protonated complexes have greater stability in alcohols and aprotic solvents such as DMF. These complexes react with good donors such as Cl^- and Me_2SO in aprotic solvents to give ring-opened complexes of the form *cis*-[Pt(diamine)(*C2*-HAsc)L]$^{+/0}$. The ring-opened chloro-ascorbate complex rapidly converts to the C2,O5 chelate in water. The ascorbate-C^2 ligand in the analogous S-bound Me_2SO complex was found to rearrange in aqueous solution to the oxygen-bound complex *cis*-[Pt(diamine)(*O3*-HAsc)(*S*-Me_2SO)]$^+$. The low pH (<1.5) required to produce a ring-opened complex in aqueous solution precludes the formation of stable complexes as the Pt-C bond hydrolyzes under these conditions.

Acknowledgment. We thank Arthur V. Miller for experimental assistance with many aspects of this work.

Registry No. **1**, 108007-37-0; **2**, 115160-60-6; **3**, 115160-62-8; **4**, 107984-67-8; **6**, 106160-56-9; **7**, 115224-85-6; **8**, 115185-33-6; **9**, 94042-09-8; **10**, 91897-69-7; **11**, 115185-31-4; **12**, 115185-29-0; **13**, 115185-59-6; **14**, 115203-85-5; **15**, 115185-55-2; **16**, 115185-34-7; **17**-($MeSO_3$), 115226-54-5; **17**(NO_3), 115226-55-6; **22**, 115224-86-7; [Pt-(*R*,*R*-dach)Cl_2], 61848-66-6; [Pt(^{15}en)(H_2O)Cl](NO_3), 115160-65-1; [Pt(^{15}en)Cl_2], 115160-63-9; [Pt(^{15}en)(H_2O)(*S*-Me_2SO)]$(NO_3)_2$, 115185-61-0; *cis*-[Pt($^{15}NH_3$)$_2$(H_2O)$_2$]$(NO_3)_2$, 78022-63-6; *cis*-[Pt-($^{15}NH_3$)$_2$(H_2O)Cl](NO_3), 78039-63-1; *cis*-[Pt($^{15}NH_3$)$_2$$Cl_2$], 78017-69-3; *cis*-[Pt($^{15}NH_3$)$_2$(*S*-Me_2SO)(H_2O)]$(NO_3)_2$, 115204-01-8; [Pt(*R*,*R*-dach)(*S*-Me_2SO)Cl]Cl, 115185-56-3; [Pt(*R*,*R*-dach)(*S*-Me_2SO)(H_2O)]$(NO_3)_2$, 115185-58-5; ^{195}Pt, 14191-88-9.

Supplementary Material Available: A listing of ^{13}C NMR data for the complexes relevant to this study (1 page). Ordering information is given on any current masthead page.

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Synthesis, Redox Behavior, Magnetic Properties, and Crystal Structure of a Nickel(II)-Semiquinone Adduct with an Unusually Strong Ferromagnetic Coupling

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$Ni(CTH)^{2+}$ (CTH = *dl*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) forms with the anion of 3,5-di-*tert*-butylsemiquinone, DTBSQ, stable complexes of formula [Ni(CTH)DTBSQ]Y (Y = ClO_4, $B(C_6H_5)_4$, PF_6). The formulation as a nickel(II)-semiquinone complex is confirmed by redox behavior and structural, spectral, and magnetic properties. The last show that the coupling between nickel(II), $S = 1$, and semiquinonate, $S = {}^1/_2$, is exceptionally strong in such a way that no evidence of population of the excited doublet state is observed at room temperature. The electronic structure of the complex is also studied through single-crystal EPR spectra. $[Ni(CTH)DTBSQ]PF_6$ crystallizes in the monoclinic system, space group $P2_1/n$. The lattice constants are a = 11.896 (4) Å, b = 32.98 (5) Å, c = 9.697 (9) Å, and β = 101.01 (8) with Z = 4. Least-squares refinement converged to a conventional R value of 0.0836. The asymmetric unit comprises a $Ni(CTH)DTBSQ^+$ cation and the PF_6^- anion.

Introduction

The search for conditions under which separate paramagnetic centers can interact strongly to yield the highest spin multiplicity state as the ground state has been actively undertaken. Interesting results have been obtained for aromatic hydrocarbons,[1,2] charge-transfer complexes,[3] and metal ion pairs,[4-6] as well as for systems containing coupled transition-metal ions and stable organic radicals.[7-13] The exchange interactions responsible for the parallel alignment of the spins are rather different. When the magnetic orbitals are orthogonal to each other, with fairly large overlap density at some common atom,[14] the exchange mechanism is called either direct or superexchange. A second type of interaction, which in the physical literature is called double exchange,[15] is observed in mixed-valence species.[16] In the case of organic radicals ferromagnetic coupling can be obtained either by Heitler-London exchange between positive spin density on a radical and negative spin density on another or by admixing of a virtual low excited state with the ground state for a chain of alternating radical-cation donors and radical-anion acceptors.[17,18]

The interactions between metal ions and stable organic radicals acting as a ligand are particularly simple to interpret. In this case in fact the magnetic orbitals of the two interacting centers are well-defined and, if they are kept orthogonal to each other, strong ferromagnetic coupling may be achieved. The magnetic interactions between metal and ligand spins in metalloporphyrin π cation radicals have been easily justified on the basis of these considerations.[11]

Among the organic radical ligands there has been a growing interest in nitroxides[7,8,10,19-23] and semiquinones.[24-31] The latter

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are much stronger ligands than the former; therefore, any interaction may be predicted to be more intense for semiquinones than for nitroxides. Recently a copper–semiquinone complex was reported to show a fairly strong ferromagnetic coupling, with the triplet lying ca. 200 cm^{-1} below the singlet.[12] Since the magnetic orbital of the semiquinone is π^*, the interaction is expected to be even stronger with octahedral nickel(II) because the d^8 metal ion has two σ magnetic orbitals, which should be orthogonal to the magnetic orbital of the ligand.

