[12]N_3)(TCCat) \xrightleftharpoons{-e^-} [Cu^{II}(Me_3[12]N_3)(TCSQ)]^+ \xrightleftharpoons{ET} [Cu^{I}(Me_3[12])(TCQ)]^+$$

The second oxidation process then involves a metal-centered electron transfer:

$$Cu^{I}(Me_3[12]N_3)(TCQ) \xrightleftharpoons{-e^-} Cu^{II}(Me_3[12]N_3)(TCQ)$$

Electronic Spectra

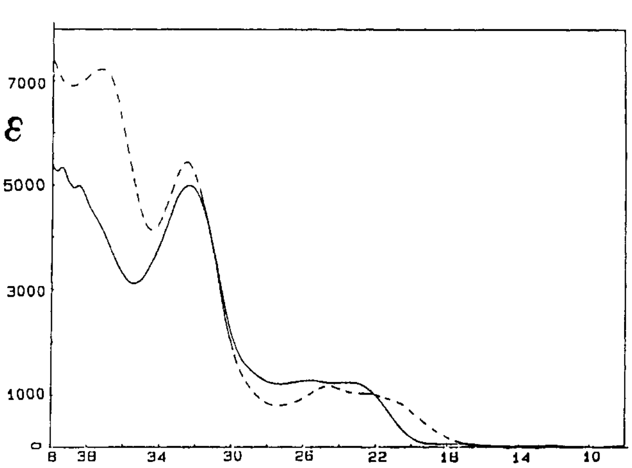

Figure 3. Electronic spectra of $Ni(Me_3[12]N_3)(DTBCat)$ (---) and $Ni(Me_3[12]N_3)(TCCat)$ (—) in acetonitrile solution.

Table II. Electronic Spectra of $[M(Me_3[12]N_3)(diox)]^{n+}$ (M = Ni, Cu; *n* = 0, 1) in Acetonitrile–0.1 M NBu_4PF_6[a]

compd	DTBCat	TCCat	proposed assgnt
$Ni(Me_3[12]N_3)(Cat)$	7.2 (1.70)	7.1 (1.70)	d–d
	13.2 (1.30)	13.0 (1.40)	d–d
	17.5 (1.90)		d–d
	22.5 (3.04)	23.4 (3.09)	LMCT
	24.7 (3.09)	25.7 (3.11)	LMCT
	32.5 (3.70)	32.5 (3.74)	$\pi^*-\pi^*$
	38.5 (3.70)	37.5 (3.86)	$\pi^*-\pi^*$
	39.5 (3.73)		
$Cu(Me_3[12]N_3)(Cat)$	11.0 (1.7)	10.0 (1.6)	d–d
	16.8 (2.28)	16.1 (2.13)	d–d
	22.9 (2.40)	22.5 (2.08)	LMCT
	26.7 sh		
	32.7 (3.81)	32.1 (3.90)	$\pi^*-\pi^*$

compd	DTBSQ	TCSQ	proposed assgnt
$[Ni(Me_3[12]N_3)(SQ)]^+$	7.5 (1.71)	7.40 (1.76)	d–d
	12.2 sh	10.5 sh	n–π^*
	13.6 (2.54)	11.8 (2.53)	*b*
	13.1 sh		*b*
	18.7 (2.57)	18.8 sh	d–d
	20.8 sh	21.1 sh	d–d
	22.6 sh		d–d
	24.8 (3.58)	23.6 (3.42)	MLCT
		25.5 sh	$\pi-\pi^*$
		26.8 sh	*b*
		28.0 sh	*b*
	30.6 sh	29.8 (3.75)	$\pi^*-\pi^*$
	33.2 (3.68)	32.3 sh	$\pi^*-\pi^*$
	36.0 sh	35.0 sh	$\pi^*-\pi^*$
$[Cu(Me_3[12]N_3)(SQ)]^+$	11.2 sh		n–π^*
	12.6 sh		*b*
	14.0 sh		*b*
	15.2 sh		*b*
	17.5 (2.66)		d–d or CT
	23.3 (3.12)		CT
	26.9 (3.18)		$\pi-\pi^*$
	28.1 sh		*b*
	29.3 sh		*b*
	33.2 (3.92)		$\pi^*-\pi^*$
	37.0 sh		$\pi^*-\pi^*$
$[Cu(Me_3[12]N_3)(TCQ)]^+$	21.0 (3.85)		
	36.0 (3.74)		
	37.5 sh		

