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Antiferromagnetic Coupling in a Six-Coordinate High Spin Cobalt(II)–Semiquinonato Complex

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The 3,5-di-*tert*-butyl-catecholato and 9,10-phenanthrenecatecholato adducts of the cobalt-tetraazamacrocycle complex Co(Me$_4$cyclam)$^{2+}$ (Me$_4$cyclam = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) were synthesized and oxidized. The oxidation reaction products were isolated in the solid state as hexafluorophosphate derivatives. Both these complexes can be formulated as 1:1 cobalt(II)–semiquinonato complexes, that is, Co(Me$_4$cyclam)(DBSQ)PF$_6$ (**1**) and Co(Me$_4$cyclam)(PhSQ)PF$_6$ (**2**), in the temperature range 4–300 K, in striking contrast with the charge distribution found in similar adducts formed by related tetraazamacrocycles. The synthesis strategy and the structural, spectroscopic, and magnetic properties are reported and discussed. The crystallographic data for **2** are as follows: monoclinic, space group $P2_1$/a, no. 14, $a = 14.087(4)$ Å, $b = 15.873(4)$ Å, $c = 14.263$ (7) Å, $\alpha = 89.91(3)°$, $\beta = 107.34(2)°$, $\gamma = 90.08(2)°$, $Z = 4$. Both these complexes are characterized by triplet electronic ground states arising from the antiferromagnetic coupling between the high-spin d^7 metal ion and the radical ligand.

Introduction

Among the molecular systems that undergo valence tautomerism, cobalt−dioxolene complexes are the most attractive from a magnetic point of view.[1−19] In all of the examples reported to date, the interconversion involves an intramolecular electron transfer between a six-coordinate diamagnetic cobalt(III) metal ion and a coordinated catecholato ligand yielding a cobalt(II)−semiquinonato species, the metal ion being in the high spin electronic configuration. In the simplest case, that is, a 1:1 cobalt−dioxolene complex, the valence tautomeric transition is associated with a change from a diamagnetic to a paramagnetic compound. As observed for spin crossover systems, the process is essentially entropy driven, the cobalt(III)−catecholato species and the cobalt(II)−semiquinonato one being favored at low and high temperatures, respectively. The magnetic properties of the cobalt(II)−semiquinonato species, however, are rather poorly understood, and their magnetic ground state is unknown. This deficiency is essentially due to complications associated with the electronic configuration of the metal ion which in octahedral coordination has a large unquenched orbital contribution. The nature of the magnetic interaction can be obtained in principle from the temperature dependence of the magnetic susceptibility, but at low temperature, most six-coordinate cobalt−dioxolene complexes are low spin cobalt(III) derivatives. Some of us in the past predicted that an antiferromagnetic exchange interaction should be operative in a cobalt(II)−semiquinonato complex,[20] and this prediction