The Ni(CTH)$^{2+}$ (CTH = *dl*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) cation is well-known to form stable cis-octahedral adducts with a variety of ligands;[32] therefore, we decided to synthesize semiquinone adducts of this acceptor in order to test if the predictions of strong ferromagnetic coupling were correct.

In this paper the synthesis, the crystal structure, and the physical properties of solid complexes containing the Ni(CTH)DTBSQ$^+$ cation (DTBSQ = anion of 3,5-di-*tert*-butylbenzosemiquinone) are reported.

Experimental Section

Synthesis of [Ni(CTH)DTBSQ]Y (Y = ClO$_4$, PF$_6$, BPh$_4$). These complexes were obtained by the same general procedure. A 2-mmol sample of sparingly soluble Ni(CTH)Y$_2$ (Y = ClO$_4$ or PF$_6$) (α form)[33] was suspended in a warm methanolic solution (30 mL) containing an equimolar amount of 3,5-di-*tert*-butylcatechol. The suspension was stirred, and 4 mmol of sodium hydroxide in methanol was slowly added. Following the basic addition, the yellow solid disappeared and the color of the solution turned to deep brown. The addition of an aqueous solution of sodium perchlorate, potassium hexafluorophosphate, or sodium tetraphenylborate induced the precipitation of a black-green solid.

The perchlorate derivative was recrystallized from dichloromethane–*n*-pentane mixtures, whereas the hexafluorophosphate and the tetraphenylborate were conveniently purified by recrystallization from either methanol or a methanol–water mixture.

Anal. Calcd for [Ni(CTH)(DTBSQ)]ClO$_4$, C$_{30}$H$_{56}$ClN$_4$NiO$_6$: C, 54.35; H, 8.51; N, 8.45. Found: C, 54.1; H, 8.8; N, 8.4. Calcd for [Ni(CTH)(DTBSQ)]PF$_6$, C$_{30}$H$_{56}$F$_6$N$_4$NiO$_2$P: C, 50.86; H, 7.97; N, 7.91. Found: C, 51.4; H, 8.3; N, 7.9. Calcd for [Ni(CTH)(DTBSQ)]BPh$_4$·2CH$_3$OH, C$_{56}$H$_{84}$N$_4$NiO$_4$B: C, 70.90; H, 8.91; N, 5.90. Found: C, 71.3; H, 8.7; N, 5.9.

The following procedure was found to be more appropriate for obtaining a pure sample of the perchlorate derivative. The green solid [Ni(CTH)(OH)]$_2$(ClO$_4$)$_2$·*n*H$_2$O, obtained by treating the yellow α-diperchlorate with concentrated aqueous sodium hydroxide, was allowed to react with a dichloromethane solution of the catechol. The solution was filtered, and *n*-pentane was added until the solution became turbid. A microcrystalline solid appeared in few minutes.

Attempts to obtain the same compounds starting from nickel(I) derivatives and the parent quinone under inert atmosphere were unsuccessful.

X-ray Structure Determination. A crystal of dimensions 0.50 × 0.35 × 0.15 mm was mounted on a Philips PW 1100 automated diffractometer equipped with a Mo Kα X-ray tube and a graphite monochromator for crystal and intensity data collection. Details of crystal and experimental data are given in Table I. Cell parameters were obtained from 25 reflections in the range $2.5° < \theta < 20°$. The intensities of three test reflections were measured every 120 min, revealing no decay during the data collection.

Corrections for Lorentz and polarization effects but not for absorption were made. Systematic absences ($h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$) were only compatible with the monoclinic space group $P2_1/n$.

Table I. Crystal Data and Experimental Parameters for [Ni(CTH)DTBSQ]PF$_6$

formula	NiC$_{30}$H$_{56}$F$_6$N$_4$O$_2$P
mol wt	702.41
cryst system	monoclinic
space group	$P2_1/n$
cell params	a = 11.896 (4) Å, b = 32.98 (5) Å, c = 9.697 (9) Å, β = 101.01 (8)°, V = 3736.08 Å^3
density (calcd)	1.25 g cm^{-3}
cryst size	0.50 × 0.35 × 0.15 mm
temp	295.5 K
radiation	wavelength = 0.7107 Å (Mo Kα); graphite monochromator
scan	mode: ω–2θ range: $2.5° < \theta < 25°$ speed: 0.5°/min
test reflns	3 reflns every 120 min
measd reflns	$-11 < h < 10$, $0 < k < 34$, $0 < l < 10$ total no.: 5331 $F > 6\sigma(F)$: 1675
refinement	R = 0.0836 R_w = 0.0764

The Patterson map allowed the localization of the nickel atom; the positions of the other non-hydrogen atoms were found by successive Fourier and difference Fourier syntheses.

The structural parameters were refined by using the SHELX76 package[34] and assuming the nickel, the carbons of the methyl substituents on the CTH, the carbons of the *t*-Bu group on the DTBSQ ligand, and the atoms of the PF$_6^-$ anion to be anisotropic.

