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Magnetic exchange interaction between paramagnetic transition metal ions and radical ligands. A 9,10-dioxophenanthrenesemiquinonato adduct of a nickel(II)–tetraazamacrocycle complex and DFT description

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The 9,10-dioxophenanthrenesemiquinonato adduct of a nickel(II)–CTH acceptor (CTH = *dl*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) was synthesized and structurally characterized. Temperature dependent magnetic susceptibility measurements show that this compound has a quartet electronic ground state arising from the strong ferromagnetic coupling between the $S = 1$ metal ion and the radical ligand. A computational DFT study carried out using the broken symmetry approach supports the observed magnetic properties as well those of the other nickel(II)–semiquinonato analogues. These results elucidate the electronic properties of the related cobalt–dioxolene complexes when undergoing valence tautomerism.

Introduction

The development of molecular materials is based on the possibility of tuning the physical properties of the substances. Prior to this development, deep understanding of the microscopic origin of the macroscopic interactions is required. Many efforts have been made in synthesizing and characterizing molecular aggregates that mimic atomic behaviour seen in larger systems, such as inorganic and organometallic solids or biological macromolecules. In the framework of magnetism this approach opened the field of molecular magnetism.[1–7] The lesson we may learn from the analysis of small molecules is an important step for a rational design of a multidimensional collection of mutually interacting molecular systems having appropriate properties. Some of us have exploited the peculiar electronic properties of metal–semiquinonato complexes for obtaining polynuclear magnetic systems behaving as molecular magnets and molecular switches.[8,9] However, notwithstanding these successful synthetic events, some reflections are necessary.

The nature of magnetic coupling in complexes formed by 3d, and, more recently, 4f metal ions and paramagnetic *o*-semiquinonate ligands is qualitatively well understood.[10–19] Indeed the large amount of work of the last two decades indicates that redox active ligands such as dithiolenes and diazine, yield metal complexes in which the metal–ligand interaction can be described as the result of a significant mixing of the frontier orbitals of the two counterparts.[10,11] This often infers some ambiguities in the correct description of these derivatives, first of all a rational, if unconventional, assessment of the oxidation states of both the metal and the ligand.[20,21] It is currently believed that the description of the *o*-dioxolene complexes is rather easy. Indeed there are several experimental evidences that the complexes of these ligands can be properly described in terms of localized structures and often the catecholato, semiquinonato or quinone character of the coordinated ligand can be simply attributed on the basis of its structural parameters.[10,11,22] This paradigm is helpful and of relevant significance, but sometimes it involves an oversimplification of the analysis of the experimental data. As far as dioxolene complexes of transition metal ions in relatively high oxidation states are considered, there are several hints in the physical and chemical properties of these adducts indicating the relative reliability of the localized electronic description. Indeed, the anomalous electronic spectra and EPR parameters,[23,24] redox potentials, reactivity properties,[25] as well as magnetic and valence tautomeric behaviours[26–31] exhibited by some dioxolene derivatives are better explained by assuming an extensive or non-negligible mixing of the metal and ligand orbitals.[32–34] In this sense the experimental data warn us to beware ambiguous analogies. This aspect is particularly relevant, as an example, when the formulation of a correct spin Hamiltonian is needed in order to fit the magnetic susceptibilities and the ESR spectra.

The theoretical bases for understanding the magnetic interactions between paramagnetic centres are well known, however their quantitative evaluation is still a challenge in modern computational chemistry. The electronic structure of an exchange coupled system is characterized by the presence of manifold states with different spin multiplicities separated by some tenths or few hundreds of wavenumbers at the most. The search of a reliable procedure for obtaining a reasonably accurate description, with reasonable computer resources, is currently under discussion. Indeed the main difficulty in handling magnetic problems is the accuracy with which electron correlation can be taken into account. MC-SCF calculations (also called CAS-SCF) are surely the best way of considering the static correlation effects, provided that the active space is appropriately chosen. A difference-dedicated configuration interaction (DDCI)[35–38] approach was found appropriate to include the rest of the correlation, the dynamical one, with sufficient accuracy in dinuclear copper(II),[36,37] nickel(II),[39] and chromium(III) complexes.[40] However this method can be practically applied only to small molecular systems and cannot be used for the most part of currently synthesized paramagnetic systems. For this reason the density functional theory (DFT)[41] is one of the most widely used computational tool in this context, since most of the dynamical correlation is included in the functional for exchange-correlation potential, and several approaches, namely the broken symmetry (BS) technique, the single determinant (SD) method and the spin projection (SP) method have been proposed to include at least part of the static correlation effects.[42]

