On the "Brown-Ring" Reaction Product via Density-Functional Theory

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On the basis of the density-functional theory, the properties of the reaction product $[Fe(H_2O)_5(NO)]^{2+}$ of the classical "brown-ring" reaction are studied via the B3LYP hybrid method. Here we have found that the Fe–N–O bond in the optimized structure of $[Fe(H_2O)_5(NO)]^{2+}$ is linear. In addition, the vibrational frequency, atomic net charges, and spin density are analyzed and then the solvent effects are incorporated via the polarized continuum model self-consistent reaction field. Furthermore, the excitation energies are evaluated using the CIS method. Results when compared with experimental data indicate that the spin-quartet ground state of $[Fe(H_2O)_5(NO)]^{2+}$ is best described by the presence of Fe^{II} ($S = 2$) antiferromagnetically coupled to NO ($S = {}^1/_2$), yielding $[Fe^{II}(H_2O)_5(NO)]^{2+}$. This is clearly different from either $[Fe^{III}(H_2O)_5(NO^-)]^{2+}$ or conventional textbook $[Fe^I(H_2O)_5(NO^+)]^{2+}$ assignment.

Introduction

The reactions of nitric oxide (NO) coordinated to transition metals have both theoretical and experimental interests due to their biological and environmental importance.[1,2] Nitric oxide has been shown to play significant roles in intracellular signaling, cytotoxic immune response, vasodilatation, and blood pressure regulation.[3,4] The NO can bind reversibly to the ferrous center of an iron enzyme and generate stable nitrosyl complex. It can also be used as a probe of a non-heme iron active site.[5,6] Understanding the interaction between NO and metal targets is key to understanding the in vivo chemistry of nitric oxide. The radical character of NO can function as an electron donor, giving NO^+, an electron acceptor, giving NO^- (isoelectronic with O_2), or as a neutral NO• radical.[7–9]

Recently, Wanat et al. have studied the classical "brown-ring" displacement reaction of coordinated water on Fe^{II} by NO.[10] Their IR peak at 1810 cm^{-1} was only slightly shifted to the $Fe^{II}(L)NO$ complex (L = $edta^{4-}$), which is known to bind NO as Fe^{III}–NO^-.[5] In the X-band electron paramagnetic resonance (EPR) spectrum of nitrosylated solution, similar subspectra were observed for solutions of other $S = {}^3/_2$ ground states of the {FeNO}[7] species. On the basis of the resemblance of Mössbauer, EPR, and IR parameters of the $[Fe(H_2O)_5(NO)]^{2+}$ product to those of {FeNO}[7] units in other well-characterized nitrosyl complexes,[5,6,11,12] they concluded that the reaction product $[Fe(H_2O)_5(NO)]^{2+}$ is best described as $[Fe^{III}(H_2O)_5(NO^-)]^{2+}$.

However, the conclusion of Wanat et al. is in conflict with the classical $[Fe^I(H_2O)_5(NO^+)]^{2+}$ assignment[13] usually quoted in undergraduate textbooks. Meanwhile, we believe the spectral evidence of Wanat et al. is not strong enough to support their $[Fe^{3+}$ ($S = {}^5/_2$)–NO^- ($S = 1$)] claim. The reasons are 3-fold. First, the IR peak observed at 1810 cm^{-1} was closer to the 1871 cm^{-1} peak of free NO instead of NO^-.[2,5,14] Second, the EPR absorption peak around $g = 1.9$ is typical of the NO radical.

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Finally, 58% zero-field Mössbauer spectrum peak (Figure 3 in ref 10b) was assigned as Fe^{II}. The large equilibrium constant K_{NO} value for the reaction of $[Fe(H_2O)_6]^{2+}$ and NO indicating the main spectrum peak should be arising from the product $[Fe(H_2O)_5(NO)]^{2+}$.