The final least-squares refinement, performed by introducing hydrogen atoms in idealized positions, converged with R = 0.0836. The presence in the difference Fourier synthesis of at least two extra peaks at a distance from the phosphorus atom corresponding to that of a P–F bond seems to indicate the presence of disorder in the PF$_6^-$ anion. We attributed to this the high value of R and the particularly large values of the thermal ellipsoids of the fluorine atoms resulting from the anisotropic refinement. The presence of disorder in the structure is also confirmed by the decay of the intensities for θ values over 22.5°. Attempts to find models of the disorder in the PF$_6^-$ moiety, attributing fractional site occupation factors to the different peaks present in the difference Fourier synthesis, resulted in failure, showing that the disorder present in our crystal is not easy to rationalize.

Physical Measurements. Polycrystalline-powder and single-crystal EPR spectra were recorded with a Bruker ER200 spectrometer working at X-band frequency. Single-crystal spectra were obtained by mounting a crystal, previously oriented on a CAD4 Enraf-Nonius diffractometer, on a Perspex rod and rotating it with a one-circle goniometer.

Variable-temperature magnetic susceptibility data were measured by using a fully automatized Aztec DSM5 susceptometer equipped with an Oxford CF1200S continous-flow cryostat and a Bruker B-E15 electromagnet. The apparatus was calibrated by measuring the magnetic susceptibilities of a pure sample of (NH$_4$)$_2$Mn(SO$_4$)$_2$·6H$_2$O at several temperatures between 4.2 and 300 K. The susceptometer was operated at a magnetic field strength of 13.5 T. Diamagnetic corrections were estimated from Pascal's constants and subtracted from the experimental susceptibility data.

Electronic spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer. IR spectra were recorded on a Perkin-Elmer 283 infrared spectrometer.

Cyclic voltammetry experiments used an electrochemical unit consisting of an Amel 553 potentiostat equipped with the Amel 863, 560/A, 568, and of a classical three-electrode cell. The working electrode was a platinum microsphere; the auxiliary electrode was a platinum disk and an SCE reference electrode. Before each experiment the solution was carefully deareated with a nitrogen flow. All potentials reported here are referenced against the SCE, and they were not corrected for junction potential and/or IR potential drops due to the internal resistance of the system.

Results

Synthesis of the Complexes. Air oxidation of basic solutions containing the Ni(CTH)$^{2+}$ cation (α form) and 3,5-di-*tert*-butylcatechol in equimolar amounts yields brown solutions from which black-green solid derivatives that analyze satisfactorily for

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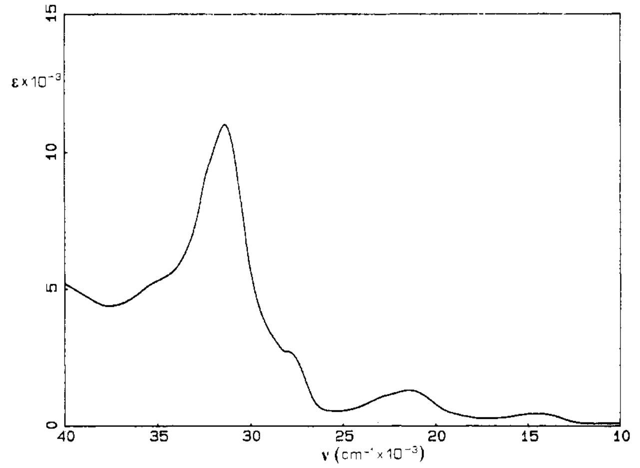

Figure 1. Electronic spectrum of $[Ni(CTH)DTBSQ]PF_6$ in 1,2-dichloroethane solution.

$[Ni(CTH)DTBSQ]Y$ ($Y = ClO_4$, PF_6, BPh_4) are obtained by adding aqueous solutions containing a slight excess of the appropriate anion. All of these compounds are sparingly soluble in water but very soluble in the most common organic solvents.

The perchlorate and hexafluorophosphate complexes are crystalline solids and are stable in the atmosphere. They can be stored for long periods without any change of their physical properties and chemical reactivities. By contrast, the tetraphenylborate derivative is not stable and decomposes in a few days. Thus, the characterization of the $Ni(CTH)DTBSQ^+$ cation was carried out for the first two derivatives only.

We suggest that the oxidation occurs at the catecholate ligand, on the basis of spectral and structural evidence. The infrared spectra of coordinated catecholates are characterized by an intense absorption near 1480 cm^{-1} (ring stretching mode involving the C–C bond between the coordinated oxygen atoms) and 1250 cm^{-1} (C–O stretching mode).[29,35-37] Coordinated semiquinones on the other hand exhibit a band in the range 1420–1460 cm^{-1}, attributable to the C–O stretching mode.[29,37,38] In addition, C–O absorption is also observed near 1250 cm^{-1}, although it is weaker than that observed for the catecholate derivatives. Finally, coordinated quinones are expected to show C=O stretching frequencies in the range 1600–1620 cm^{-1}, about 60 cm^{-1} lower than the values observed for the free ligand.[39] In the spectra of our compounds the lack of strong absorptions in the 1600- and 1250-cm^{-1} regions indicates, on the basis of the above considerations, the absence of coordinate *o*-quinone and catecholate anion, thus indirectly suggesting semiquinone coordination. Unfortunately, the strong broad absorption of the macrocycle in the region near 1450 cm^{-1} precludes the possibility of observing directly the C–O stretching mode of vibration. However, the presence of a weak band at 1250 cm^{-1} might support this suggestion.