Our interest originates from the necessity of an accurate description of the electronic structure of cobalt–semiquinonato adducts in order to identify the orbital interactions which

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determine the electronic ground state. The interest of this system arises from the fact that the cobalt(III)–catecholato complex can be involved in a valence tautomeric interconversion to its *hs*-cobalt(II)–semiquinonato electronic isomer and that this equilibrium can be controlled by external perturbations like temperature, pressure and light irradiation, thus offering the opportunity of its use for the development of electronic devices.[26–31,43–50] However the electronic structure of the *hs*-cobalt(II)–semiquinonato complex is not clear. Some of us have recently found experimental evidence that a weak antiferromagnetic coupling characterizes this system, as a result of both ferromagnetic and antiferromagnetic contributions.[13] However this suggestion does not agree with the conclusions drawn from other research groups.[15] Further it should be mentioned that a femtosecond spectroscopy investigation shows that these systems are characterized by several electronic states close in energy.[50]

The [Co(CTH)(PhenSQ)]Y (CTH = *dl*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, PhenSQ = 9,10-dioxophenanthrene) is the simplest complex to date investigated since it contains a 1 : 1 metal–dioxolene moiety. This compound was found to undergo temperature, pressure and light irradiation valence tautomeric equilibrium.[47,51] A DFT study on this system is in progress,[52] but though it has been possible to determine the structural parameters of the Co(III)–catecholato species, the crystal structure of the *hs*-Co(II)–semiquinonato one is unknown since the tautomeric interconversion is far from complete at room temperature. In order to obtain a comparable set of structural and computational data, the [Ni(CTH)(PhenSQ)]Y complexes (Y = PF_6, ClO_4) were synthesized and characterized. Here we report the synthesis of these complexes as well as the crystal structure of the PF_6 derivative. Their physical properties were measured and discussed on the basis of the results of a computational DFT study obtained using the BS approach. A similar study performed on the previously reported[53] complex [Ni(CTH)(DBSQ)]PF_6 (DBSQ = 3,5-di-*tert*-butyl-*o*-semiquinonato) provides a further support for the quantitative description of the magnetic interaction occurring between the two paramagnetic acceptor and donor counterparts. Indeed it was found that this compound experiences a ferromagnetic coupling so large that it was not possible to evaluate the exchange coupling constant of the pair of paramagnetic centres. In addition it has been found that the nickel(II)–semiquinonato moiety may act as a building block for the synthesis of an extended network of paramagnetic centres behaving as molecular magnets.[9]

Experimental

Synthesis

The [Ni(CTH)(PhenSQ)]Y (Y = ClO_4, PF_6) complexes can be obtained by oxidation of the parent catecholate, either with atmospheric dioxygen or ferrocenium hexafluorophosphate under inert atmosphere. The latter procedure allows the isolation of a more pure product. An efficient synthetic alternative uses the redox reaction between [Ni(CTH)BH_4]PF_6 and the 9,10-phenanthrenequinone in methanol solution. Slow evaporation of methanol solutions of the hexafluorophosphate derivative allows the isolation of crystals suitable for X-ray structural characterization. Anal. [Ni(CTH)(PhenSQ)]PF_6·H_2O, found: C, 50.49; H, 6.39; N, 7.69%. $C_{30}H_{46}F_6N_4NiO_3$ requires: C, 50.44; H, 6.49; N, 7.84%. [Ni(CTH)(PhenSQ)]ClO_4·0.5H_2O, found: C, 54.69; H, 6.88; N, 8.47%. $C_{30}H_{45}ClN_4NiO_{6.5}$ requires: C, 54.61; H, 6.87; N, 8.49%.

Physical measurements

Magnetic measurements were performed on a polycrystalline powder using a Cryogenic S600 SQUID magnetometer. Measurements were corrected for the diamagnetic contribution calculated from Pascal's constants.