[a] Absorption maxima in $cm^{-1} \times 10^{-3}$; log ε in parentheses; sh = shoulder. [b] Vibronic progression.

Catecholate Complexes. The electronic spectra of acetonitrile solutions of the two tetrachlorocatecholate derivatives and of the di-*tert*-butylcatecholate analogues, prepared by controlled-potential electrolysis from the parent semiquinone derivatives, are shown in Figures 3 and 4. The spectral parameters are shown in Table II. They are strictly similar to those observed in other solvents like acetone and 1,2-dichloroethane. Apparently no processes involving ligand dissociation or solvent coordination occur for these chromophores.

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(48) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980.
(49) Balch, A. L. *J. Am. Chem. Soc.* **1973**, *95*, 2723.
(50) Girgis, A. Y.; Sohn, Y. S.; Balch, A. L. *Inorg. Chem.* **1975**, *14*, 2327.
(51) Stallings, M. D.; Morrison, M. M.; Sawyer, D. T. *Inorg. Chem.* **1981**, *20*, 2655.
(52) Connelly, N. G.; Manners, I.; Protheroe, J. R. C.; Witheley, M. W. *J. Chem. Soc., Dalton Trans.* **1984**, 2713.
(53) Haga, M.; Dodsworth, E. S.; Lever, A. B. P. *Inorg. Chem.* **1986**, *25*, 447.
(54) Bianchini, C.; Masi, D.; Mealli, C.; Meli, A.; Martini, G.; Laschi, F.; Zanello, P. *Inorg. Chem.* **1987**, *26*, 2643.
(55) Harlmaker, S.; Jones, S. E.; Sawyer, D. T. *Inorg. Chem.* **1983**, *22*, 2790.

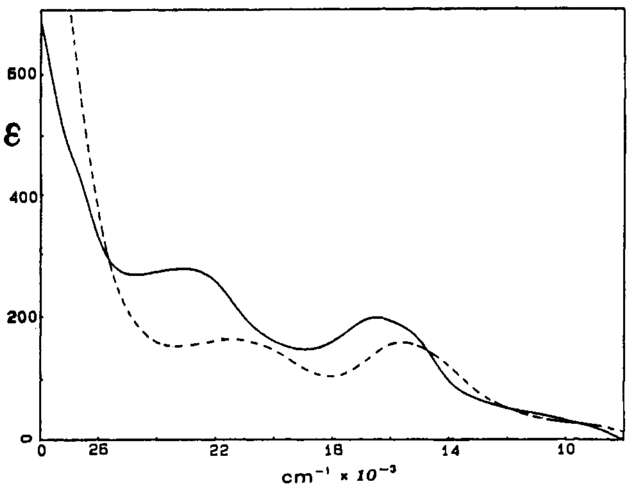

Figure 4. Electronic spectra of Cu(Me$_3$[12]N$_3$)(DTBCat) (—) and Cu(Me$_3$[12]N$_3$)(TCCat) (---) in acetonitrile solution.

The sets of bands appearing in the low-energy region of the spectrum exhibit the expected pattern of energies and intensities characterizing distorted trigonal-bipyramidal high-spin five-coordinate nickel(II)[56-58] and copper(II)[59,60] chromophores. In particular these spectra are closely related to those of other nickel(II)- and copper(II)-Me$_3$[12]N$_3$ derivatives, whose structures have been determined by X-ray analysis.[35,61] It should pointed out that the spectral parameters for the two copper(II) chromophores indicate a somewhat different distortion of the coordination polyhedra.

