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Consideration of spin states in determining the structure and decomposition of the transition metal pentazoles $FeClN_5$, $Fe(N_5)_2$, $Fe(H_2O)_4ClN_5$, and $Fe(NH_3)_4ClN_5$†

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Optimised geometries and energies have been calculated for the unidentate, bidentate, and ferrocene-like structures of Fe(II) pentazoles of the form MN_5 and $M'(N_5)_2$, (M = FeCl, M′ = Fe) using the UB3LYP DFT method with basis sets up to 6-311+G(3df) in order to study the effect of an unfilled d shell on the stability of the singlet, triplet, and quintet states; the ground state is a quintet and the quintet has a lower barrier to decomposition than the singlet.

The quest for high energy compounds has generated intense interest in the synthesis of nitrogen-rich compounds. Theoretical studies at the *ab initio* level on the mechanism of their formation began in 1974 with tetrazole,[1] pentazole,[2] and the pentazole anion, N_5^-. High level calculations leading to information about the aromaticity,[3,4] structure, and physical properties of the N_5^- anion and LiN_5 began appearing in the early 1990s. N_5^- is calculated to be thermodynamically less stable than its decomposition products, the N_3^- anion and N_2, although a sizable activation energy has been found, *ca.* 20 kcal mol^{-1}. Recently, theoretical studies have been considered for other metals and $M(N_5)_2$ ferrocene-like structures.[5–11] To our knowledge, no study has included the effect of spin. This might seem reasonable since ferrocene has long been known to exist as a singlet in the ground state for Fe^{2+}.

Two experiments have detected the presence of N_5^-, one within a tandem mass spectrometer at high collision voltages[12] and the other using laser desorption ionisation (LDI) time-of-flight (TOF) mass spectroscopy.[13] The first synthesis of the pentazole anion in solution was reported by Butler *et al.*[14] Prior theoretical calculations[8] suggested that Zn^{2+} might provide an effective counterion compared to Group I or II cations, due to the higher covalent character of Zn^{2+}. It is not known what effect the presence of transition metal ions with incomplete d-shell occupation can have on the energy barrier to decomposition of the N_5^- species into N_3^- and N_2. The effect of the spin state of transition metals on the structure and decomposition of MN_5 has not been investigated until now, but should be considered for high energy substances in the solid state or solution.

Optimised geometries for the monodentate (**I**), bidentate (**II**), and ferrocene-like (**V**) structures (Fig. 1) in the singlet, triplet, and quintet states have been calculated. The effect of spin on decomposition energy barriers was also examined. Structures **I** and **II** for $FeClN_5$ have C_{2v} symmetry, those for $Fe(N_5)_2$ have D_{2d} or D_{2h} symmetry with the rings perpendicular or coplanar, respectively.

The stability of the spin-restricted wavefunction to mixing with states of different spin is of primary concern when calculating the properties of many transition metal complexes and there is still considerable controversy about the use of unrestricted methods such as UB3LYP DFT, which permit such mixing for these cases.[4,15] In cases where the ground state is a spin eigenfunction, the ordering of the other spin states can be found using approaches such as the symmetry-adapted cluster/configuration interaction (SAC-CI) method.

The DFT calculations were carried out using the Gaussian98 A11.2 series of programs.[16] The Gaussian03 A1.1[17] series was employed with the SAC-CI method to confirm the ordering of the spin states. The B3LYP hybrid functional[18] method supplied with Gaussian98 was used, along with the 6-311+G(d) and 6-311+G(3df) basis sets. Three procedures for all calculations on singlet species were employed, RB3LYP, UB3LYP, and the mixing of the HOMO and LUMO in the trial vectors in order to destroy α–β and spatial symmetries. Stability calculations were performed on unmixed, singlet species to verify RHF to UHF and internal stabilities. A vibrational analysis was carried out in each case to ascertain the nature of each stationary point found. Since MN_5 species are expected in solution, the effect of spin state has been calculated for two coordination compounds, $FeClN_5(H_2O)_4$ and $FeClN_5(NH_3)_4$.