To investigate the electronic structure of the ground state $[Fe(H_2O)_5(NO)]^{2+}$ product ($S = {}^3/_2$), we have performed the density-functional theory (DFT)[15] calculations. A variety of the electronic structures of the $[Fe(H_2O)_5(NO)]^{2+}$ ($S = {}^3/_2$) product are possible. They are listed according to the 1+, 2+, or 3+ charge on the Fe atom as follows: (a) $[Fe^+$ d^7 ($S = {}^3/_2$)–NO^+ ($S = 0$)], (b) $[Fe^{2+}$ d^6 ($S = 1$)–NO^0 ($S = {}^1/_2$)] ferromagnetically coupled or $[Fe^{2+}$ d^6 ($S = 2$)–NO^0 ($S = {}^1/_2$)] antiferromagnetically coupled, and (c) $[Fe^{3+}$ d^5 ($S = {}^1/_2$)–NO^- ($S = 1$)] ferromagnetically coupled and $[Fe^{3+}$ d^5 ($S = {}^3/_2$)–NO^- ($S = 0$)] or $[Fe^{3+}$ d^5 ($S = {}^5/_2$)–NO^- ($S = 1$) antiferromagnetically coupled.

According to the above charge and spin combinations, there are four possible charge and spin characters for the NO ligand, namely, NO^+ ($S = 0$), NO^0 ($S = {}^1/_2$), NO^- ($S = 1$), and NO^- ($S = 0$). To identify the character for the NO ligand, the DFT calculations are performed on the free nitric oxide NO^0 ($S = {}^1/_2$) and its ions NO^+ ($S = 0$), NO^- ($S = 1$), and NO^- ($S = 0$), respectively. The geometry of the reactant $[Fe(H_2O)_6]^{2+}$ ($S = 2$) is also optimized to compare the net charge on the Fe atom with the product $[Fe(H_2O)_5(NO)]^{2+}$ ($S = {}^3/_2$).

Computational Method

Calculations based on DFT are carried out in this investigation. Here we use the unrestricted B3LYP hybrid method involving the three-parameter Becke exchange functional[16] and a Lee–Yang–Parr correlation functional.[17] All calculations are performed using the Gaussian 98 program.[18] The gas-phase geometry optimizations are performed at 6-31G(d,p), 6-311G-(d,p), 6-311G+(d,p), and 6-311G++(d,p) Gaussian-type basis sets. Solvent effects of $[Fe(H_2O)_5(NO)]^{2+}$ ($S = {}^3/_2$) in water are taken into account for the optimized geometries[19] via the self-consistent reaction field (SCRF) method using the Tomasi's polarized continuum model (PCM).[20] For all PCM calculations,

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TABLE 1: Optimized Bond Distances (Å) of Fe−N Bonds for [Fe(H$_2$O)$_5$NO]$^{2+}$ ($S = {}^3/_2$) and Average Fe−O Bonds for [Fe(H$_2$O)$_6$]$^{2+}$ ($S = 2$) Using Different Basis Sets

basis set	R_{Fe-N} ([Fe(H$_2$O)$_5$NO]$^{2+}$)	R_{Fe-O} ([Fe(H$_2$O)$_6$]$^{2+}$)
6-31G(d,p)	1.78	2.14
6-311G(d,p)	1.79	2.14
6-311+G(d,p)	1.81	2.16
6-311++G(d,p)	1.81	2.16

TABLE 2: Optimized Bond Distances (Å) of N−O Bonds for [Fe(H$_2$O)$_5$NO]$^{2+}$ ($S = {}^3/_2$), NO^0 ($S = {}^1/_2$), NO$^+$ ($S = 0$), NO$^-$ ($S = 1$), and NO$^-$ ($S = 0$) Using Different Basis Sets