Table II. Positional Parameters ($\times 10^4$) and Isotropic Thermal Factors ($Å^2 \times 10^3$) for Non-Hydrogen Atoms of $[Ni(CTH)DTBSQ]PF_6$[a]

	x	y	z	U_{eq}/U_{iso}
Ni	2320 (2)	1405 (1)	2912 (2)	45
N1	505 (10)	1343 (5)	2150 (14)	52 (4)
N2	1997 (11)	1692 (4)	4714 (14)	52 (4)
N3	4078 (11)	1547 (4)	3755 (13)	45 (4)
N4	2206 (10)	1902 (4)	1555 (14)	45 (4)
O1	2675 (8)	872 (3)	4013 (11)	47 (3)
O2	2437 (8)	1014 (3)	1284 (11)	47 (3)
C1	−271 (16)	1235 (6)	3126 (20)	67 (6)
C2	−101 (14)	1508 (6)	4400 (17)	56 (6)
C3	1063 (14)	1492 (6)	5396 (17)	59 (6)
C4	3088 (15)	1678 (7)	5714 (21)	76 (7)
C5	4052 (15)	1810 (6)	4987 (19)	60 (6)
C6	4831 (14)	1700 (5)	2813 (19)	53 (5)
C7	4270 (15)	2046 (5)	1868 (18)	59 (6)
C8	3180 (13)	1969 (5)	820 (17)	46 (5)
C9	1122 (14)	1852 (6)	565 (19)	57 (6)
C10	183 (14)	1722 (5)	1329 (19)	54 (5)
C11	−26 (18)	794 (6)	3549 (22)	79 (7)
C12	−1558 (17)	1273 (6)	2365 (23)	106 (8)
C13	958 (21)	1687 (7)	6756 (24)	116 (9)
C14	5105 (15)	1344 (6)	1912 (19)	58 (5)
C15	6002 (14)	1831 (6)	3680 (20)	70 (6)
C16	2994 (16)	2319 (5)	−223 (19)	61 (6)
C17	2780 (12)	565 (5)	3189 (16)	39 (5)
C18	2996 (13)	163 (5)	3734 (20)	48 (5)
C19	2993 (15)	−138 (6)	2756 (20)	60 (6)
C20	2807 (14)	−59 (7)	1363 (22)	64 (6)
C21	2626 (13)	311 (5)	691 (18)	46 (5)
C22	2603 (21)	649 (5)	1706 (16)	40 (5)
C23	3158 (21)	−581 (7)	3346 (25)	81 (7)
C24	3325 (34)	−613 (7)	4917 (26)	148
C25	2100 (22)	−825 (7)	2727 (43)	123
C26	4180 (25)	−770 (9)	2866 (40)	161
C27	2417 (19)	369 (7)	−825 (22)	69 (6)
C28	2522 (37)	−29 (9)	−1604 (40)	162
C29	1210 (22)	525 (11)	−1322 (28)	125
C30	3235 (26)	674 (8)	−1270 (28)	108
P	1642 (6)	2929 (2)	3754 (7)	78
F1	503 (12)	3167 (5)	3711 (18)	161
F2	1774 (19)	2842 (9)	5254 (20)	237
F3	2777 (14)	2704 (5)	3775 (20)	204
F4	1623 (17)	3046 (9)	2314 (18)	237
F5	2280 (17)	3295 (7)	4283 (30)	251
F6	996 (15)	2562 (6)	3345 (44)	333

[a] Standard deviations in the last significant digit are in parentheses. Standard deviations in the thermal factors are indicated only for isotropic atoms.

Table III. Selected Bond Distances (Å) and Angles (deg) for $[Ni(CTH)DTBSQ]PF_6$[a]

	Distances		
Ni–N1	2.15 (1)	Ni–N2	2.08 (2)
Ni–N3	2.15 (1)	Ni–N4	2.09 (1)
Ni–O1	2.06 (1)	Ni–O2	2.06 (1)
O1–C17	1.31 (2)	O2–C22	1.28 (2)
C17–C18	1.44 (2)	C22–C21	1.49 (2)
C18–C19	1.37 (2)	C21–C20	1.38 (2)
C19–C20	1.35 (2)	C17–C22	1.44 (2)
	Angles		
N2–Ni–N1	89.8 (5)	N3–Ni–N1	172.3 (6)
N4–Ni–N1	85.3 (5)	N4–Ni–N2	99.8 (6)
N4–Ni–N3	90.5 (5)	O1–Ni–N1	100.9 (5)
O1–Ni–N2	90.3 (5)	O1–Ni–N3	84.3 (5)
O1–Ni–N4	168.1 (5)	O2–Ni–N1	83.6 (5)
O2–Ni–N2	167.0 (5)	O2–Ni–N3	103.0 (5)
O2–Ni–N4	90.8 (5)	O2–Ni–O1	79.9 (4)
Ni–O1–C17	112 (1)	Ni–O2–C22	112 (1)
O1–C17–C22	117 (2)	O2–C22–C17	119 (2)

[a] Standard deviations in the last significant digits are in parentheses.

The electronic spectrum of a 1,2-dichloroethane solution of $[Ni(CTH)(DTBSQ)]PF_6$ (Figure 1) shows bands at 12 950 (log $\epsilon = 2.66$), 21 170 (log $\epsilon = 3.12$), and 32 380 cm^{-1} (log $\epsilon = 4.02$), with shoulders at ca. 23 500, 28 500, 33 500, and 36 800 cm^{-1}. Owing to their intensities, none of the observed absorptions can be attributed to d–d transitions but must be related to either internal ligand transitions involving the DTBSQ electronic levels or charge-transfer transitions associating the metal ion and the DTBSQ moiety itself. The similarity of this spectrum to that reported for the free 3,5-di-*tert*-butylsemiquinone[40] again is in agreement with the formulation of this compound as a nickel(II)–semiquinone adduct. Tentatively, the absorption band oc-