The two nickel(II) catecholate complexes show two relatively intense bands at 22 500 and 24 700 cm^{-1} in the DTBCat derivative and 23 400 and 25 700 cm^{-1} in the TCCat one. These bands cannot be attributed to d–d transitions and are absent also in the spectra of some related six-coordinate zinc(II) and nickel(II) chromophores containing a single chelated catecholate ligand.[27] Therefore, we attribute these transitions to charge-transfer bands. The blue shift of the bands on passing from the DTBCat to the TCCat chromophore is consistent with a ligand-to-metal charge-transfer (LMCT) character of the transitions.

The bands occurring in the UV region are attributed to internal transitions of the dioxolene ligands, by comparison with the spectra of other catecholate derivatives.[27,51]

The spectra of the copper(II) complexes exhibit bands at 22 900 (DTBCat) and 22 500 cm^{-1} (TCCat), which again cannot be assigned to d–d transitions. We suggest that also these transition have a LMCT character.

Semiquinonate Complexes. The spectra of [Ni(Me$_3$[12]N$_3$)(DTBSQ)]ClO$_4$ and of the solution of Ni(Me$_3$[12]N$_3$)(TCCat) electrolyzed at +0.45 V are shown in Figure 5. The ESR spectrum of the latter solution shows a broad signal at g = 2.52, which is consistent with the presence of the [Ni(Me$_3$[12]N$_3$)(TCSQ)]$^+$ species. In fact the same type of analysis developed above for [Ni(Me$_3$[12]N$_3$)(DTBSQ)]$^+$ yields g_{Ni} = 2.4, which agrees with a five-coordinate structure.[47]

Apparently five-coordination of the nickel(II) chromophores is maintained as indicated by the band at 7500 cm^{-1}, but the assignment of the other bands appearing in the spectra of these chromophores is not straightforward. However, we can make a reasonable attempt along the lines of a spectroscopic investigation carried out recently on some optically active zinc(II) and nickel(II) complexes with chelated semiquinonate derivatives.[27] On this basis we assign the group of bands centered at 13 600 and 11 800 cm^{-1} in the spectra of nickel(II)–DTBSQ and nickel(II)–TCSQ derivatives, respectively, to the 9a$_1$–3b$_1$ transition of the ligand. Both bands exhibit the typical pattern of subbands characterizing a vibronic progression. The separation energy of 1200–1300 cm^{-1} may be reasonably associated with the C–O stretching vibration mode. Indeed we previously showed that this band is characteristic of semiquinonate adducts.[27]

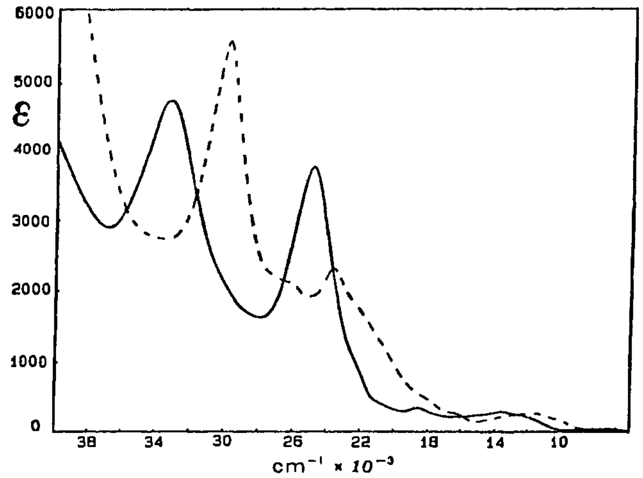

Figure 5. Electronic spectra of [Ni(Me$_3$[12]N$_3$)(DTBSQ)]$^+$ (—) and [Ni(Me$_3$[12]N$_3$)(TCSQ)]$^+$ (---) species in acetonitrile solution.