	R_{N-O}				
basis set	[Fe(H$_2$O)$_5$-NO]$^{2+}$	NO^0 ($S = {}^1/_2$)	NO$^+$ ($S = 0$)	NO$^-$ ($S = 1$)	NO$^-$ ($S = 0$)
6-31G(d,p)	1.15	1.16	1.07	1.28	1.28
6-311G(d,p)	1.14	1.15	1.06	1.27	1.27
6-311+G(d,p)	1.13	1.15	1.06	1.26	1.25
6-311++G(d,p)	1.13	1.15	1.06	1.26	1.25

TABLE 3: Calculated Vibrational Frequency (cm^{-1}) for [Fe(H$_2$O)$_5$NO]$^{2+}$ ($S = {}^3/_2$), NO^0 ($S = {}^1/_2$), NO$^+$ ($S = 0$), NO$^-$ ($S = 1$), and NO$^-$ ($S = 0$) Using Different Basis Sets^a

basis set	[Fe(H$_2$O)$_5$NO]$^{2+}$	NO^0 ($S = {}^1/_2$)	NO$^+$ ($S = 0$)	NO$^-$ ($S = 1$)	NO$^-$ ($S = 0$)
6-31G(d,p)	1895	(1908)	1892	2356	1394	1400
6-311G(d,p)	1901	(1906)	1889	2369	1372	1380
6-311+G(d,p)	1896	(1901)	1880	2367	1344	1375
6-311++G(d,p)	1898	(1902)	1880	2367	1344	1375

^{a} Values in parentheses are results with solvation effects.

TABLE 4: Atomic Net Charges (Q in e$^-$) on the Fe Atom for [Fe(H$_2$O)$_6$]$^{2+}$ ($S = 2$) and on the Fe Atom and NO Ligand for [Fe(H$_2$O)$_5$NO]$^{2+}$ ($S = {}^3/_2$), Respectively, via NBO Population Analysis^a

	[Fe(H$_2$O)$_6$]$^{2+}$	[Fe(H$_2$O)$_5$NO]$^{2+}$	
basis set	Q_{Fe}	Q_{Fe}	Q_{NO}
6-31G(d,p)	1.63	1.73 (1.78)	−0.12 (−0.19)
6-311G(d,p)	1.67	1.68 (1.73)	−0.04 (−0.10)
6-311+G(d,p)	1.59	1.45 (1.49)	0.12 (0.05)
6-311++G(d,p)	1.59	1.45 (1.49)	0.12 (0.05)

^{a} Values in parentheses are results with solvation effects.

the number of initial tesserae/atomic spheres was set to 60 as in the default.

The vibrational frequencies of the optimized structure are calculated to compare with the IR experimental data.[10] The electronic structures have also been analyzed using the nature bond orbital (NBO) partition scheme.[21] An important feature of the NBO method is that the presence of diffuse functions in the basis sets does not affect the results. To analyze the UV−vis properties[10] qualitatively, we perform the singles CI (CIS) method based on the unrestricted B3LYP [Fe(H$_2$O)$_5$(NO)]$^{2+}$ ground state ($S = {}^3/_2$) wave functions.

Results and Discussions

The gas-phase geometry optimizations are performed for [Fe(H$_2$O)$_5$NO]$^{2+}$ ($S = {}^3/_2$), [Fe(H$_2$O)$_6$]$^{2+}$ ($S = 2$), and the free nitric oxide NO^0 ($S = {}^1/_2$) and its ions NO$^+$ ($S = 0$), NO$^-$ ($S = 1$), and NO$^-$ ($S = 0$), respectively. The optimized bond distances of Fe−N bonds for [Fe(H$_2$O)$_5$NO]$^{2+}$ ($S = {}^3/_2$) and average Fe−O bonds for [Fe(H$_2$O)$_6$]$^{2+}$ ($S = 2$) are listed in Table 1. The optimized geometries converge when using the larger basis sets such as 6-311+G(d,p) and 6-311++G(d,p). For instance, the Fe−N distance converges to 1.81 Å for [Fe(H$_2$O)$_5$(NO)]$^{2+}$ and the average Fe−O distance to 2.16 Å for [Fe(H$_2$O)$_6$]$^{2+}$.