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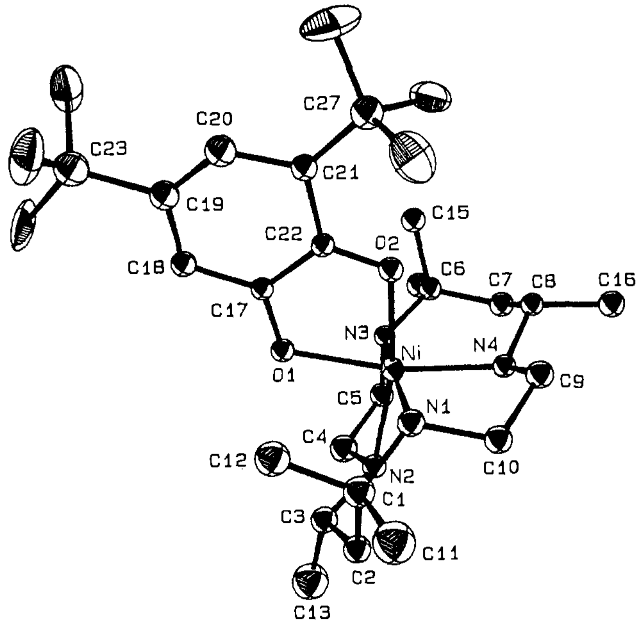

Figure 2. View of the structure of the $[Ni(CTH)DTBSQ]^+$ cation.

curring at 21 000 cm^{-1} may be attributed to a charge-transfer transition.

Description of the Structure. The crystal structure of the title compound comprises $Ni(CTH)DTBSQ^+$ units, showing a distorted cis-octahedral coordination geometry around the nickel ion, and PF_6^- ions. A view of the structure of the cation is shown in Figure 2. Atomic coordinates, bond distances, and bond angles are reported in Tables II and III.

The two oxygen atoms of the semiquinone ligand occupy two cis-equatorial positions of the inner coordination sphere of the metal; the two Ni–O distances, which are equal to 2.06 (1) Å, compare well with the values (ranging between 2.028 and 2.100 Å) previously reported for the one structure of a nickel–semiquinone complex thus far published.[41] The four nitrogen atoms of the CTH ligand occupy the two remaining equatorial and the two axial positions. The two axial bond distances, Ni–N1 and Ni–N3 (2.15 (1) Å), are significantly longer than the equatorial ones, suggesting that the coordination polyhedron can be described as an elongated octahedron. The metal–nitrogen distances are in agreement with those of analogous cis-octahedral complexes of nickel(II) with CTH.[42–45]

The semiquinone ligand is rather asymmetric, although the relatively large indeterminateness in the bond distances and angles does not allow us to speculate on this point. So, for instance, the carbon–oxygen distances, C17–O1 = 1.31 (1) Å and C22–O2 = 1.28 (2) Å, although different from each other, overlap within the standard deviation. These values may be compared with 1.302 and 1.294 Å in $Mn_4(DTBSQ)_8$[24] and with 1.297 Å in the semiquinone ligand of the Co(bpy)(DTBCat)(DTBSQ)[41] complex, which have been considered as typical of the semiquinone ligand. The same conclusion can be reached also from the C17–C22 bond distance, 1.44 (2) Å, which is again typical of semiquinones.[24,37–41] The six-membered ring of the DTBSQ is fairly flat, the maximum deviation being 0.01 Å, and forms an angle of about 10° with the N2-N4-Ni-O1-O2 least-squares plane.

The shortest distance between nickel ions in the cell is 11.8 Å. A view of the unit cell in Figure 3 shows the stacking between two semiquinone units of two different cations. The distance between the planes of the two rings is 7.37 Å, much larger than would be required for any interaction between them.[41]

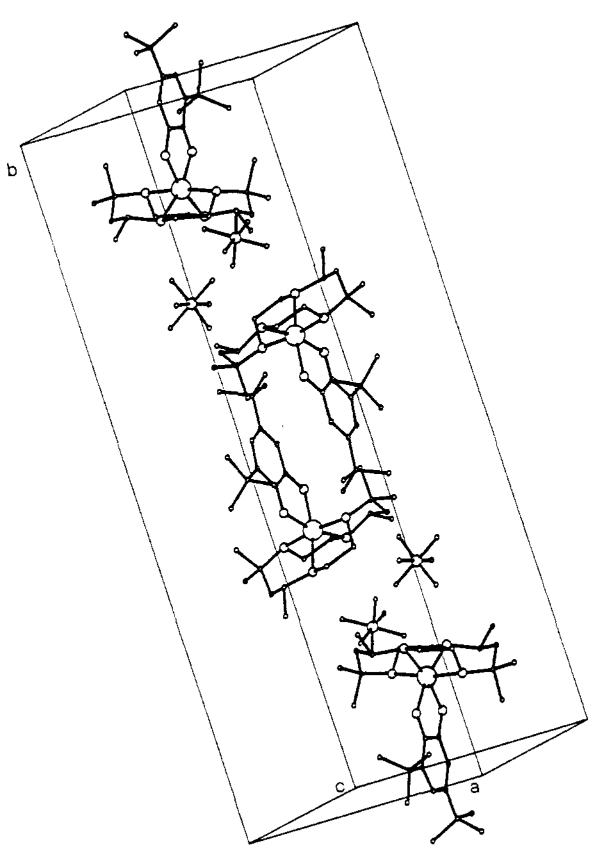

Figure 3. Unit cell view of $[Ni(CTH)DTBSQ]PF_6$.