Table 1 Crystal data and structure refinement for compound $NiC_{30}H_{45.8}F_6N_4O_{2.9}P$

Formula weight/g mol^{-1}	712.79
Temperature/K	298(2)
Wavelength/Å	0.71069
Crystal system, space group	Monoclinic, *C*2/*c*
a, *b*, *c*/Å	20.133(3), 12.803(3), 29.393(5)
α, β, γ/°	90, 103.140(1), 90
Volume/Å^3	7378(2)
Z	8
Calculated density/mg m^{-3}	1.283
Absorption coefficient/mm^{-1}	0.633
Reflections collected/unique [*R*(int)]	6508/5365 [0.0394]
Final R_1, wR_2 [$I > 2\sigma(I)$]	0.0769, 0.1864
R_1, wR_2 (all data)	0.1251, 0.2239

X-Ray data collection was performed on a Siemens P4-RA diffractometer, Cu Kα radiation and graphite monochromator. Structure was successfully solved by direct methods (SIR97)[54] to obtain the position of all non-hydrogen atoms, and later was refined by successive Fourier difference syntheses using SHELXL97.[55] Hydrogen atoms were added in calculated positions assuming idealised bond geometries. Anisotropic thermal factors were used for all non-hydrogen atoms. Details of data collection and structure refinement are given in Table 1.

CCDC reference number 196876.

See http://www.rsc.org/suppdata/dt/b3/b300970j/ for crystallographic data in CIF or other electronic format.

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). All potentials are reported for cyclic voltammograms of 10^{-3} M 1,2-dichloroethane solutions of the complexes as referenced *vs.* the ferrocinium/ferrocene couple. Under the experimental conditions used (25 °C, 0.1 M NBu_4PF_6) this couple lies at +0.455 V *vs.* SCE.

Electronic spectra were recorded in the range 5000–30000 cm^{-1} on a Perkin-Elmer Lambda 9 spectrophotometer.

Computational details

The program package NWChem (Version 4.1)[56] was used in all the calculations. SCF-DFT calculations were performed at two different levels of approximation, that is using the local Slater exchange potential[57] with the correlation potential (functional *V*) of Vosko–Wilk–Nusair (VWN)[58] and the hybrid exchange-correlation potential B3LYP.[59] These two approximations are generally referred to as the local density approximation (LDA) and the adiabatic connection approach. All the calculations were spin unrestricted. Cartesian coordinates obtained from the experimental structures of [Ni(CTH)(DBSQ)]PF_6[53] and of [Ni(CTH)(PhenSQ)]PF_6 measured at room temperature with X-ray diffraction methods were used. The overall symmetry of the complexes was C_1. Gaussian type LANL2DZ[60] basis sets with the LANL2 effective core potential[61,62] were used. The Ahlrichs[63,64] charge density fitting basis set was used for evaluating the Coulomb potential.

Results and discussion

The X-ray structure of [Ni(CTH)(PhenSQ)]$^+$ cation is shown in Fig. 1. Selected bond distances and angles for the compound are reported in Tables 2 and 3. The crystal structure shows distorted *cis*-octahedral coordination geometry around the nickel ion. The two oxygen atoms of the semiquinonato ligand occupy two *cis* equatorial positions of the inner coordination sphere of

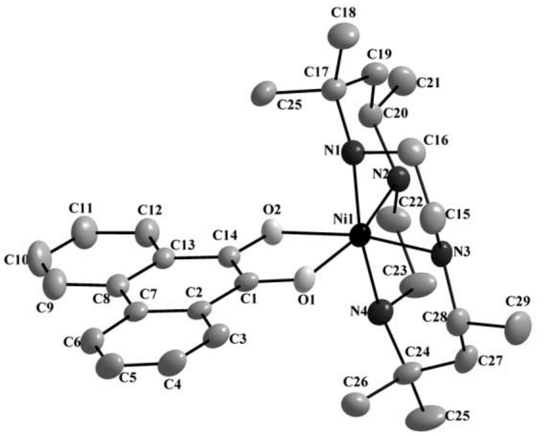


Fig. 1 Molecular structure of [Ni(CTH)(PhenSQ)]$^+$. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at 20% probability.