TABLE 5: Total Atomic Spin Densities for [Fe(H$_2$O)$_5$NO]$^{2+}$ ($S = {}^3/_2$) Using Different Basis Sets^a

basis set	Fe	NO	H$_2$O$_{ax}$	(H$_2$O)$_{4,eq}$
6-31G(d,p)	3.87 (3.92)	−1.04 (−1.10)	0.02 (0.03)	0.14 (0.15)
6-311G(d,p)	3.82 (3.86)	−0.98 (−1.02)	0.02 (0.03)	0.14 (0.13)
6-311+G(d,p)	3.74 (3.80)	−0.90 (−0.98)	0.02 (0.03)	0.14 (0.15)
6-311++G (d,p)	3.73 (3.79)	−0.90 (−0.98)	0.02 (0.03)	0.15 (0.16)

^{a} Values in parentheses are results with solvation effects.

TABLE 6: UB3LYP/6-311++G(d,p) NAO Occupations^a for [Fe(H$_2$O)$_5$NO]$^{2+}$ ($S = {}^3/_2$)

atom	NAO	α spin-orbital occupancy	β spin-orbital occupancy
Fe	4s	0.12 (0.12)	0.11 (0.11)
	3d$_{xy}$	0.99 (0.99)	0.05 (0.05)
	3d$_{xz}$	0.97 (0.98)	0.51 (0.47)
	3d$_{yz}$	0.97 (0.98)	0.54 (0.52)
	3d$_{x^2-y^2}$	0.99 (0.99)	0.13 (0.14)
	3d$_{z^2}$	0.98 (0.98)	0.14 (0.15)
N	2s	0.80 (0.80)	0.75 (0.75)
	2p$_x$	0.43 (0.41)	0.65 (0.67)
	2p$_y$	0.43 (0.41)	0.62 (0.64)
	2p$_z$	0.57 (0.57)	0.56 (0.56)
O	2s	0.85 (0.85)	0.86 (0.86)
	2p$_x$	0.59 (0.61)	0.84 (0.86)
	2p$_y$	0.59 (0.61)	0.83 (0.84)
	2p$_z$	0.71 (0.71)	0.70 (0.70)

^{a} Values in parentheses are results with solvation effects.

All optimized Fe−N−O angles in [Fe(H$_2$O)$_5$(NO)]$^{2+}$ are 180°. As described in the literature,[6,22] the linear Fe−N−O is usually being viewed as Fe$^+$ and NO$^+$, and the bent Fe−N−O as Fe$^-$ and NO$^-$ for the {FeNO}^{7} complex. Notice that our Fe−NO bond for [Fe(H$_2$O)$_5$(NO)]$^{2+}$ is linear but the bonds of the Fe^{3+}−NO$^-$ complexes in refs 5 and 6 are bent.

Table 2 illustrates the optimized N−O bond distances for [Fe(H$_2$O)$_5$(NO)]$^{2+}$ ($S = {}^3/_2$) and the nitric oxide NO^0 ($S = {}^1/_2$) and its ions NO$^+$ ($S = 0$), NO$^-$ ($S = 1$), and NO$^-$ ($S = 0$), respectively. Notice that in Table 2, the N−O distances converge to 1.13, 1.15, 1.06, 1.26, and 1.25 Å for [Fe(H$_2$O)$_5$(NO)]$^{2+}$, NO^0 ($S = {}^1/_2$), NO$^+$ ($S = 0$), NO$^-$ ($S = 1$), and NO$^-$ ($S = 0$), respectively. The converged N−O distance for [Fe(H$_2$O)$_5$-(NO)]$^{2+}$ ranging between those of NO$^+$ ($S = 0$) and NO^0 ($S = {}^1/_2$) is closest to that of NO^0 ($S = {}^1/_2$). The converged N−O distance for both NO$^-$ ($S = 1$) and ($S = 0$) are too long when compared with that of the [Fe(H$_2$O)$_5$(NO)]$^{2+}$.