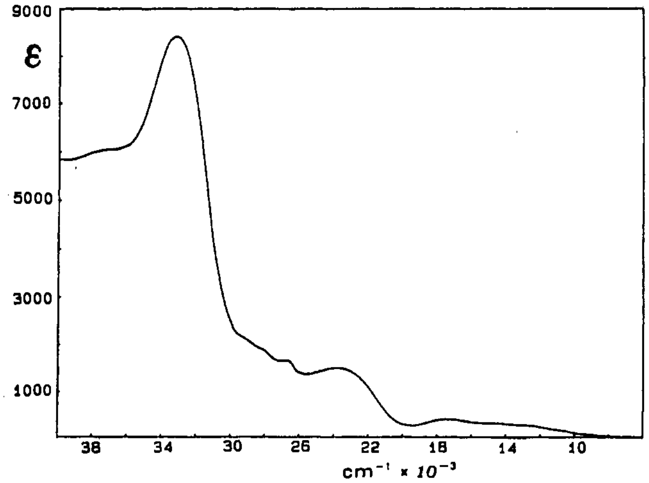

Figure 6. Electronic spectrum of [Cu(Me$_3$[12]N$_3$)(DTBSQ)]ClO$_4$ in acetonitrile solution.

In the same way the bands occurring in the UV region are assigned to internal transitions of the ligand. In the spectrum of the TCSQ derivative a vibronic progression of ca. 1200 cm^{-1} (at 25 500, 26 800, 28 000 cm^{-1}) is resolved.

In addition to the bands of the ligands, the spectra of the two chromophores show bands at 18 600 (log ϵ = 2.58) and 24 900 (log ϵ = 3.58), with shoulders at 20 600 and 22 300 cm^{-1}, for the DTBSQ derivative and 23 600 cm^{-1} (log ϵ = 3.42), with shoulders at 18 400, 20 600 and 22 000 cm^{-1}, for the TCSQ derivative. The more intense transition is red-shifted on passing from DTBSQ to TCSQ and therefore is reasonably assigned to a transition having MLCT character. The other bands do not vary significantly in energy on passing from a chromophore to the other and are characterized by similar and relatively intense molar absorption coefficients. One of these bands might be assigned to the 7b$_2$–3b$_1$ semiquinone transition, but although this hypothesis cannot be discarded, it has been shown that this transition can be easily observed only in the CD but not in the electronic spectra.[27] Furthermore, the close similarity of the pattern of bands in the two electronic spectra leads us to suggest that they arise from

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(56) Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier: Amsterdam, 1984.

(57) Sacconi, L.; Mani, F.; Bencini, A. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, England, 1987; Vol. 5, p 1.

(58) Banci, L.; Bencini, A.; Dei, A.; Gatteschi, D. *Inorg. Chem.* **1981**, *20*, 393.

(59) Hathaway, B. J.; Duggan, M.; Murphy, A.; Mullane, J.; Power, C.; Walsh, A.; Walsh, B. *Coord. Chem. Rev.* **1981**, *36*, 267.

(60) Hathaway, B. J. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, England, 1987; Vol. 5, p 533.

(61) Davis, R. J.; Einstein, F. W. B.; Curtis, N. F.; Martin, J. W. L. *J. Am. Chem. Soc.* **1978**, *100*, 6258.