Table 2 Selected bond lengths (Å) for [Ni(CTH)(PhenSQ)]PF_6

Ni(1)–O(1)	2.081(4)	Ni(1)–O(2)	2.087(4)
Ni(1)–N(1)	2.148(6)	Ni(1)–N(2)	2.092(6)
Ni(1)–N(3)	2.105(6)	Ni(1)–N(4)	2.128(7)
O(1)–C(1)	1.280(8)	O(2)–C(14)	1.284(7)
C(1)–C(14)	1.430(9)	C(2)–C(1)	1.448(9)
C(14)–C(13)	1.452(9)		

Table 3 Bond angles (°) for [Ni(CTH)(PhenSQ)]PF_6

N(2)–Ni(1)–N(1)	89.8(3)	N(3)–Ni(1)–N(1)	84.0(3)
N(4)–Ni(1)–N(1)	171.8(3)	N(2)–Ni(1)–N(3)	100.0(3)
N(2)–Ni(1)–N(4)	84.7(2)	N(3)–Ni(1)–N(4)	91.0(3)
O(1)–Ni(1)–O(2)	79.4(2)	O(1)–Ni(1)–N(2)	167.8(2)
O(2)–Ni(1)–N(2)	90.4(2)	O(1)–Ni(1)–N(3)	90.7(2)
O(2)–Ni(1)–N(3)	168.8(2)	O(1)–Ni(1)–N(4)	101.0(2)
O(2)–Ni(1)–N(4)	86.0(2)	O(1)–Ni(1)–N(1)	85.6(2)
O(2)–Ni(1)–N(1)	100.1(2)	C(14)–O(2)–Ni(1)	111.6(4)
C(1)–O(1)–Ni(1)	111.5(4)	O(1)–C(1)–C(14)	118.9(6)
O(2)–C(14)–C(1)	118.3(6)		

the metal; the two Ni–O distances, which are equal to 2.081 and 2.087 Å, are in the range usually observed for nickel(II)–semiquinonato complexes.[22,53] The four nitrogen atoms of the CTH ligand occupy the two remaining equatorial and the two axial positions of the coordination polyhedron. The two axial bond distances, Ni–N1 (2.148Å) and Ni–N4 (2.128 Å) are significantly longer than the equatorial ones, suggesting that the chromophore 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 this tetraazamacrocycle.[53] The structural parameters of the coordinated dioxolene ligand well agree with those observed for metal–semiquinonato complexes. Indeed the C1–O1 (1.280 Å), C14–O2 (1.284 Å) and the C14–C1 bond distances, 1.430 Å, are strongly indicative of the metal(II)–semiquinonato charge distribution nature of the dioxolene adduct.[22] When the structural features of this cation are compared with the previously reported ones of the [Co(CTH)(PhenSQ)]$^+$ complex at room temperature,[47] it is rather clear that the cobalt complex can be properly described as containing both Co(III)–catecholato and Co(II)–semiquinonato species. In particular we stress that the Co–O bond distances are 2.01 Å, a value intermediate between catecholato and semiquinonato species. The shortest distance between nickel ions in the cell is 9.085 Å and the distance between the planes of two rings of the semiquinone ligand is 7.06 Å.

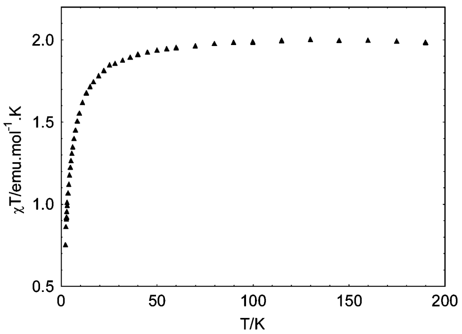


Fig. 2 χT *vs.* T curve for [Ni(CTH)(PhenSQ)]PF_6.

The temperature dependence of the magnetic susceptibility in the range 190–2 K is shown in Fig. 2. The χT *vs.* T curve is essentially flat in most of the temperature range, the value being 2.11 emu mol^{-1} K, with a slight decrease in the low temperature edge. These results are in striking correspondence with the one observed for the [Ni(CTH)(DBSQ)]Y (Y = ClO_4, PF_6, BPh_4) complexes.[53] Again the magnetic data provide clear indication that this complex is characterized by a quartet ground state as a result of ferromagnetic interaction between the nickel(II) $S = 1$ metal ion and the $S = ½$ semiquinonato ligand. In addition these data provide evidence that only one multiplet is populated up to room temperature. As a consequence these data do not provide a basis for the establishing the value of the exchange coupling constant J between the two paramagnetic centres. Thus, as discussed for DBSQ complex, we conclude that this value is larger than 400 cm^{-1}.