The calculated vibrational frequencies for optimized [Fe(H$_2$O)$_5$(NO)]$^{2+}$ ($S = {}^3/_2$), NO^0 ($S = {}^1/_2$), NO$^+$ ($S = 0$), NO$^-$ ($S = 1$), and NO$^-$ ($S = 0$) are listed in Table 3. Because of the well-recognized overestimation of the vibrational frequencies by the SCF method, all frequencies are scaled down by a factor of 0.95. According to Table 3, the gas-phase N−O stretching modes are 1898, 1880, 2367, 1344, and 1375 cm^{-1} for [Fe(H$_2$O)$_5$(NO)]$^{2+}$, NO^0 ($S = {}^1/_2$), NO$^+$ ($S = 0$), NO$^-$ ($S = 1$), and NO$^-$ ($S = 0$), respectively, when using the 6-311++(d,p) basis set. The N−O stretching mode for [Fe(H$_2$O)$_5$(NO)]$^{2+}$ ranging between those of NO$^+$ ($S = 0$) and NO^0 ($S = {}^1/_2$) is closest to NO^0 ($S = {}^1/_2$). The N−O stretching modes for both NO$^-$ ($S = 1$) and ($S = 0$) are too low when compared with those of [Fe(H$_2$O)$_5$(NO)]$^{2+}$. The N−O stretching modes for [Fe(H$_2$O)$_5$(NO)]$^{2+}$ in solution are almost the same as those of the gas phase.

On the basis of the above N−O bond distance and vibration frequency results, the characteristics of the NO ligand in [Fe(H$_2$O)$_5$(NO)]$^{2+}$ ($S = {}^3/_2$) are more likely to be NO^0 ($S = {}^1/_2$) than the others. Hence, it is only possible to couple with Fe^{2+} in [Fe(H$_2$O)$_5$(NO)]$^{2+}$ ($S = {}^3/_2$).

TABLE 7: Excitation Energies and Oscillator Strengths^a for [Fe(H$_2$O)$_5$NO]$^{2+}$ ($S = ^3/_2$) via CIS Method under 6-311++G(d,p) Basis Set

	excitation energy (nm)				
	323 (0.110)	415 (0.001)	416 (0.001)	501 (0.001)	525 (0.001)
Main orbital excitation^c from → to	$42\beta \rightarrow 44\beta$ (0.52) $43\beta \rightarrow 45\beta$ (0.50) $38\alpha \rightarrow 47\alpha$ (-0.39) $38\alpha \rightarrow 48\alpha$ (−0.35)	$43\beta \rightarrow 48\beta$ (0.94)	$42\beta \rightarrow 48\beta$ (0.94) $42\beta \rightarrow 48\beta$ (0.35)	$42\beta \rightarrow 47\beta$ (0.93)	$43\beta \rightarrow 47\beta$ (0.95)
exp^b	336		451		585

^{a} Values in parentheses are oscillating strengths. ^{b} Reference 10. ^{c} Values in parentheses are the coefficients, c_i, of the wave function for each excitation. Here, only the square of $c_i \geq 0.10$ is given.