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(1) Pierpont, C. G.; Lange, C. W. *Prog. Coord. Chem.* **1993**, *41*, 381.
(2) Gütlich, P.; Dei, A. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2734.
(3) Buchanan, R. M.; Pierpont, C. G. *J. Am. Chem. Soc.* **1980**, *102*, 4951.
(4) Adams, D. M.; Dei, A.; Rheingold, A. L.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1993**, *115*, 8221.
(5) Hendrickson, D. N.; Adams, D. M.; Wu, C.-C.; Aubin, S. M. J. In *Magnetism: a supramolecular function*; Kahn, O., Ed.; Kluwer Academic: Dordrecht, The Netherlands, 1996; C, 484, p 357.
(6) Abakumov, G. A.; Cherkasov, V. K.; Bubnov, M. P.; Ellert, O. G.; Dobrokhotova, Z. B.; Zakharov, L. N.; Struchovkov, Y. T. *Dokl. Akad. Nauk.* **1993**, *328*, 12.
(7) Jung, O. S.; Pierpont, C. G. *Inorg. Chem.* **1994**, *33*, 2227.
(8) Jung, O. S.; Pierpont, C. G. *J. Am. Chem. Soc.* **1994**, *116*, 1127.
(9) Attia, A. S.; Pierpont, C. G. *Inorg. Chem.* **1995**, *34*, 1172.
(10) Jung, O. S.; Jo, D. H.; Lee, Y. A.; Sohn, Y. S.; Pierpont, C. G. *Angew. Chem., Int. Ed. Eng.* **1996**, *35*, 1694.
(11) Pierpont, C. G.; Jung, O. S. *Inorg. Chem.* **1995**, *34*, 4281.
(12) Adams, D. M.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1996**, *118*, 11515.
(13) Roux, C.; Adams, D. M.;. Itiè, J. P.; Polian, A.; Hendrickson, D. N.; Verdaguer, M. *Inorg. Chem.* **1996**, *35*, 2846.
(14) Jung, O. S.; Jo, D. H.; Lee, Y. A.; Conklin, B. J.; Pierpont, C. G. *Inorg. Chem.* **1997**, *36*, 19.
(15) Adams, D. N.; Noodleman, L.; Hendrickson, D. N. *Inorg. Chem.* **1997**, *36*, 3966.
(16) Caneschi, A.; Cornia, A.; Dei, A. *Inorg. Chem.* **1998**, *37*, 3419.
(17) Ruiz, D.; Yoo, J.; Guzei, I. A.; Rheingold, A. N.; Hendrickson, D. N. *Chem. Commun.* **1998**, 2089.
(18) Ruiz-Molina, D.; Veciana, J.; Wurst, K.; Hendrickson, D. N.; Rovira, C. *Inorg. Chem.* **2000**, *39*, 617.
(19) Pierpont, C. G. *Coord. Chem. Rev.* **2001**, *216*, 99.

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has been supported by the temperature-dependent magnetic data on a five-coordinate high spin cobalt(II)−semiquinonato complex.[21] However, a ferromagnetic interaction was more recently suggested to be operative in the high spin six-coordinate Co(bpy)(DBSQ)(DBCat)$^-$ complex anion,[17] and therefore, the nature of the magnetic interaction between the cobalt(II) ion and the semiquinonato ligand remains unclear.

With this in mind, we tried to isolate a 1:1 cobalt−dioxolene derivative existing as cobalt(II)−semiquinonato at low temperature. This in principle can be done by properly tuning the redox potentials of the metal ion and the dioxolene ligand. The use of an easily oxidized catecholato ligand as well as the use of a poorer donor ancillary ligand is expected to favor the cobalt(II)−semiquinonato valence tautomer with respect to the cobalt(III)−catecholato one. For instance, we have shown that complexes of general formula Co(CTH)(diox)Y (CTH = DL-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, Y = I, ClO_4, PF_6) are stable in the cobalt(III)−catecholato form using the di-*tert*-butyl-*o*-dioxolene ligand,[22] whereas temperature and pressure dependent valence tautomeric interconversion characterizes the phenanthrene-9,10-dioxolene derivative, in agreement with the fact that the redox potentials of the two ligands differ by about 200 mV.[23] The charge distribution of the complexes Co(N−N)$(diox)_2$ (N−N = diazine ligand) was found to be strongly affected by the electron donor ability of the diazine ancillary ligand.[4] We have therefore used a macrocyclic ligand which is expected to increase the redox potential of the Co(III)/Co(II) couple, that is, 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (Me_4cyclam), and we have synthesized its 1:1 dioxolene adducts. Here, we wish to report the structural, spectroscopic, and magnetic characterization of the Co(Me_4cyclam)(diox)PF_6 systems (diox = DBSQ (**1**), PhenSQ (**2**)), showing that indeed the synthetic strategy works and that the compounds are stable in the Co(II)−SQ form down to 4 K. The reported results here are believed to be very important for offering a rationale for the intriguing photochemical properties of the cobalt−dioxolene complexes.[24]

Experimental Section

Synthesis of Co(Me_4cyclam)(CH_3CO_2)PF_6. A solution of cobalt(II) acetate (3 mmol) in methanol (50 mL) was added to a solution of Me_4cyclam (3.3 mmol, Aldrich) under stirring. The resulting solution was gently warmed for 0.5 h and then treated with an aqueous solution of KPF_6. The volume of the resulting mixture was reduced and then filtered and cooled at room temperature. Subsequent storage at 5 °C afforded a pink-violet crystalline material. Yield: 78%. ($C_{16}H_{35}CoF_6N_4O_2P$ requires C = 37.00, H = 6.79, N = 10.79. Found: C = 36.25, H = 6.34, N = 10.23).