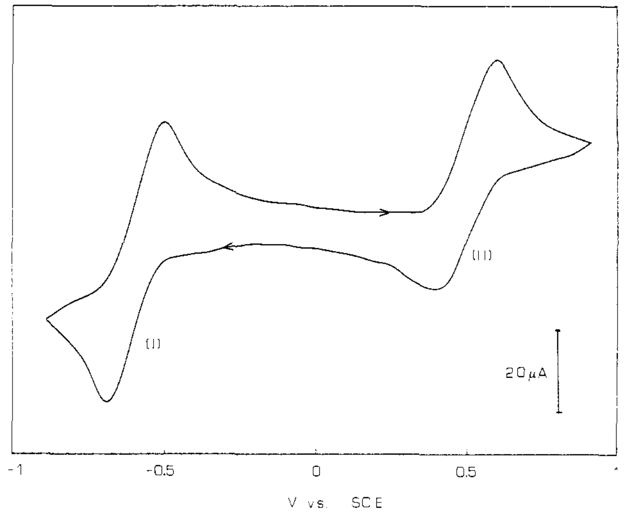

Figure 4. Cyclic voltammogram of $[Ni(CTH)DTBSQ]PF_6$ in 1,2-dichloroethane 0.1 M in $(NBu_4)PF_6$.

Electrochemistry. The cyclic voltammogram of a deaerated dichloroethane solution of $[Ni(CTH)DTBSQ]PF_6$ shows two redox couples (Figure 4), at −0.58 and +0.48 V. The potentials are taken as the average of anodic and cathodic peak potentials vs SCE. These two redox processes can be reasonably attributed to the semiquinonate–catecholate (I) and to the quinone–semiquinonate (II) couples, since oxidation and reduction processes involving the nickel(II) ion are expected to occur at significantly more positive and more negative potentials, respectively.[47,48] The electrochemical behavior is in agreement with the two ligand-

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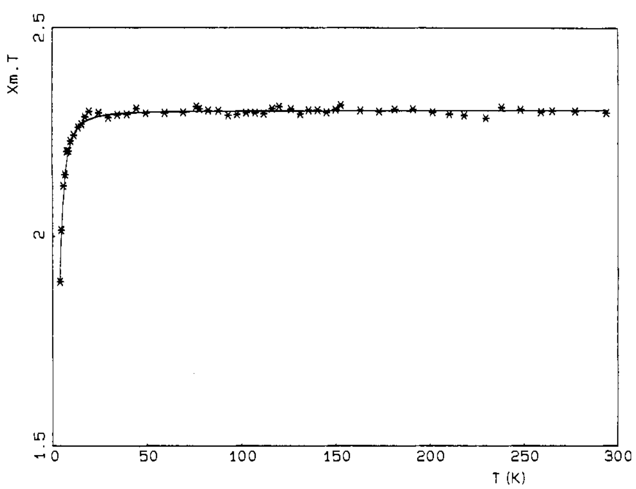

Figure 5. Variation of the χT product with temperature in the range 4–300 K for [Ni(CTH)DTBSQ]PF_6. The curve represents the best fit (see text).

centered one-electron-transfer processes observed for other metal dioxole adducts.[49-52] If this interpretation is correct, it can be concluded that the coordinated ligands undergo redox processes at potentials that are about 0.7–0.9 V more positive compared with those of the free ligands.[40]

Cyclic voltammetry at scan rates v ranging from 0.02 to 0.5 V s^{-1} shows that the semiquinonate–catecholate redox process at –0.58 V has the typical features of an uncomplicated reversible one-electron charge transfer, the ratio i_c/i_a being equal to 1 and the ratio $i/v^{1/2}$ being constant. Furthermore, the peak-to-peak separation approaches the value of 60 mV at low scan rates.[53]

The voltammetric analysis of the redox process at +0.48 V reveals that $i_c/i_a \leq 1$, the ratio decreasing as the scan rate is lowered. Furthermore, the peak-to-peak separation strongly increases with increasing scan rate (being 130 mV at 0.02 V s^{-1} and 280 mV at 0.5 V s^{-1}).

Finally, as the i_c value decreases, a new reduction peak appears in the voltammogram. These data indicate that a homogeneous chemical reaction follows the one-electron reversible semiquinonate–quinone oxidation. The occurrence of an increasing reduction signal at –0.45 V could be attributed to the reduction of the free quinone ligand, and thus the nonreversible character of the couple could be reasonably attributed to the instability of the Ni–DTBSQ adduct. A similar study carried out in acetonitrile indicates that in this medium the couple is irreversible. Thus it can be concluded that the synthesis of a stable Ni(CTH)(DTBSQ)$^+$ adduct is not possible at room temperature.

Magnetic Susceptibility Data. The temperature dependence of the magnetic susceptibility of [Ni(CTH)DTBSQ]PF_6 in the range 4–300 K is shown in Figure 5. The χ^{-1} vs T curve follows Curie–Weiss behavior, with $C = 2.279$ emu mol^{-1} K and $\Theta = 0.16$ K. The C value agrees well with an $S = {}^3/_2$ spin, and $g = 2.201$. The χT vs T curve is essentially flat in most of the temperature range, the value being 2.28 emu mol^{-1} K. There is no significant deviation in the high-temperature range, while a slight decrease of the χT value is observed at the low-temperature edge. The magnetic data for the other derivatives are similar to those of the hexafluorophosphate in the range 77–300 K.

EPR Spectra. The polycrystalline-powder spectrum of [Ni(CTH)(DTBSQ)]PF_6 at X-band frequency is shown in Figure 6. It is typical of a Kramers doublet with the principal g values $g_1 = 5.8$, $g_2 = 2.4$, and $g_3 = 1.7$.