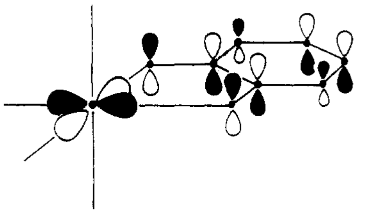


Figure 7. Schematic drawing of the magnetic orbitals of the copper(II)–semiquinonate moiety.

transitions mainly d–d in character, presumably to doublet states deriving either from singlet to triplet nickel(II) states coupled to the radical.[29]

The spectra of the copper derivative, as said above, indicate that different chemical species are present in solution upon one-electron oxidation of the two copper(II)–catecholate complexes. The spectrum of $[Cu(Me_3[12]N_3)(DTBSQ)]ClO_4$, reported in Figure 6, shows the typical pattern of bands characterizing a semiquinone derivative, i.e. 14 000 and 33 200 with shoulders at 26 900, 28 100, 29 300 (vibronic progression), and 36 800 cm^{-1}. The band at 23 200 cm^{-1} is probably a charge-transfer transition, but the impossibility to compare it with other semiquinone derivatives does not allow us to establish its character. The band at 17 500 cm^{-1} is significantly more intense than that occurring in the catecholate, and its nature is rather uncertain. The comparison with the spectra reported for other copper(II)–semiquinone derivatives[41,55] could suggest that also this transition has a charge-transfer character.

The spectrum of a solution of $Cu(Me_3[12]N_3)(TCCat)$, after exhaustive electrolysis at +0.45 V, on the other hand shows only a band at 21 000 cm^{-1} with $\log \epsilon = 3.85$. Since 1 mol of electrons is stoichiometrically required for the complete oxidation of the reagent, and no bands attributable either to copper(II) derivatives or semiquinonate species are detected, we suggest that copper(I) species are produced in the oxidation process. As a further support to this hypothesis, the electrolyzed solution is ESR silent. The band at 21 000 cm^{-1} is close to that observed in the spectrum of the free quinone ligand under the same conditions, which shows an absorption at 22 800 cm^{-1} with $\log \epsilon = 3.3$. The difference between the two spectra suggests a bound quinone, and therefore these data are consistent with the presence of a copper(I)–quinone adduct in solution. Indeed it has been shown that adducts of this kind are stable and can be isolated in the solid state.[44]

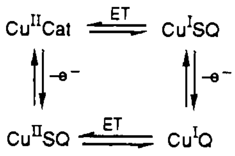
Electronic Structure of the Compounds

The magnetic and spectral data clearly indicate that all the isolated nickel(II)- and copper(II)–dioxolene complexes are five-coordinated. The oxidation of nickel(II)–catecholate occurs at the ligand, yielding stable nickel(II)–semiquinonate species, which in the case of the DTBSQ ligand can also be isolated in the solid state. The failure in isolating solid complexes containing TCSQ is due probably either to thermodynamic factors or to the existence of side reactions, which we are currently attempting to investigate.

The magnetic data of the semiquinonate derivatives indicate that the coupling is ferromagnetic for copper(II). This result requires that the magnetic orbitals of the semiquinone and of the metal ion are orthogonal to each other as previously reported (Figure 7).[24-27] As compared to that of the square-planar (di-2-pyridylamine)(3,5-di-*tert*-butyl-*o*-semiquinonato)copper(II) perchlorate,[24] the ferromagnetic coupling is smaller in the present case. This may be due to the fact that the orthogonality of the magnetic orbitals is less rigorously obtained in the present case. On the other hand, since the electronic spectra clearly indicate that the nickel(II) is in a high-spin form, the coupling is antiferromagnetic in the nickel(II)–semiquinonate adduct. This requires that at least one magnetic orbital of the metal ion strongly overlaps with the radical. This can occur in a distorted trigonal-bipyramidal geometry, where the magnetic orbitals are z^2 and xz (yz).

The bands of the nickel(II)–catecholate adducts that we have assigned to LMCT are much more intense than the corresponding bands of the copper(II) complexes. Our interpretation is that these bands involve the transition between the HOMO of catecholate, which is also the HOMO of semiquinone,[27,54,62] to the metal orbital containing the unpaired electron(s). In charge-transfer processes the optical transition intensity is proportional to the overlap of the involved orbitals; therefore, the LMCT bands must be less intense in the copper(II) complex, where the magnetic properties of the semiquinone adduct show that the metal and ligand orbitals are orthogonal, than in the nickel(II) complex (Figure 7), where the magnetic properties of the semiquinonate adduct show that the magnetic orbitals have large nonzero overlap.