Synthesis of Co(Me_4cyclam)(DBSQ)PF_6 (1). A solution of 3,5-di-*ter*-butylcatechol (1 mmol) in methanol (20 mL) was mixed under inert atmosphere with a solution of Co(Me_4cyclam)(CH_3CO_2)PF_6 (1 mmol) in the same solvent (30 mL). After the addition of solid NaOH (2 mmol), the resulting mixture was gently warmed for 0.5 h and then mixed with a solution of ferrocinium hexafluorophosphate (1 mmol) in acetone. A blue microcrystalline material was obtained after the addition of an aqueous solution of KPF_6. Recrystallization from dichloromethane/pentane mixtures afforded a blue crystalline product. ($C_{28}H_{52}CoF_6N_4O_2P$ requires C = 49.41, H = 7.70, N = 8.23. Found: C = 49.73, H = 7.81, N = 7.96.)

Synthesis of Co(Me_4cyclam)(PhSQ)PF_6 (2). This compound was prepared following the same procedure as for **(1)** by using 9,10-di-hydroxy-phenanthrene. Recrystallization from dichloromethane/pentane mixtures afforded brown-green crystals. Subsequent storage of the filtrate at −20 °C yielded single crystals suitable for X-ray structural investigations. ($C_{28}H_{44}CoF_6N_4O_2P$ requires C = 50.00, H = 6.59, N = 8.33. Found: C = 49.81, H = 6.22, N = 8.06.)

Physical Measurements. The magnetic susceptibility of polycrystalline powders of **1** and **2** was measured between 2 and 300 K and an applied magnetic field of 0.1 and 1 T using a Cryogenic S600 SQUID magnetometer. Data were corrected for the magnetism of the sample holder which was determined separately in the same temperature range and field, and diamagnetism correction was estimated from Pascal's constants. Magnetization measurements were performed on the same sample at 2.5 and 4.5 K with field up to 6 T.

Infrared spectra were recorded on a Perkin-Elmer BX spectrometer. Electronic spectra were recorded in the range 5000−30000 cm^{-1} on a Perkin-Elmer Lambda 9 spectrophotometer. The electrochemical analysis by cyclic voltammetry was carried out by using an electrochemical unit (Amel model 553 potentiostat equipped with Amel 860, 560 and 568 elements) and a classical three-electrode cell. The working electrode was a platinum microsphere, the auxiliary electrode was a platinum disk, and the reference electrode was a calomel electrode in aqueous saturated KCl (SCE). Before each experiment, the solution was carefully deaerated with an argon flow. All potentials are reported as referenced versus ferrocinium/ferrocene couple. Under the experimental conditions used, this couple lies at +0.455 V vs SCE.

X-ray Structure Determination. The X-ray crystal structure was solved for compound **2**. The ORTEP diagram is shown in Figure 1. Crystallographic data are reported in Table 1, and selected bond distances and angles are reported in Table 2. No decay was observed for 5338 reflections measured, 4014 independent reflections collected by ω scan ($2.5° < \theta < 24.99°$). The structure was solved by direct methods[25] and refined[26] by full matrix least-squares on F^2. All non-hydrogen atoms were treated anisotropically while the hydrogen atoms were treated as fixed contributions in calculated positions with isotropic thermal parameters fixed and equal for all the atoms (U = 0.05 Å^2). The quite high final R values can be partially attributed to the disorder present on the fluorine atoms of the PF_6^- moiety and on the macrocycle, where some atoms present high thermal factors due to disorder and thermal agitation. C16 and C26 were refined as double positions with partial occupational factor (C16−C16′ 0.5−0.5, C26−C26′ 0.6−0.4, respectively). An absorption correction was based on ψ scan.

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(20) Dei, A.; Gatteschi, D. *Inorg. Chim. Acta* **1992**, *198−200*, 813.

(21) Ruf, M.; Noll, B. C.; Groner, M. D.; Yee, G. T.; Pierpont, C. G *Inorg. Chem.* **1997**, *36*, 4860.