The total 6-311+G(3df) energies for the **II** structure of the $FeClN_5$ and $Fe(N_5)_2$ species, and the 6-311+G(d) energies for $FeClN_5(H_2O)_4$ and $FeClN_5(NH_3)_4$ are given in Table 1 for singlet, triplet, and quintet states. Structure **II** was chosen for the starting point in the geometry optimisations of the H_2O and NH_3 coordination compounds, but structure **I** resulted in all cases. Also included is the number of imaginary frequencies found for each calculation. The energies for all structures with the various basis sets can be found in the ESI†.

Several **I**, **II**, and TS structures had the Cl atom above the plane of the Fe and N atoms, retaining a C_s structure for **I** and **II**. Representative structures are given in Fig. 1. Full geometric details will be given in a forthcoming article that will include results for Cr, Ni, and Cu compounds.

For every $FeClN_5$ structure, the quintet is the ground state, the singlet is the highest energy state, and the triplet lies between the quintet and the singlet. The wavefunction for every singlet $FeClN_5$

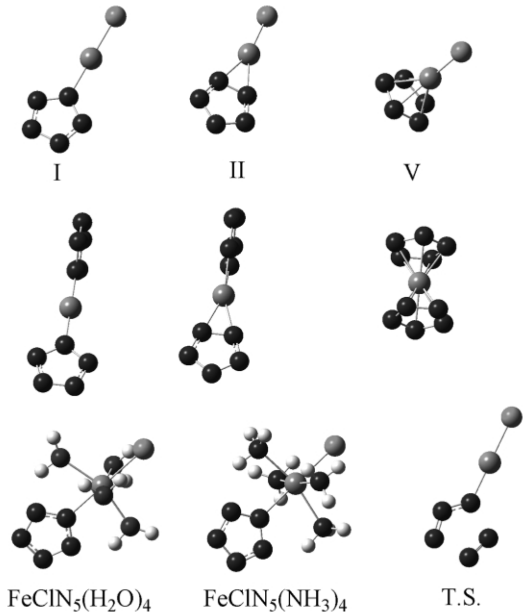

Fig. 1 Principle structures for $FeClN_5$, the transition state for decomposition, $Fe(N_5)_2$, and the complexes $FeClN_5(H_2O)_4$ and $FeClN_5(NH_3)_4$.

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† Electronic supplementary information (ESI) available: energies for all structures with the various basis sets. See http://www.rsc.org/suppdata/cc/b3/b315812h/

Table 1 Energies (in hartrees) for the optimised structures.[a] Two kinds of ΔE are reported, the activation energies (kcal mol^{-1}) TS–**II** for $FeClN_5$ and the singlet–quintet energy differences for the two complexes. The B3LYP and SAC-CI values are the relative energies (in hartrees) from the quintets

Compound (structure)	Spin state	*E*	TS	ΔE	B3LYP	SAC-CI
$FeClN_5$ (**II**)	Singlet 6-311+G(3df)	0.677650	0.641967(1)	22.39	0.098	0.157
	Triplet 6-311+G(3df)	0.725958			0.050	0.078
	Quintet 6-311+G(3df)	0.775690	0.750467(1)	15.83	0.000	0.000
$Fe(N_5)_2$ (**II**)	Singlet 6-311+G(3df)	1.209000			0.054	0.151
	Triplet 6-311+G(3df)	1.164263			0.099	0.079
	Quintet 6-311+G(3df)	1.263396			0.000	0.000
$FeCl(N_5)(H_2O)_4$ (**I**)	Singlet 6-311+G(d)	1.615553		24.72		
	Quintet 6-311+G(d)	1.654942				
$FeCl(N_5)(NH_3)_4$ (**I**)	Singlet 6-311+G(d)	1.170529		5.40		
	Quintet 6-311+G(d)	1.179127				

[a] Energies are to be subtracted from −1997 hartrees for $FeClN_5$, −1810 hartrees for $Fe(N_5)_2$, −2302 hartrees for $FeCl(N_5)(H_2O)_4$, and −2223 hartrees for $FeCl(N_5)(NH_3)_4$.