Another important feature of the present data is the different nature of the one-electron oxidation products of the copper(II) complexes with two different catecholate ligands. This result provides a further example of how the metal and quinone frontier electron levels are close in energy. It was previously found that hard donor atoms, like oxygen or nitrogen,[42,55,63-66] stabilize copper(II)–catecholate adducts, whereas soft donors, like phosphorus,[63,67] stabilize copper(I)–semiquinonate adducts. For example, it has been reported that the addition of phosphine ligands to some copper(II)–catecholate yields a copper(I)–semiquinonate species.[42,63] In a similar way the addition of pyridine under nitrogen atmosphere to copper(II)–semiquinonate derivatives yields quinone, through the stabilization of copper(I) complexes.[41] At the same time, however, the DTBQ molecule can yield oxidative addition to copper(I) complexes giving the stable semiquinonate adduct.[41,42] Our present data show that also the π-acceptor properties of the dioxolene ligand play a major role in determining the charge distribution in the complex: the stronger acceptor properties of TCQ in fact provide stabilization of a copper(I) adduct, while with DTBQ the copper(II)–semiquinonate form is preferred. In summary, the reactivity properties of copper–dioxolene moieties can be described as deriving by one-electron-transfer reactions between two isoelectronic couples, i.e. copper(II)–catecholate/copper(I)–semiquinonate and copper(II)–semiquinonate/copper(I)–quinone, according to the scheme



The species connected by the ET processes have never been found up to now to be in thermal equilibrium in the case of copper, although this has been observed for other metal ions.[68,69] However, we may assume that the two ET equilibria, as depicted in the scheme, are shifted either to the left or to the right depending on the nature of the dioxolene and the counterligand.

These processes can be related to the charge shift occurring in $Ni^{II}(Me_3[12]N_3)(TCCat)$ upon addition of TCQ. The resulting adduct was described, on the basis of its structural parameters, as $Ni^{I}(Me_3[12]N_3)(TCSQ)(TCQ)$, rather than a simple charge-transfer complex.[26] Indeed the LMCT character of the bands at relatively low energy observed in the present nickel(II)- and copper(II)–catecholate derivatives justify the observed charge shifts.

This view is consistent with that proposed by Thompson and Calabrese[42] about the catalytic role of the copper(II) ion in the

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(62) Gordon, D. J.; Fenske, R. F. *Inorg. Chem.* **1982**, *21*, 2907.

(63) Buchanan, R. M.; Wilson-Blumberg, C.; Trapp, C.; Larsen, S. K.; Greene, D. L.; Pierpont, C. G. *Inorg. Chem.* **1986**, *25*, 3070.

(64) Drown, D. G.; Reinprecht, J. T.; Vogel, G. C. *Inorg. Nucl. Chem. Lett.* **1976**, *12*, 399.

(65) Brown, D. G.; Hughes, W. J. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1979**, *34B*, 1408.

(66) Brown, D. G.; Hughes, N. J.; Knerr, G. *Inorg. Chim. Acta* **1980**, *53*, 2847.

(67) Razuvaev, G. A.; Cherkasov, V. K.; Abakumov, G. A. *J. Organomet. Chem.* **1978**, *160*, 361.

(68) Lynch, M. W.; Hendrickson, D. N.; Fitzgerald, B. J.; Pierpont, C. G. *J. Am. Chem. Soc.* **1984**, *106*, 2041.