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

(23) Caneschi, A.; Dei, A.; Fabrizi de Biani, F.; Gütlich, P.; Hoefer, A.; Ksenofontov, V.; Levchenko, G.*Chem.−Eur. J.* **2001**, *7*, 3926.

(24) Neuwahl, F. V. R.; Righini, R.; Dei, A. *Chem. Phys. Lett.* **2002**, *352*, 408.

(25) *SIR92*: Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr*. **1994**, *27*, 435.

(26) Sheldrick, G. M. *SHELX93*; University of Göttingen, Göttingen, Germany, 1993.

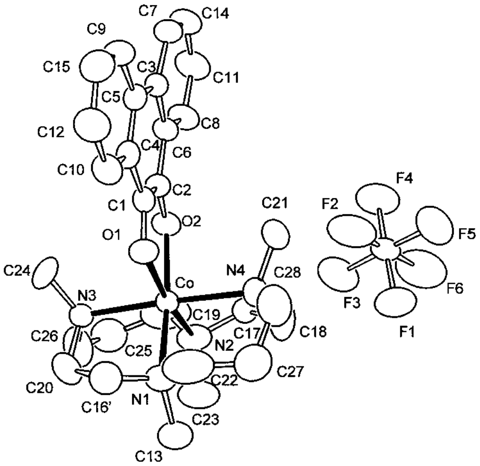

Figure 1. ORTEP plot of Co(Me$_4$cyclam)(PhenSQ)PF$_6$ (**2**). The hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]. Co−O1 2.098(4), Co−O2 2.118(5), Co−N4 2.177(6), Co−N3 2.191(5), Co−N1 2.225(6), Co−N2 2.226(5), O1−Co−O2 77.4(2), O2−Co−N4 89.6(2), O1−Co−N3 90.2(2), O2−Co−N3 92.7(2), N4−Co−N3 177.1(2), O1−Co−N1 90.8(2), O2−Co−N1 168.1(2), N4−Co−N1 92.2(2), N3−Co−N1 85.9(2), O1−Co−N2 169.4(2), O2−Co−N2 92.3(2), N4−Co−N2 85.7(2), N3−Co−N2 92.5(3), N1−Co−N2 99.6(2).

Table 1. Crystal Data and Structural Refinement Parameters for Co(Me$_4$cyclam)(PhenSQ)PF$_6$ (**2**)

empirical formula	$CoC_{28}H_{40}F_6N_4O_2P$
fw	668.54
nnit cell dimensions	$a = 14.087(4)$ Å
	$b = 15.873(4)$ Å
	$c = 14.263(7)$ Å
	$\alpha = 89.91(3)°$
	$\beta = 107.34(2)°$
	$\gamma = 90.08(2)°$
	$V = 3044.3(19)$ Å^3
Z	4
space group	$P2_1/a$, N°14
T(K)	293
radiation	Mo Kα, $\lambda = 0.71069$ Å
d (calcd)	1.459 Mg/m^3
abs coeff	0.686 mm^{-1}
F(000)	1392
final R indices [$I > 2\sigma(I)$]	R1 = 0.0867, wR2 = 0.2674
R indices (all data)	R1 = 0.1087, wR2 = 0.2958

Table 2. Selected Bond Lengths [Å] and Angles [deg] for Co(Me$_4$cyclam)(PhenSQ)PF$_6$ (**2**)

Co−O1 2.098(4)	Co−O2 2.118(5)	Co−N4 2.177(6)
Co−N3 2.191(5)	Co−N1 2.225(6)	Co−N2 2.226(5)
O1−Co−O2 77.4(2)	O2−Co−N4 89.6(2)	O1−Co−N3 90.2(2)
O2−Co−N3 92.7(2)	N4−Co−N3 177.1(2)	O1−Co−N1 90.8(2)
O2−Co−N1 168.1(2)	N4−Co−N1 92.2(2)	N3−Co−N1 85.9(2)
O1−Co−N2 169.4(2)	O2−Co−N2 92.3(2)	N4−Co−N2 85.7(2)
N3−Co−N2 92.5(3)	N1−Co−N2 99.6(2)	