To verify the oxidation state of the Fe atom in the [Fe(H$_2$O)$_5$-(NO)]$^{2+}$ ($S = ^3/_2$) ion, the atomic net charges on the Fe atom for the reactant [Fe(H$_2$O)$_6$]$^{2+}$ ($S = 2$) and the [Fe(H$_2$O)$_5$(NO)]$^{2+}$ ($S = ^3/_2$) ion are studied. The calculated atomic net charges on the Fe atom of [Fe(H$_2$O)$_6$]$^{2+}$ ($S = 2$) and Fe atom and NO ligand of [Fe(H$_2$O)$_5$(NO)]$^{2+}$ ($S = ^3/_2$) via NBO population analysis are illustrated in Table 4. For the gas phase, the net charges on Fe atoms for [Fe(H$_2$O)$_6$]$^{2+}$ and [Fe(H$_2$O)$_5$(NO)]$^{2+}$ are 1.59 and 1.45 e for the larger 6-311+G(d,p) and 6-311++G(d,p) basis sets, respectively. The net charges of Fe atom for both +2 iron complexes are almost the same; the oxidation state of the Fe atom for [Fe(H$_2$O)$_5$(NO)]$^{2+}$ should also be the same as that for [Fe(H$_2$O)$_6$]$^{2+}$ ($S = 2$), that is, +2. According to Table 4, the net charge of the NO ligand is + 0.12 e via larger basis sets indicating slightly partial positive and nearly neutral character of the NO ligand. Notice that in Table 4, when the solvation effects are taken into account, the net charges on the Fe atom and the NO ligand for [Fe(H$_2$O)$_5$(NO)]$^{2+}$ are very close to those of the gas phase. Therefore, the Fe^{2+} coupled with NO^0 are most likely the structures for the [Fe(H$_2$O)$_5$(NO)]$^{2+}$ complex.

The total atomic spin densities for [Fe(H$_2$O)$_5$NO]$^{2+}$ ($S = ^3/_2$) are listed in Table 5. Our z axis is defined by the Fe−N bond; the H$_2$O ligand along the z axis is written as (H$_2$O)$_{ax}$ and the other four H$_2$O ligands are written as (H$_2$O)$_{4,eq}$. The total spin densities using the 6-311++G(d,p) basis set are 3.73 and −0.90 (3.79 and −0.98) in the gas phase (with solvation effects) for Fe and NO, respectively. This result indicates that the idealized total spin $S = 2$ on the Fe atom and $S = ^1/_2$ on the NO ligand.

Table 6 indicates the natural atomic orbitals (NAO) for [Fe-(H$_2$O)$_5$NO]$^{2+}$ ($S = ^3/_2$) when using the 6-311++G(d,p) basis set only. The results for other basis sets are similar. For the Fe atom in the gas phase (with solvation effects), the α NAO configuration is 4s$^{0.12}$d$^{4.90}$ (4s$^{0.12}$d$^{4.92}$) and the β NAO configuration is 4s$^{0.11}$d$^{1.37}$ (4s$^{0.11}$d$^{1.32}$), giving net α spin of +3.54 (+3.61) that corresponds to an idealized Fe^{2+} d^6 ($S = 2$) configuration. For the NO ligand in the gas phase (with solvation effects), the net result is a 0.84 (0.96) β electron located in the π^* orbital of NO, giving an idealized total $S = ^1/_2$ of NO.

In the combination of both Tables 5 and 6, results indicate that Fe^{2+} ($S = 2$) is antiferromagnetically coupled NO^0 ($S = 1/2$). The values of $\langle S^2 \rangle$ for the gas phase (with solvation effects) population analyses range within 3.92−3.96 (3.96−3.99) for all basis sets. These values are close to the ideal $S(S + ^1/_2)$ expectation value 3.75, indicating low-spin contamination.[23]

The excitation energies (nm) and oscillator strengths for [Fe-(H$_2$O)$_5$NO]$^{2+}$ ($S = ^3/_2$) are calculated by using the CIS method based on the unrestricted B3LYP wave functions. The obtained results using the representative 6-311++G(d,p) basis set are shown in Table 7. The predicted excitation energies allow us to qualitatively describe the three broad regions centered at 336, 451, and 585 nm observed in the UV−vis spectra of ref 10. Our calculated excitation energy at 322 nm corresponds to the experimental 336 nm, which has the largest absorbance. The