(69) Buchanan, R. M.; Pierpont, C. G. *J. Am. Chem. Soc.* **1980**, *102*, 4951.

oxidative processes of catechols. It is apparent that under the conditions used in the synthesis, the process can be reasonably thought to proceed by successive one-electron-transfer steps (oxidation of the copper(II)–catecholate complex to copper–semiquinonate, followed by internal electron transfer within the product). In the overall process, according to Rogic and Demmin,[39,40] no dioxygen is required, since an additional cupric species (the bis(pyridine)cupric chloride in the synthetic procedure) is sufficient to act as on electron acceptor. The problem remains open about the factors determining the successive oxidation process that involves the cleavage of a carbon–carbon bond.

Acknowledgment. The financial support of the Ministry of Public Education and of the CNR is gratefully acknowledged.

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Electrochemistry and Spectroelectrochemistry of 1,8-Naphthalene- and 1,8-Anthracene-Linked Cofacial Binuclear Metallophthalocyanines. New Mixed-Valence Metallophthalocyanines

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Received March 20, 1990

1,8-Naphthalene- or 1,8-anthracene-linked cofacial dizinc, dicopper, and dicobalt diphthalocyanines have been studied by solution and surface electrochemistry, spectroelectrochemistry, and electron spin resonance (ESR). These derivatives are mixtures of syn and anti isomers that have very similar electrochemistry except where we comment specifically. The phthalocyanine ring first oxidation Pc(−1)/Pt(−2), the Co(III)/Co(II), and the Co(II)/Co(I) redox couples split into two couples as a consequence of intra-ring exchange interactions. The spectra of the electrochemically oxidized or reduced species and, in particular, those of the mixed-valence species are recorded. Exciton coupling energies are derived and are seen to be related to the ground-state mixed-valence splitting energies. These are discussed in terms of structure and inter-ring distance. Cobalt derivatives immobilized onto ordinary pyrolytic graphite catalyze the electroreduction of oxygen by two electrons to hydrogen peroxide.

Introduction

There is considerable interest in the electrochemistry and spectroelectrochemistry of binuclear metalloporphyrins[4–7] and binuclear[8–10] and polynuclear[8d,g,9,10] metallophthalocyanines. When two macrocyclic units are spaced closely to each other, properties that are not seen in mononuclear units often emerge. Most striking of these is the splitting of some redox couples, generating mixed-valence species whose properties have been discussed for several systems.[4,6,7c,8a,b,g,10] Mixed-valence behavior has been observed with some zinc derivatives of flexible clamshell phthalocyanines,[8g] but not with analogous cobalt derivatives.

We report the electrochemical and spectroelectrochemical properties of rigidly linked 1,8-naphthalene- and 1,8-anthracene-bridged cofacial binuclear metallophthalocyanines

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(4) (a) Mest, Y. L.; L'Her, M.; Collman, J. P.; Kim, K.; Helm, S.; Hendricks, N. H. *J. Electroanal. Chem. Interfacial Electrochem.* **1987**, *234*, 277; **1987**, *220*, 247. (b) Collman, J. P.; Prodolliet, W.; Leidner, R. *J. Am. Chem. Soc.* **1986**, *10*,, 2916. (c) Le Mest, Y.; Courtot-Coupez, J.; Collman, J. P.; Evitt, E. R.; Bencosme, C. S. *J. Electroanal. Chem. Interfacial Electrochem.* **1985**, *184*, 331. (d) Collman, J. P.; Marrocco, M.; Elliot, C. M.; L'Her, M. L. *J. Electroanal. Chem. Interfacial Electrochem.* **1981**, *124*, 113. (e) Collman, J. P.; Kim, K.; Leidner, C. R. *Inorg. Chem.* **1987**, *26*, 1152. (f) Ngameni, E.; Le Mest, Y.; L'Her, M.; Collman, J. P.; Hendricks, N. H.; Kim, K. *J. Electroanal. Chem. Interfacial Electrochem.* **1987**, *220*, 247.

(5) Cowan, J. A.; Saunders, J. K. M. *J. Chem. Soc., Perkin Trans. 1* **1987**, 2395.