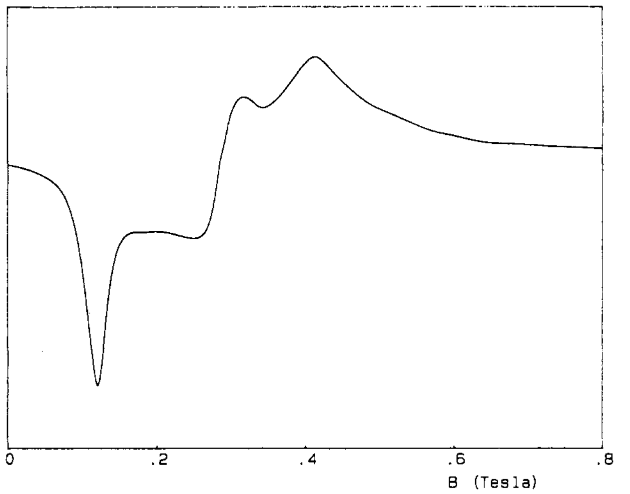

Figure 6. X-Band polycrystalline-powder EPR spectrum of [Ni(CTH)DTBSQ]PF_6 at room temperature.

The spectra are practically independent of temperature down to 4.2 K. The spectra of the other derivatives are also similar, with the following principal values: [Ni(CTH)DTBSQ]ClO_4, $g_1 = 5.0$, $g_2 = 3.4$, $g_3 = 1.9$; [Ni(CTH)DTBSQ]BPh_4, $g_1 = 5.7$, $g_2 = 2.6$, $g_3 = 1.8$.

In order to obtain the principal directions of the **g** tensor, we recorded single-crystal spectra of [Ni(CTH)DTBSQ]PF_6. Only one signal was observed for every crystal orientation with very broad lines. Very accurate attempts were made to detect other transitions at room temperature, but they were unsuccessful. One principal direction is parallel to b, the other two being in the ac plane. The g_b value is 2.4, while in the ac plane the two extremes correspond to $g = 1.7$ and 5.6. These values compare well with those obtained from the powder spectra. The principal direction of the lowest g value makes an angle of ca. 4° with a^*.

Discussion

The magnetic and EPR data of [Ni(CTH)DTBSQ]PF_6 provide a clear indication that only one spin multiplet is populated up to room temperature. Since the value of the Curie constant clearly indicates that three unpaired electrons are present, we must conclude that a strong ferromagnetic coupling between nickel(II), $S = 1$, and the semiquinonate ligand, $S = {}^1/_2$, is operative. The alternative formalism as a nickel(III)–catecholate complex, already discarded on the basis of structural and spectral data, would require a high-spin configuration of the nickel(III) ion, which has never been observed. The value of the exchange-coupling constant J cannot be accurately obtained because we do not observe any significant deviation from Curie behavior at high temperature, but a lower limit can be established. As the energy separation between the ground quartet and the excited doublet is ${}^3/_2J$, if we assume a J value of 400 cm^{-1}, a χT value of 2.27 emu K mol^{-1} at 100 K and of 2.22 emu K mol^{-1} at 300 K are calculated, setting $g = 2.20$. The experimental χT values do not show such a behavior; therefore, 400 cm^{-1} can be estimated as a lower limit to the true value of J. A confirmation of this comes also from the EPR spectra, where we observe only transitions within the $S = {}^3/_2$ manifold, and not those of $S = {}^1/_2$, even at room temperature.

The low-temperature data show a significant decrease of χT, which at 4.2 K for [Ni(CTH)DTBSQ]PF_6 reaches the value of 1.89 emu mol^{-1} K. In principle, this may be due either to intermolecular effects or to the zero-field splitting of the ground quartet state. On the basis of EPR evidence (see below), we prefer the latter hypothesis. A quantitative fit was obtained using for χ the expression valid for $S = {}^3/_2$ in a rhombic environment. The best fit values are $g = 2.22$ (1), $|D| = 2.54$ (3) cm^{-1}, and $E/D = 0.30$ (5).

The EPR spectra are typical for a spin $S = {}^3/_2$ with a zero-field splitting larger than the microwave quantum. The signal that is observed can be attributed to transitions between the $M_S = \pm{}^1/_2$ states. The fact that the transitions within the $M_S = \pm{}^3/_2$ states

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are not observed can be due to their intensities, which are expected to be much less than the others, even in a rhombic environment.

In a monoclinic cell two magnetically nonequivalent sites are expected to be present, but we observe only one signal in all the crystal orientations. This shows that intermolecular exchange is operative to average the two signals. Therefore, we cannot compare directly the crystal principal directions with the molecular ones. However, if we look at the structure, we see that the overall symmetry of the cation is not far from C_{2v}, the symmetry axis being the bisector of the O1–Ni–O2 angle. This axis makes an angle of ca. 15° with *b*, which is sufficiently small to make the principal axes of the two sites almost parallel to each other, in such a way that even a comparatively small intermolecular exchange is enough to average the two signals.

From the observed principal directions we see that g_2 is parallel to *b*, i.e. very close to the bisector of the O1–Ni–O2 angle, g_3 is orthogonal to it in the equatorial plane of the complex, and g_1 is very close to the N1–Ni–N3 direction.

The observed *g* values are effective *g* values for the fictitious $S = {}^1/_2$ spin. From these, it is possible to obtain the true *g* values of the $S = {}^3/_2$ spin and the rhombic asymmetry parameter E/D on the assumption that the **g** tensor is axial.[54] With this procedure, we calculate for the hexafluorophosphate derivative $g_{\parallel} = 2.17$, $g_{\perp} = 2.17$ and $E/D = 0.293$. The identity of the $g_{\parallel}$ and $g_{\perp}$ values is most probably fortuitous. The *g* and E/D values compare well with the analysis of the magnetic data.