TABLE 8: Main and Percent Compositions and Energies (ϵ, in eV) of Some Frontier Molecular Orbitals for [Fe(H$_2$O)$_5$NO]$^{2+}$ ($S = ^3/_2$) via UB3LYP/6-311++G(d,p)

	main	percent composition				
MO^a	composition	Fe	NO	H$_2$O$_{ax}$	(H$_2$O)$_{4,eq}$	ϵ (eV)
38α O	Fe(d$_{xz}$)	74	9	0	17	−19.3
39α O	Fe(d$_{yz}$)	81	6	8	5	−19.2
40α O	(H$_2$O)$_{4,eq}$, Fe(d$_{x^2-y^2}$)	28	3	5	64	−18.5
41α O	(H$_2$O)$_{4,eq}$	2	0	0	98	−18.4
42α O	(H$_2$O)$_{4,eq}$, Fe(d$_{xy}$)	18	0	0	82	−18.2
43α O	H$_2$O$_{ax}$, Fe(d$_{yz}$)	12	0	86	2	−18.0
44α O	(H$_2$O)$_{4,eq}$, Fe(d$_{xz}$)	18	0	0	82	−17.9
45α O	Fe(d$_{x^2-y^2}$), (H$_2$O)$_{4,eq}$	42	0	2	56	−17.7
46α O	Fe(d$_{z^2}$)-NO(σ)	47	19	10	24	−17.2
47α V	NO(π_y^*)	6	83	0	11	−11.2
48α V	NO(π_x^*)	6	90	0	4	−11.2
49α V	Fe(s), (H$_2$O)$_5$	37	5	15	43	−8.6
50α V	(H$_2$O)$_{4,eq}$	5	2	0	93	−7.6
51α V	(H$_2$O)$_{4,eq}$	7	1	0	92	−7.4
38β O	(H$_2$O)$_{4,eq}$	2	2	0	96	−18.4
39β O	(H$_2$O)$_{4,eq}$	2	2	0	96	−18.2
40β O	(H$_2$O)$_{4,eq}$	2	4	2	92	−18.1
41β O	H$_2$O$_{ax}$	2	0	94	4	−18.1
42β O	Fe(d$_{yz}$) + NO(π_y^*)	43	52	2	3	−15.6
43β O	Fe(d$_{xz}$) + NO(π_x^*)	39	54	0	7	−15.5
44β V	Fe(d$_{yz}$) − NO(π_y^*)	38	53	1	8	−11.6
45β V	Fe(d$_{xz}$) − NO(π_x^*)	43	54	0	3	−11.5
46β V	Fe(d$_{xy}$)	93	0	0	7	−11.5
47β V	Fe(d$_{x^2-y^2}$), (H$_2$O)$_{4,eq}$	55	0	1	44	−10.6
48β V	Fe(d$_{z^2}$)-NO(σ)	45	27	9	19	−10.0
49β V	Fe(s), (H$_2$O)$_5$	35	8	19	38	−8.5
50β V	(H$_2$O)$_{4,eq}$	6	2	0	92	−7.6
51β V	(H$_2$O)$_{4,eq}$	7	1	0	92	−7.4

^{a} O and V represent occupied and virtual MOs, respectively.

two values 415 and 416 nm are very close and correspond to the broad UV−vis region centered at 451 nm. The values 501 and 525 nm correspond to the broader and weakest absorbance region centered at 585 nm. Hence, our calculated excitation energies are qualitatively in agreement with the experimental values.

According to Table 7, the main orbital excitation corresponding to the excitation energy 323 nm is from molecular orbital (MO) $42\beta \rightarrow 44\beta$, $43\beta \rightarrow 45\beta$, $38\alpha \rightarrow 47\alpha$, and $38\alpha \rightarrow 48\alpha$. The main-orbital excitation corresponding to the excitation energies 415 and 416 nm are from $43\beta \rightarrow 48\beta$ and $42\beta \rightarrow 48\beta$, respectively. Similarly, the main-orbital excitation corresponding to the excitation energies 501 and 525 nm are from $42\beta \rightarrow 47\beta$ and 48β and $43\beta \rightarrow 47\beta$, respectively.