Results and Discussion

The reactions between Co(Me$_4$cyclam)(CH$_3$COO)PF$_6$ and 3,5-di-*t*-butylcatechol or 9,10-di-hydroxy-phenanthrene in alkaline methanol under inert atmosphere yield solid catecholato complexes, Co(Me$_4$cyclam)(Cat). Solid compounds of formula Co(Me$_4$ cyclam)(diox)PF$_6$ can be isolated from acetone−methanol mixtures as a result of the addition of a stoichiometric amount of ferrocenium hexafluorophosphate. One-electron oxidation of the cobalt(II)−catecholato moiety may yield either the cobalt(III)−catecholato derivative or the cobalt(II)−semiquinonato one. So far, it has been found that for 1:1 metal−dioxolene complexes the metal centered oxidation process is favored.[22] As said previously, exceptions are the five coordinate Tp$^{\mathrm{Cum,Me}}$Co(DBSQ) and Co(bpy)(DBSQ)(DBCat)$^-$ complexes.[17,21] Evidence is presented here that the Co(Me$_4$cyclam)(diox)PF$_6$ complexes we have isolated can be formulated as containing high spin cobalt(II)−semiquinonato derivatives.

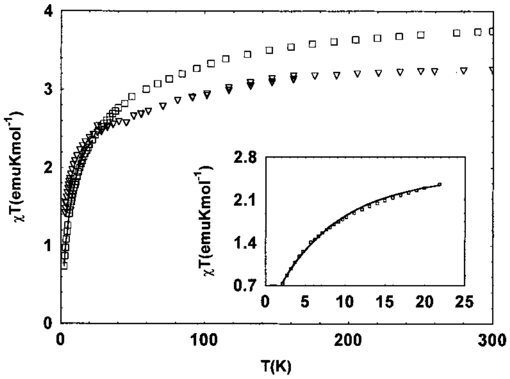

Figure 2. χT vs T plot for: Co(Me$_4$cyclam)(DBSQ)PF$_6$ (**1**), □, and Co(Me$_4$cyclam)(PhenSQ)PF$_6$ (**2**), ▼. The fit reported in the insert was obtained as described in the text using the following parameters: $J_z = 26$ cm^{-1}, $J_{xy}/J_z = 0.12$ cm^{-1}, $g_z = 7.94$, $g_{xy}/g_z = 0.35$.

The results of the crystal structure determination of the Co(Me$_4$cyclam)(PhenSQ)PF$_6$ complex are shown in Figure 1; selected bond distances and angles are reported in Table 2. The cobalt ion is six coordinated, the macrocyclic ligand is bound in a folded configuration, and the PhenSQ acts as bidentate ligand. The features of the coordination sphere are fully consistent with the formulation of the cation as a Co(II)−semiquinonate complex, the C−O distances (average 1.273 Å), C1−C2 (1.434(9) Å), and Co−O distances (average 2.109 Å) being in agreement with those usually observed in other M(II)−semiquinonate complexes.[1,3] As mentioned in the Experimental Section, the final *R* value is quite high because of the disorder present on the fluorine atoms of the counterion. However, X-ray data collection using three different crystals does not improve the quality of the structure.

Magnetic susceptibility measurements recorded in the temperature range 300−2 K are in agreement with the cobalt(II)−semiquinonato charge distribution for both complexes. The χT versus T plot shown in Figure 2 indicates that the complexes are paramagnetic in the whole temperature range investigated, thus ruling out the existence of valence tautomeric interconversion to a diamagnetic cobalt(III)−catecholato species. The experimental χT values at 300 K for the DBSQ and PhSQ complexes, are, respectively, 3.3 and 3.6 emu K mol^{-1}. Both values are reasonable for systems containing high spin cobalt(II) ions and a semiquinonate radical ligand. The experimental χT values drop down on decreasing temperature reaching a value of 1.4 emu K mol^{-1} at 2 K for the DBSQ derivative and 0.8 emu K mol^{-1} for the PhSQ one.