If we assume that the system is in the strong-exchange regime, i.e. $J \gg D$, we can calculate the *g* values of nickel from those of the $S = {}^3/_2$ state,[55] finding $g_{Ni} = 2.25$, in good agreement with the values expected for octahedral nickel(II) complexes. A similar analysis can be performed also on the perchlorate and the tetraphenylborate derivatives, yielding $g_{Ni} = 2.19$ and $E/D = 0.128$ for the former and $g_{Ni} = 2.22$ and $E/D = 0.263$ for the latter. The main difference in the series is given by the E/D ratio, which reflects the symmetry of the ligand field around the nickel ion.

The angular overlap model is extremely well suited for interpreting the spectral and magnetic behavior of low-symmetry transition-metal complexes.[56] We performed simple calculations for nickel(II) in a C_{2v} symmetry environment. We fixed the values of the e_σ parameters of the nitrogen donors, on the basis of the comparison with other nickel complexes,[56] and let the e_σ and e_π parameters of the semiquinone ligand vary freely. We found that essentially only e_π can affect the E/D ratio, thus suggesting that the observed variation in the series of complexes may be due to variations in this parameter. The best agreement with the experimental values of the *g* and E/D values can be obtained for positive e_π value, i.e. when the semiquinone orbitals determine a π-antibonding effect on the nickel orbitals.[57]

The estimated value of $J > 400$ cm^{-1} is the largest so far reported for molecular compounds involving metal ions. A ground quartet state, with no evidence of populated excited doublet states, was reported for a nickel(I)–nickel(II) pair.[58,59] However, in that case the stabilization of the high-spin state is due to the mixed-valence nature of the pair rather than to exchange interactions.

The origin of such a large coupling can be easily understood on the basis of an orbital model. The magnetic orbitals of nickel(II) are d_{xy} and d_{z^2}, both with a σ-bonding character, while the magnetic orbital of the semiquinone is a π^* orbital. According to the geometry observed in the structure of [Ni(CTH)DTBSQ]PF_6, the orthogonality between the two sets of orbitals is preserved; therefore, according to the well-established rules,[14,60] a ferromagnetic coupling must be observed. In this respect, the situation here is similar to that observed for instance in copper(II)–oxovanadium(IV)[4,6] and copper(II)–chromium(III)[5] pairs and in copper–semiquinonate complexes.[11]

According to the above analysis, it seems established that both experimentally and theoretically a strong ferromagnetic interaction can occur between octahedral nickel(II) and a semiquinone, provided that they bind in such a way to keep the relative magnetic orbitals orthogonal. However against this stand the reported[41] magnetic properties of Ni(phenSQ)$_2$(py)$_2$, where two semiquinonates bind to nickel, keeping their π^* orbitals approximately orthogonal to the magnetic orbitals of the metal. In fact, in that case it was suggested that the coupling between nickel(II) and the semiquinonate is exceedingly small, and the observed temperature dependence of χT was attributed to the intermolecular interaction between two semiquinonates that have their molecular planes parallel at a distance of 3.3 Å. We want to show here that an alternative explanation of the magnetic data of Ni(phenSQ)$_2$(py)$_2$[41] is possible, which gives a coupling constant between nickel and semiquinonate that is closer to our present interpretation of the magnetic data of Ni(CTH)DTBSQ$^+$. Indeed, the χT value is substantially constant at high temperature and decreases gradually at low temperature. The room-temperature value of 2.205 emu K mol^{-1} is very close to the value expected for free spin with $S = {}^3/_2$, 1.875 emu mol^{-1} K. Although this may be fortuitous, a possible explanation can be attempted by assuming that the intermolecular interaction between the two semiquinonates that have short contacts is strong enough to essentially pair the spins in such a way that the two semiquinonate ligands must be considered as a single diamagnetic ligand. In this hypothesis, if the interaction between the nickel ion and the remaining semiquinonate is ferromagnetic, as in Ni(CTH)DTBSQ$^+$, then the room-temperature χT value corresponds to $S = {}^3/_2$, with $g = 2.17$. The decrease of χT on a decrease in temperature may be due to weak antiferromagnetic superexchange interaction between the two Ni(phenSQ)$_2$(py)$_2$ moieties or to intermolecular exchange. In order to test the feasibility of this hypothesis, we performed extended Hückel calculations on two semiquinonates possessing the same relative geometry observed in Ni(phenSQ)$_2$(py)$_2$. We found that the overlap between the two π^* magnetic orbitals at a distance of 3.33 Å is 0.0195. For comparison, we also calculated the overlap between the two π^* orbitals of two nitroxides at a distance of 3.56 Å and found a value of 0.0019. Since the latter were found to interact antiferromagnetically[61] with $J = 15$ cm^{-1} and since the antiferromagnetic component of J, J_F, is expected to be proportional to square of the overlap, these calculations do suggest a strong pairing of the spins on the two semiquinonates.

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Registry No. [Ni(CTH)(DTBSQ)]ClO_4, 115140-63-1; [Ni(CTH)(DTBSQ)]PF_6, 115223-63-7; [Ni(CTH)(DTBSQ)]BPh_4, 115223-64-8; Ni(CTH)$(ClO_4)_2$, 51372-01-1; Ni(CTH)$(PF_6)_2$, 115224-77-6; Ni(CTH)$(BPh_4)_2$, 115223-65-9; [Ni(CTH)(OH)]$_2$$(ClO_4)_2$, 115140-65-3; 3,5-di-*tert*-butylcatechol, 1020-31-1.

Supplementary Material Available: Tables SI and SII, listing thermal parameters and hydrogen positional parameters for [Ni(CTH)DTBSQ]PF_6 (4 pages); Table SIII, listing calculated and observed structure factors (8 pages). Ordering information is given on any current masthead page.

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