The electronic spectrum of a 1,2-dichloroethane solution of the [Ni(CTH)(PhenSQ)]PF_6 complex is shown Fig. 3. It shows strong transitions at 20400, 21600, 25800, 29200 and 31400 cm^{-1} with shoulders at 17200, 18000, 21000, 22600, 25000, and 27100 cm^{-1}. Although the full assignment of the spectral features is not straightforward, some useful indication can be obtained by the comparison of this spectrum with the one of the [Zn(CTH)(PhenSQ)]ClO_4 analogue. The spectrum of this compound shows a weak transition at 19800 cm^{-1} followed by two strong absorptions at 24700 and 31000 cm^{-1}.[65] Since it is reasonable to attribute these transitions to the coordinated semiquinonato ligand, it follows that the strong transitions observed at 20400, 21600 and 29200 cm^{-1} are charge transfer in character and, as suggested from CD data concerning the DBSQ and TCSQ analogues,[66] (TCSQ = *o*-tetrachlorosemiquinonato) are presumably MLCT in origin.

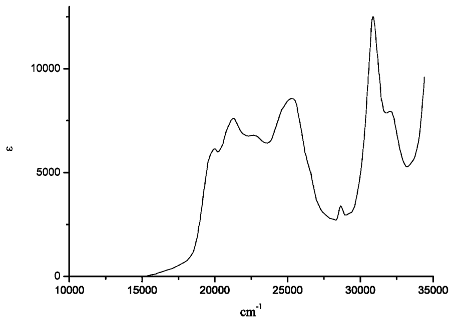
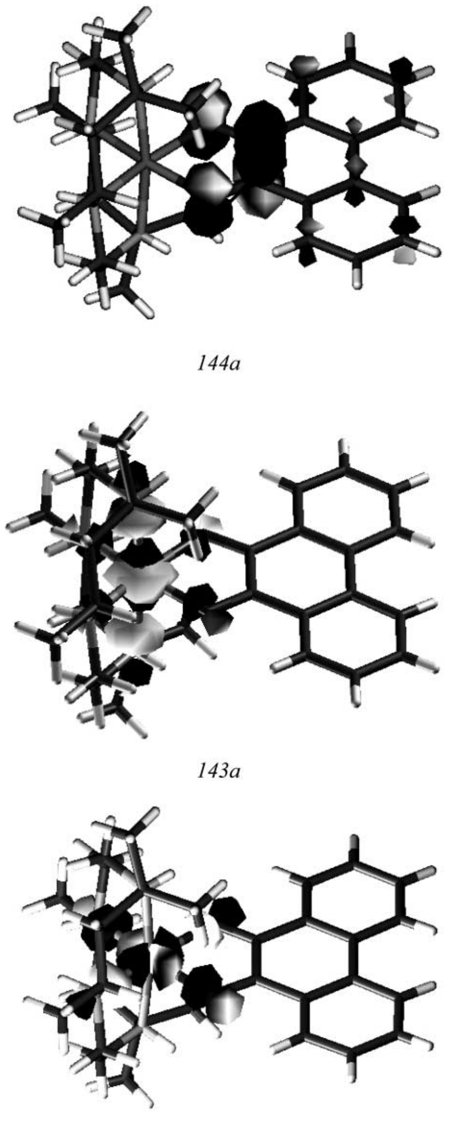


Fig. 3 Electronic spectrum of [Ni(CTH)(PhenSQ)]PF_6 at 25 °C.

Cyclic voltammetry experiments in acetonitrile solutions show that the [Ni(CTH)(PhenSQ)]$^+$ cation undergoes a reversible redox process at −1.10 V *vs.* Fc$^+$/Fc which can be attributed to the semiquinonato/catecholato couple. This value is rather similar to that reported for the cobalt complex (−1.08 V *vs.* Fc$^+$/Fc).[47] A further redox process, irreversible in character, is observed at −0.18 V *vs.* Fc$^+$/Fc. Again it may be suggested that this process is ligand centred and may be attributed to the quinone/semiquinonato couple. This result is in striking analogy with the ones observed in the previously investigated nickel(II) and zinc(II)–semiquinonato complexes.[53,66]