A quantitative interpretation of the magnetic data is not straightforward because of the orbital degeneracy of octahedral Co(II). We have attempted an analysis on the basis of the following considerations. Degeneracy of the $^4T_{1g}$

ground state of the octahedral Co(II) ion is removed by the action of axial and rhombic distortions of the crystal field, as well as by spin−orbit coupling. The overall effect of low-symmetry crystal-field components and spin−orbit coupling produces up to six Kramers doublets and results in a doublet ground state. Because the same doublet energy level remains lowest in energy for all values of the applied field strength, and because the energy difference between the two lowest-lying doublets is relatively large with respect to thermal energy present at low temperatures ($<$ 30 K), cobalt(II) systems may be described as having an effective spin of $^1/_2$ with large anisotropy. At higher temperatures, thermal population of the higher-energy Kramers doublets becomes significant, and the magnetic problem becomes more difficult. The general quantum mechanical operator can be written explicitly as

$$\mathbf{H} = J[aS_1^z S_2^z + b(S_1^x S_2^x + S_1^y S_2^y)] + \sum_i B\cdot g_i\cdot S_i \ (i = 1 - 2)$$

where the effective spin is $S_{\mathrm{Co(II)}} = S_{\mathrm{SQ}} = {}^1/_2$, and the assumption of axial J ($J_x = J_y$, J_z) and $g_{\mathrm{Co(II)}}$ ($g_x = g_y$, g_z) values was used. For the semiquinone, the g-value tensor was taken as isotropic and was fixed to 2.00. This fully anisotropic model limits its applicability to the low temperature range ($T <$ 30 K), where only the lowest lying spin doublet of Co(II) is significantly populated, but it is adequate to obtain useful information on the exchange parameter.[27] The best fit of the experimental data derived from this model gives as exchange parameter $J_z = 26.0$ cm^{-1}, $J_{xy}/J_z = 0.12$, $g_z = 7.94$, g_{xy}/g_z=0.35 for Co(Me$_4$cyclam)(PhenSQ)PF$_6$. The fitting is shown in the inset of Figure 2, in the form of $\chi_{\mathrm{M}}T$ versus T revealing the antiferromagnetic character of the interaction. Concerning the DBSQ complex, the fitted parameters are $J_z = 6.82$ cm^{-1}, $J_{xy}/J_z = 0$, $g_z = 8.04$, $g_{xy}/g_z = 0$. These data suggest an anisotropic Ising interaction.

These results therefore support the prediction that when in a 3d metal ion−radical adduct the magnetic orbitals are not strictly orthogonal to each other, the antiferromagnetic exchange interactions dominate. Thus, ferromagnetic interactions are observed in copper(II)− and nickel(II)−semiquinonato 1:1 metal complexes in agreement with the magnetic orbitals of the metal ions being σ in character and then orthogonal to the magnetic orbital of the semiquinonato ligand (π* in character).[1,17,20,21,28−32] However, antiferromagnetic interactions are observed in metal−semiquinonato complexes with metal ions whose magnetic orbitals are π in character. This statement can be verified either for metal ions characterized by a d(π)^{n}d(σ)^0 electronic ground state like vanadium(III),[33] vanadium(IV),[34] and chromium(III),[32,35−40] or those characterized by d(π)^{n}d(σ)^m electronic configurations, like high spin manganese (II),[41−43] manganese(III),[43,44] manganese (IV),[44,45] high spin iron(III),[39,44−48] or high spin cobalt(II), provided that n is greater than 0 and lower than 6. In other words, antiferromagnetic exchange is expected every time that there exists the possibility of a nonzero overlap between the magnetic orbitals. In this sense, the observed magnetic results can be easily anticipated.[20] It should be stressed, however, that the observed J values here are rather small when compared to those reported for other 1:1 metal−semiquinonato systems. For all the systems reported to date, the observed or estimated values of both ferro- or antiferromagnetic exchange coupling constants are 1 order of magnitude larger than those observed for the complexes studied in this work. It seems therefore that in this case the dominant antiferromagnetic character of the cobalt(II)−semiquinonato interaction is close to being quenched by a ferromagnetic one. In this sense, if these data are compared with those reported by Hendrickson and co-workers for the Co(bpy)(DBCat)(DBSq)$^-$ complex anion[17] which shows a ferromagnetic interaction, it could be concluded that the sign of the magnetic interaction for these complexes is determined by a delicate balance between two opposite exchange pathways. Because the weight of the two contributions may change with the nature of the ligands, both ferro- and antiferromagnetic exchange behavior can be observed. This intriguing property is probably inherent to the $d_\pi{}^5 d_\sigma{}^2$ electronic configuration of the metal ion.