structure is unstable with respect to RHF to UHF change. Both procedures available in Gaussian98, *stable* = *opt* and mixing the HOMO and LUMO in the trial vector lead to ill-defined spin states with spin projected as S^2 = 3–4, indicating contamination from at least the quintet. The triplets also have projected spins of S^2 = 3–4. All quintet calculations have original S^2 values of between 6.00 and 6.01, projected to *ca*. 6.0001, indicating a stable spin state. A stationary state for the quintet **V** structure was not found, but optimisation led to **I** or **II**.

The SAC-CI method[19] has been shown to give reliable differences in excited states provided the ground state can be described by a single reference wavefunction. The quintets were used as starting ROHF functions and then singlets and triplets calculated. The coefficient for the starting ROHF determinant was 0.9997. The CI reference for the quintet included all canonical MOs with energies between −0.53 and +0.40 hartrees. The 6-31G(d) basis set was used on the quintet-optimised structure for both $FeClN_5$ and $Fe(N_5)_2$. The relative energies in hartrees are given in Table 1 for a qualitative comparison between the spin-state energy levels calculated with B3LYP and SAC-CI.

As for the calculated E_a for decomposition, (TS–**II**, Table 1) it is not valid to compare the singlet and quintet values since the singlet states contain spin contamination whereas the quintet states do not. Nevertheless, the quintet E_a values are consistently lower than the singlet values with all basis sets.

In the case of $Fe(N_5)_2$, UB3LYP singlet calculations for structure **II** contain symmetry-breaking instabilities, but interestingly, not singlet–triplet instabilities. While the quintets are lowest in energy, the singlets are now lower than the triplets. As both spin states are subject to considerable spin contamination after spin projection, this energy level ordering is suspect. When SAC-CI calculations are based on the quintet, which again is stable, the ordering as shown in Table 1 follows the same order as in $FeClN_5$, *i.e.* singlet higher than triplet higher than quintet.

Only with the smaller basis set 6-31G(d) is the singlet wavefunction stable for structure **V**, and it is only for the singlet states that equilibrium geometries (0 imaginary frequencies) could be found for structure **V**. Nevertheless, all of the **V** structures lie significantly higher than the **I** or **II** structures as previously found.[4,8]

The preference for the quintet state carries over to both example coordination compounds. Although the somewhat smaller 6-311+G(d) basis set was used for optimisation of the geometries, the results are consistent with experiment. In simple crystal field theory terms, the splitting by the NH_3 is expected to be greater than that for H_2O. This would lead to more stabilisation of the NH_3-coordinated singlet. As indicated in Table 1, the singlet–quintet energy difference is 0.0344 hartrees (21.6 kcal mol^{-1}) for NH_3 and 0.0123 hartrees (7.7 kcal mol^{-1}) for H_2O with the SVP basis set, and 0.0394 (24.72) and 0.0086 hartrees (5.39 kcal mol^{-1}), respectively, for the 6-311+G(d) basis set.

In conclusion, the spin state should be considered for pentazole anions in contact with transition metals with incomplete d shells and, in general, for all high nitrogen-content rings.[11] The stability of singlet wavefunctions to mixing with higher states for transition metals in general must be established and, if the stability is lacking at one level of theory, proper theoretical methods should be employed.[4,15] Triplet instability is not sufficient for exploration using the singlet state.

Both $FeClN_5$ and $Fe(N_5)_2$ resemble their Na, K, Mg, Ca, and Zn counterparts in their geometrical preference for mono- or bidentate binding over ferrocene-like structures.[8] The interactions of the metal ions with N atom lone pairs are more favourable than with the much lower occupied π MOs on N_5^- and this is also found to be the case in the presence of the unfilled d shell in Fe^{2+}. In a forthcoming Full Paper, we will explain how the presence of five N lone pairs makes the pentazole anion fundamentally different to the cyclopentadienyl anion.

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