DFT description of the electronic and magnetic structure of $[Ni(CTH)(DBSQ)]^+$ and $[Ni(CTH)(PhenSQ)]^+$

The nature of the singly occupied molecular orbitals (SOMOs) for the $[Ni(CTH)(PhenSQ)]^+$ cation computed using the LDA approximation is pictorially shown in Fig. 4 for the $S = \frac{3}{2}$ state that is the ferromagnetic, F, highest spin state. The results obtained for the $[Ni(CTH)(DBSQ)]^+$ cation are close to those obtained for the $[Ni(CTH)(PhenSQ)]^+$ cation; the B3LYP functional also gives close results. The SOMOs are almost localized on the Ni(II) ion (142a and 143a) and on the SQ^- radical anion (144a). The 142a and 143a orbitals are mainly formed by the two σ-type 3d metal orbitals (e_g in O_h symmetry) that interact with the σ-type orbitals of the N and O donor atoms. The interaction with the oxygen atoms of the SQ^- ligand is more important for the in-plane σ orbital (x^2–y^2-like) and causes a significant delocalization of the unpaired spin density onto the oxygens. The 144a orbital is mainly a C–O π* molecular orbital, weakly interacting with one of the π-type 3d atomic orbitals of Ni(II) (xz-like). Since all of these orbitals result quite well localized onto the two magnetic centres, namely Ni(II) ($S_{Ni} = 1$) and SQ^- ($S_{SQ} = ½$), they can be identified with the natural magnetic orbitals, which, in the active electron approximation description of molecular magnetism, are widely used to qualitatively rationalize the properties of molecular magnets.[1] At lower energy we can identify three closely spaced, mainly 3d metal orbitals, which are of π-type (t_{2g}-like in O_h) and two σ-type orbitals of the SQ^- anion. A detailed description of the molecular orbitals of semiquinone-type radical ligand has been reported,[67] and will not further discussed here. Spin polarization effects cause large energy differences between majority (α) and minority (β) spin-orbitals.



144a

143a

142a

Fig. 4 Magnetic orbitals for the $[Ni(CTH)(PhenSQ)]^+$ complex.

The observed ferromagnetism of the $[Ni(CTH)(DBSQ)]^+$ and $[Ni(CTH)(PhenSQ)]^+$ cations can be qualitatively rationalized looking at the composition of the magnetic orbitals 142a, 143a and 144a and following the recipes of O. Kahn.[1] In the idealized C_{2v} symmetry (z axis perpendicular to the SQ plane and x axis bisecting the O–Ni–O angle) the magnetic orbitals 142a and 143a span the a_1 irreducible representation and 144a spans b_2. An overall ferromagnetic interaction can therefore be anticipated because of the orthogonality of the magnetic orbitals. Fig. 4 also shows that the magnetic orbitals of a_1 type are significantly delocalized onto the oxygens in atomic orbitals which are orthogonal to the π system of the 144a magnetic orbital. Therefore the overlap density $\rho_{a_1b_2} = \psi^*(a_1)\psi(b_2)$ displays zones of large magnitude around the oxygens and on the metal centre, and a large ferromagnetic interaction can be expected.[68]

Spin density is an observable that receives much attention in the literature as the picture of the magnetic pathway in organic biradicals and transition metal ions. The spin densities of the $[Ni(CTH)(DBSQ)]^+$ and $[Ni(CTH)(PhenSQ)]^+$ cations, computed through the Mulliken population analysis on the $S = \frac{3}{2}$ state are reported in Table 4. Independent of the functional used, a significant delocalization of the electronic spin on the bridging oxygens and on the aromatic rings is computed.

Quantitative calculations of the magnetic exchange coupling constant for the $[Ni(CTH)(DBSQ)]^+$ and $[Ni(CTH)(PhenSQ)]^+$ cations were performed using the spin projection technique developed by Noodleman.[41,69] In this formalism the energy of the doublet state is computed by spin projection from the energy of the so called broken symmetry state (BS) that is obtained from an unrestricted SCF calculation on a Slater determinant in which spin up (α) electrons are localized on the nickel(II) centre and the spin down (β) electrons on the organic radical. This determinant, often referred also as the antiferromagnetic, AF, state, is not, in general, a pure doublet spin state, *i.e.* eigensolution of the $\boldsymbol{S}^2$ operator with eigenvalue 0.75, but merely an eigenstate of $\boldsymbol{S}_z$. The energy of the doublet state can be obtained by an appropriate fit of the DFT energy of the BS state to that obtained by the spin Hamiltonian $H_S = J\,\boldsymbol{S}_{Ni}\cdot\boldsymbol{S}_{SQ}$. In this framework, the J value can be computed from the energies of the F and AF states as $J = E_F - E_{AF}$. Spin densities computed on the BS state are also shown in Table 4. The localization of the unpaired electrons on the paramagnetic centres is apparent.