The Kohn−Sham MOs can be used in qualitative MO discussions of molecular properties.[24] The main and percent compositions of frontier MOs for [Fe(H$_2$O)$_5$NO]$^{2+}$ ($S = ^3/_2$) and the orbital energies (eV) using the representative 6-311++G-(d,p) basis set are listed in Table 8. There are 46 α and 43 β occupied spin-unrestricted MOs. For α spin MOs, occupied 46α is the HOMO. Its main contribution comes from a metal of d$_{z^2}$. There is also a σ-antibonding interaction between the Fe (d$_{z^2}$)

and the NO σ. Occupied MO 38α is essentially a metal of d_{xz} ($\sim$75%), and there is a slight π-antibonding interaction between Fe and NO π. Occupied MO 39α is essentially a metal of d_{yz} ($\sim$81%) and has a slight π-antibonding interaction between Fe and NO π. Virtual MOs 47α and 48α are the same in energy. Virtual MOs 47α and 48α are mainly NO π_y* and NO π_x*, respectively.

For β spin MOs, occupied MOs 42β and 43β are fairly close in energy. MO 42β corresponds to a strong π-bonding interaction between Fe (d_{yz}) and NO π_y*, and MO 43β corresponds to strong π-bonding interaction between Fe (d_{xz}) and NO π_x*. Virtual MO 44β, the LUMO, is almost equally distributed between iron and the NO ligand. The orbital corresponds to a strong π-antibonding interaction between Fe (d_{yz}) and NO π_y*. Virtual MO 45β corresponds to a strong π-antibonding interaction between Fe (d_{xz}) and NO π_x*. Virtual MO 46 β is essentially a metal of d_{xy} symmetry. Virtual MO 47 β is essentially a metal of $d_{x^2-y^2}$ symmetry and contributions from $(H_2O)_{4,eq}$. Virtual MO 48 β is mainly from Fe d_{z^2} antibonding with the NO σ.

By analysis of the properties of MOs and CIS excitation results, the UV–vis region centered at 336 nm can thus be assigned as mainly due to a Fe ($d_{yz,xz}$) + NO ($\pi*$) → Fe ($d_{yz,xz}$)– NO ($\pi*$) transition and the metal to ligand Fe ($d_{xz,yz}$) → NO ($\pi*$) charge transfer. The region centers at 451 nm can be assigned as a Fe ($d_{yz,xz}$) + NO ($\pi*$) → Fe (d_{z^2})–NO (σ) transition and at 585 nm as a Fe ($d_{yz,xz}$) + NO ($\pi*$) → Fe ($d_{x^2-y^2}$) transition.

Conclusion

The results of optimized structure, atomic net charges on the Fe atom and the NO ligand, and vibrational frequency analysis indicate that nearly neutral character of the NO ligand and the Fe^{2+}–NO^0 complex are the most likely electronic structures of $[Fe(H_2O)_5(NO)]^{2+}$ even though there is a slight partial positive charge on NO ligand. Results of spin densities and NBO valence electron configurations indicate that the Fe^{2+}–NO^0 is best described by the presence of Fe^{II} ($S = 2$) antiferromagnetically coupled to NO^0 ($S = 1/2$) yielding the $[Fe^{II}(H_2O)_5(NO)]^{2+}$ ($S = 3/2$).

Our calculated results can also explain the experimental data studied by Wanat et al. First, the calculated IR data is close to the experimental value 1810 cm^{-1}. Second, the character of NO^0 is consistent with the NO radical parameters they found in EPR spectrum. Third, the 58% zero-field Mössbauer spectrum peak (Figure 3 in ref 10b), which can be assigned as Fe^{II}, is mainly from $[Fe^{II}(H_2O)_5(NO)]^{2+}$. Finally, the calculated excitation energies are qualitatively in agreement with the UV–vis experimental values. Hence, we conclude that Fe^{II} ($S = 2$) is antiferromagnetically coupled to NO^0 ($S = 1/2$), yielding the $[Fe^{II}(H_2O)_5(NO)]^{2+}$ ($S = 3/2$) structure.

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