The physical characterization in solution indicates that the charge distribution found in the solid state is maintained in solution. Cyclic voltammetry experiments show that the Co(Me$_4$cyclam)(PhenSQ)PF$_6$ complex undergoes a reversible redox process at −1.00 V versus Fc$^+$/Fc and an irreversible one at −0.19 V. The DBSQ analogue exhibits a similar behavior, the reversible oxidation process falling at −0.85 V and the irreversible one at +0.05 V versus Fc$^+$/Fc. This result is similar to that observed by Pierpont and co-workers

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(27) Clemente-Juan, J. M.; Coronado, E. *Coord. Chem. Rev.* **1999**, *193−195*, 361.
(28) Kahn, O.; Prins, R.; Redijk, J.; Thompson, J. *Inorg. Chem.* **1987**, *26*, 3557.
(29) Benelli, C.; Dei, A.; Gatteschi, D.; Pardi, L. *Inorg. Chem.* **1988**, *27*, 2831.
(30) Benelli, C.; Dei, A.; Gatteschi, D.; Pardi, L. *Inorg. Chem.* **1990**, *29*, 3409.
(31) Speier, G.; Csihony, J.; Whalen, A. M.; Pierpont, C. G. *Inorg. Chem.* **1996**, *35*, 3519.
(32) Caneschi, A.; Dei, A.; Lee, H.; Shultz, D. A.; Sorace, L. *Inorg. Chem.* **2001**, *40*, 408.
(33) Buchanan, R. M.; Downs, H. H.; Shorthill, W. B.; Pierpont, C. G.; Kessel, S. L.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1978**, *100*, 4318.
(34) Bruni, S.; Caneschi, A.; Cariati, F.; Delfs, C.; Dei, A.; Gatteschi, D. *J. Am. Chem. Soc.* **1994**, *116*, 1388.
(35) Buchanan, R. M.; Kessel, S. L.; Downs, H. H.; Pierpont, C. G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1978**, *100*, 7894.
(36) Sofen, S. R.; Ware, D. C.; Raymond, K. N. *Inorg. Chem.* **1979**, *18*, 234.
(37) Buchanan, R. M.; Claflin, J.; Pierpont, C. G. *Inorg. Chem.* **1983**, *22*, 2552.
(38) Benelli, C.; Dei, A.; Gatteschi, D.; Güdel, H.; Pardi, L. *Inorg. Chem.* **1989**, *28*, 3089.
(39) Dei, A.; Gatteschi, D.; Pardi, L.; Russo, V. *Inorg. Chem.* **1991**, *30*, 2589.
(40) Wheeler, D. E.; McCusker, J. K. *Inorg. Chem.* **1998**, *37*, 2296.
(41) Lynch, M. W.; Hendrickson, D. N.; Fitzgerald, B. J.; Pierpont, C. G. *J. Am. Chem. Soc.* **1984**, *106*, 2041.
(42) Caneschi, A.; Dei, A. *Angew. Chem., Int. Ed.* **1998**, *37*, 3005.
(43) Attia, A. S.; Pierpont, C. G. *Inorg. Chem.* **1995**, *34*, 1172.
(44) Attia, A. S.; Pierpont, C. G. *Inorg. Chem.* **1998**, *37*, 3051.
(45) Larsen, S. K.; Pierpont, C. G. *J. Am. Chem. Soc.* **1988**, *110*, 1827.
(46) Buchanan, R. M.; Kessel, S. L.; Down, H. H.; Pierpont, C. G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1978**, *100*, 7894.
(47) Lynch, M. W.; Valentine, M.; Henrickson, D. N. *J. Am. Chem. Soc.* **1982**, *104*, 6982.
(48) Simpson, C. L.; Boone, S. R.; Pierpont, C. G. *Inorg. Chem.* **1989**, *28*, 4379.