It must be stressed here that electrons in metal–dioxolene complexes can be strongly correlated, *i.e.* the single determinant description needed to describe the spin states in DFT can be invalid and the partial correlation included into the functional of the density and the spin projection technique can be inadequate to overcome these effects. An experimental evidence of the importance of the electron correlation in these systems is the appearance of the so-called valence tautomerism. Since these effects were not evidenced in our systems, we have been confident that application of the standard spin projection technique could be reliable in the present cases. The J values computed with the LDA and the adiabatic approximation for the two cations are shown in Table 5. The J values computed with the Vosko–Wilk–Nusair functional are much larger than those computed with the B3LYP functional as already found in the literature.[70] In any case the computed J values are big enough to yield a well isolated $S = \frac{3}{2}$ ground state, as experimentally observed. In Table 5 the average value of $\boldsymbol{S}^2$, $<\boldsymbol{S}^2>$, are also shown. It can be seen that, in the present case, the ferromagnetic state is a pure spin $S = \frac{3}{2}$ state (expected value $<\boldsymbol{S}^2>_{quartet} = 3.75$) and the antiferromagnetic one is almost a

Table 4 Mulliken spin populations[a] computed for the $[Ni(CTH)(DBSQ)]^+$ and $[Ni(CTH)(PhenSQ)]^+$ cations

Complex		DFT approach	Ni	SQ	O[b]	CTH
$[Ni(CTH)(DBSQ)]^+$	F	LDA	1.44	1.11	0.31	0.44
		B3LYP	1.60	1.11	0.29	0.31
	AF	LDA	1.38	−0.77	−0.13	0.44
		B3LYP	1.61	−0.87	−0.18	0.29
$[Ni(CTH)(PhenSQ)]^+$	F	LDA	1.44	1.15	0.29	0.47
		B3LYP	1.61	1.10	0.27	0.30
	AF	LDA	1.41	−0.82	−0.12	0.44
		B3LYP	1.62	−0.90	−0.17	0.29

[a] F: calculations performed on the ferromagnetic state; AF: calculations performed on the antiferromagnetic state; CTH: atomic population summed over atoms belonging to the external ligand; SQ: atomic population summed over carbon and hydrogen atoms of the aromatic rings of DBSQ and PhenSQ ligands. [b] Values averaged over the two oxygen atoms.

Table 5 Computed values of J and $<S^2>$[a] for the $[Ni(CTH)(DBSQ)]^+$ and $[Ni(CTH)(PhenSQ)]^+$ cations

Complex	DFT approach	J/cm^{-1}	$<S^2>_F$	$<S^2>_{AF}$
$[Ni(CTH)(DBSQ)]^+$	LDA	−885	3.76	1.75
	B3LYP	−356	3.76	1.76
$[Ni(CTH)(PhenSQ)]^+$	LDA	−514	3.76	1.75
	B3LYP	−285	3.76	1.76

[a] $<S^2>_F$ and $<S^2>_{AF}$ refer to the expectation values of S^2 for the ferro- and antiferromagnetic states, respectively.

perfect admixture of quartet and doublet states (expected value $<S^2>_{mix} = 1.75$).

Conclusions

The spin populations obtained for the BS state are in full agreement with those suggested by the usual chemical intuition. The methods used for calculating the Heisenberg coupling constant J between the two paramagnetic centres gave results in reasonable agreement with the experimental data. Since the exchange coupling constant in the Heisenberg model Hamiltonian in a trivial sense merely defines the exchange parameters between a family of states related by a spin flipping without any change in the electronic structure, *i.e.* the wave functions of the two counterparts, the present data suggest that this approximation is valid for the actual system. It should be stressed, however, that this cannot be considered a general conclusion. In particular, as mentioned above, the role of the electron correlation can be important for other magnetically exchange coupled systems.

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