(6) (a) Crossley, M. J.; Burn, P. L. *J. Chem. Soc., Chem. Commun.* **1987**, 39. (b) Buchler, J. W.; Elsasser, K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 286. (c) Williams, R. F. X.; White, D.; Hambright, P.; Schamin, A.; Little, R. G. *J. Electroanal. Chem. Interfacial Electrochem.* **1983**, *110*, 69. (d) Becker, J. Y.; Dolphin, D.; Paine, J. B. Wijesekera, T. J. *J. Electroanal. Chem. Interfacial Electrochem.* **1984**, *164*, 335.

(7) Bottomley, L. A.; Gorce, J.-N.; Landrum, J. T. *Inorg. Chim. Acta* **1986**, *125*, 135. (b) Kadish, K. M.; Cheng, J. S.; Cohen, I. A.; Summerville, D. *ACS Symp. Ser.* **1977**, *No. 38*, 65. (c) Kadish, K. M.; Larson, G.; Lexa, D.; Momenteau, M. *J. Am. Chem. Soc.* **1975**, *97*, 282.

(8) (a) Leznoff, C. C.; Lam, H.; Nevin, W. A.; Kobayashi, N.; Janda, P.; Lever, A. B. P. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1021. (b) Leznoff, C. C.; Lam, H.; Marcuccio, S. M.; Nevin, W. A.; Janda, P.; Kobayashi, N.; Lever, A. B. P. *J. Chem. Soc., Chem. Commun.* **1987**, 699. (c) Nevin, W. A.; Hempstead, M. R.; Liu, W.; Leznoff, C. C.; Lever, A. B. P. *Inorg. Chem.* **1987**, *26*, 570. (d) Nevin, W. A.; Liu, W.; Greenberg, S.; Hempstead, M. R.; Marcuccio, S. M.; Melnik, M.; Leznoff, C. C.; Lever, A. B. P. *Inorg. Chem.* **1987**, *26*, 891. (e) Liu, W.; Hempstead, M. R.; Nevin, W. A.; Melnik, M.; Lever, A. B. P.; Leznoff, C. C. *J. Chem. Soc., Dalton Trans.* **1987**, 2511. (f) Minor, P. C.; Lever, A. B. P. *Inorg. Chem.* **1983**, *22*, 826. (g) Manivannan, V.; Nevin, W. A.; Leznoff, C. C.; Lever, A. B. P. *J. Coord. Chem.* **1988**, *19*, 139. (h) Leznoff, C. C.; Greenberg, S.; Marcuccio, S. M.; Minor, P. C.; Seymour, P.; Lever, A. B. P.; Tomer, K. B. *Inorg. Chim. Acta* **1984**, *89*, L35.

(9) (a) Simic-Glavaski, B.; Tanaka, A. A.; Kenney, M. E.; Yeager, E.; *J. Electroanal. Chem. Interfacial Electrochem.* **1987**, *229*, 285. (b) Mezza, T. M.; Armstrong, N. R.; Kenney, M. *J. Electroanal. Chem. Interfacial Electrochem.* **1984**, *176*, 259. (c) Mezza, T. M.; Armstrong, N. R.; Ritter, G. W.; Iafalice, J. P.; Kenney, M. E. *J. Electroanal. Chem. Interfacial Electrochem.* **1982**, *137*, 227.

(10) Wheeler, B. L.; Nagasubramanian, G.; Bard, A. J.; Schechtman, L. A.; Dininny, D. R.; Kenney, M. E. *J. Am. Chem. Soc.* **1984**, *106*, 7404. Anderson, A. B.; Gordon, T. L.; Kenney, M. E. *J. Am. Chem. Soc.* **1985**, *107*, 192. DeWulf, D. W.; Leland, J. K.; Wheeler, B. L.; Bard, A. J.; Batzel, D. A.; Dininny, D. R.; Kenney, M. E. *Inorg. Chem.* **1987**, *26*, 266.

0020-1669/90/1329-3415$02.50/0