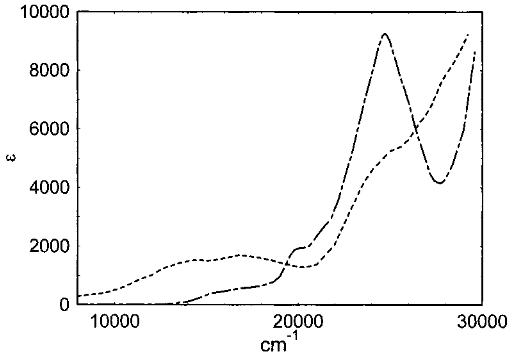

Figure 3. Electronic spectra in acetone of Co(Me$_4$cyclam)(DBSQ)PF$_6$ (**1**) (- - -) and Co(Me$_4$cyclam)(PhenSQ)PF$_6$ (**2**) (− • − •).

for the five-coordinate Tp$^{\mathrm{Cum,Me}}$Co(DBSQ) complex,[21] and like these authors, we suggest that the observed reversible redox process is associated with the semiquinonato−catecholato couple, whereas the irreversible one, to the quinone−semiquinonato one. No evidence of metal centered redox process was found. This result is in striking contrast with the ones we have observed for other cobalt-*o*-dioxolene formed by tetraazamacrocyclic ligands with secondary amine donors.[22]

The electronic spectra of both complexes are similar to the diffuse reflectance spectra and show a complicated pattern of bands whose interpretation is not straightforward (Figure 3). A partial assignment of the observed bands can be made by taking into account the internal transitions of the semiquinonato ligands. Then, the transitions occurring at 12500 and 26600 cm^{-1} in the spectrum of the DBSQ derivative can be attributed, as previously discussed, to internal ligand transitions.[29] The spectra of the PhenSQ complexes have never been discussed. However, following the spectrum of the Zn(CTH)(PhenSQ)$^+$ analogue, which shows bands at 16300 (ϵ = 110 M^{-1} cm^{-1}), 19800 (ϵ = 1200 M^{-1} cm^{-1}), 21000 (ϵ = 1400 M^{-1} cm^{-1}), and 24700 cm^{-1} (ϵ = 3300 M^{-1} cm^{-1}), we may assume that similar internal ligand transitions would characterize the cobalt complex discussed here. The other bands we observe therefore are presumably charge transfer in origin, because d−d transitions in pseudo-octahedral cobalt(II) chromophores are very weak. The transitions occurring at 14500 and 16900 cm^{-1} in the spectrum of the DBSQ derivative and at 15200 and 17100 cm^{-1} in the spectrum of the PhenSQ one are assigned to MLCT transitions in agreement with the higher oxidizing power of the DBSQ anion with respect to the PhenSQ one. The bands associated to these transitions are broad and relatively weak ($\epsilon \sim$ 400−500 M^{-1} cm^{-1}). We suggest that these transitions might involve an electron transfer between the d metal orbital and the π* SOMO of the semiquinonato ligand. The more intense transitions occurring in the violet region of the spectra of both complexes are more difficult to assign because of the overlap with the internal transition of the ligands. Tentatively, according to their intensities, they might involve charge-transfer transitions between the d metal orbitals and the same SOMO acceptor orbitals.

As a first conclusion, we want to stress how the results reported here support the predicted antiferromagnetic coupling between the high spin cobalt(II) ion and the radical semiquinonato ligand in agreement with the principle of the overlap of the magnetic orbitals of the interacting magnetic centers. However, we think that the most significant result of this work is that a cobalt(II)−semiquinonato adduct can exist in the range 4−300 K by a simple variation of the donor power of the ancillary macrocyclic ligand. This result, although not original but often forgotten, is particularly important for designing valence tautomers.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Chrystallographic Data Centre as supplementary publication n*o*. 144459. Copies of the data can be obtained free of charge on application to CCDC, 1 Union Road, Cambridge, CB21EZ, U.K. (Fax: (+44)1223-336-033. E-mail: deposit@ccdc.cam.ac.uk.)

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Supporting Information Available: Additional tables of data. This material is available free of charge via the Internet at http://pubs.acs.org.

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