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Notes

Local Density Functional Theory Analysis of the Structures and Energies of the Isomers of Low-Spin $[\mathrm{Ni(cyclam)}]^{2+}$

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The investigation of the relative energies of the configurational isomers of low-spin $[\mathrm{Ni(cyclam)}]^{2+}$ has been a recurring theme in coordination chemistry. Following initial qualitative studies, based on molecular models,[1] several groups (including ours) have applied molecular mechanics techniques in attempts to analyze this "classic" macrocyclic ligand system.[2−5] Recently we reported the failure of the PM3(tm) semiempirical method to describe adequately this series of isomers.[6]

We now present the first report of the application of density functional theory (DFT) to generate the minimized structures and absolute energies of the five configurational isomers of $[\mathrm{Ni(cyclam)}]^{2+}$. This study serves to demonstrate the geometric accuracy of the S-VWN5[7] local density functional for macrocyclic complexes of the type considered and to allow assessment of the relative energies of these isomers. It is commonly assumed that the symmetrical *trans-III* (*R,S,S,R* with respect to the nitrogen centers) isomer is the most stable form of $[\mathrm{Ni(cyclam)}]^{2+}$,[8] although molecular mechanics investigations suggest that both the *trans-I* (*R,S,R,S*) and *trans-III* (*R,R,S,S,*) forms are, within experimental error, of similar energy.[4,5] In accord with this, recent solution NMR studies indicate that both *trans-I* and *trans-III* forms coexist in aqueous solution.[9] Previously, X-ray structures have been reported for the *trans-III* and *trans-V* (*R,R,R,R*) isomers.[3,10,12,13]

Table 1. DFT and Molecular Mechanics Calculated Relative Energies between the Isomers of $[\mathrm{Ni(cyclam)}]^{2+}$

isomer	MM2[a,b]	MM2[a,c]	DFT[d]
trans-I	0.0	1.3	0.98
trans-II	6.4	5.4	10.16
trans-III	1.1	0.0	0.00
trans-IV	42.9	32.4	59.23
trans-V	14.4	9.9	24.64

[a] Steric energy in kJ/mol. [b] Data from ref 4. [c] Data from ref 3. [d] Electronic energy in kJ/mol.

Table 2. Summary of Mean Bond Lengths (Å) and Angles (deg) about Nickel in the Coordination Spheres of the DFT-Calculated and X-ray Structures for the Geometric Isomers of $[\mathrm{Ni(cyclam)}]^{2+}$

	trans-I	*trans-II*	*trans-III*[a]	*trans-IV*	*trans-V*[b]
Ni−N	1.896	1.896	1.911 (1.947)	1.908	1.891 (1.916)
N−Ni−N (90°)	90.00	90.03	90.00 (90.00)	90.19	90.08 (90.14)
N−Ni−N (180°)	177.04	177.34	179.99 (180.00)	172.81	175.68 (174.31)

[a] Values in parentheses are the means of these X-ray structures in Cambridge Crystallographic Data Base (Version 5.11, May 1996); CAFHUM, FISKEX, JIZTUX. [b] Values in parentheses are from X-ray structure.[10]

The five isomeric starting structures used in the present study corresponded to the (extended) MM2-minimized structures obtained previously.[5]

These were then geometry optimized with the DFcalc code[14] using the VWN5 functional and the 6-311G* basis set on IBM SP2 and SGI Power Challenge computer systems. No symmetry conditions were imposed during the calculations. To compare the accuracy of the DFcalc calculations, the resulting structures were subsequently refined with Gaussian 94[15] using the VWN5 functional and the 6-311G* basis set on a SGI Power Challenge computer—no significant geometric or relative energetic differences were observed between the DFcalc and G94 calculations. For all isomers, calculations were run with closed shells (multiplicity 1) and a level shift factor of 500 mhartrees was added (400 mhartrees in G94). In accord with the presumed low-spin state of these square planar nickel(II) complexes, SCF convergence could not be achieved when the calculations were repeated as open shell (multiplicity 3). The trans-*III* isomer was also studied with the gradient-corrected nonlocal functional P86.[16] However, as the optimized geometry was a slightly poorer fit to the available X-ray data than obtained with the LSDA VWN5 method, and the nonlocal functional calculations were considerably more computationally expensive than the LSDA methods, nonlocal functionals were not considered further in this work.[17]

Table 1 gives a comparison of the energies of the minimized isomers obtained in the present study with those from the previous MM investigations.[3,4] The results from the DFT

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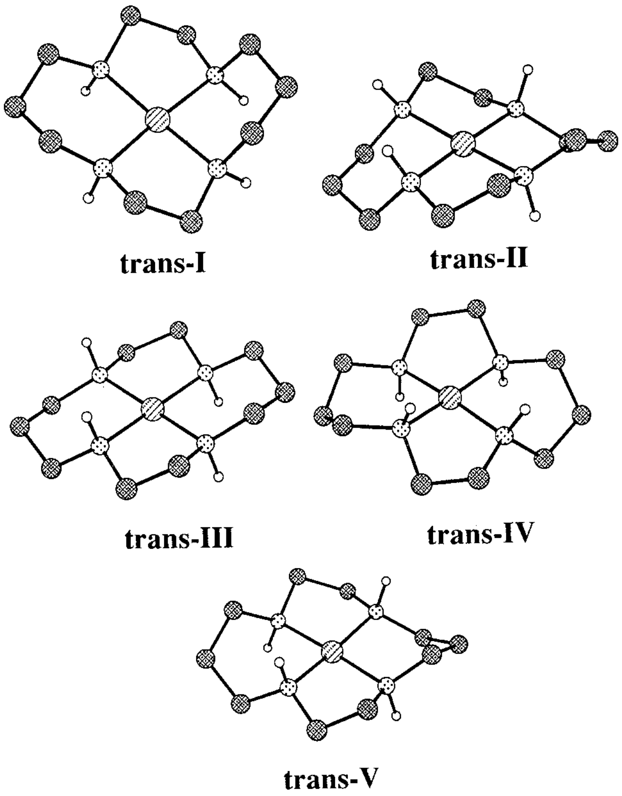

Figure 1. DFT minimum energy structures of the five configurational isomers of *trans*-[Ni(cyclam)]$^{2+}$.

calculations are in clear concordance with the corresponding results from both prior MM investigations; the relative energies of the *trans-I* and *trans-III* isomers for each set of calculations are also in keeping with recent experimental (NMR) evidence that both isomers occur in aqueous solution.[9]

To our knowledge, the above study represents the first time that high level *ab initio* calculations on a series of isomeric transition metal complexes have been available for comparison with the results from parallel molecular mechanics studies. Table 2 lists the mean bond lengths and angles around the nickel atom from the DFT-minimized (gas phase) structures (relative to those from the X-ray structures in the case of the *trans-III* and *trans-V* isomers). Overall, the agreement between the calculated and X-ray[10] structures of the *trans-III* isomer is excellent.[18] For the *trans-V* isomer, the agreement[19] is also good; even though the X-ray structure[13] in this case shows apparently anomalous C−C distances. In view of the latter, somewhat less than excellent correspondence is expected in this case.

In conclusion, it appears that the use of computational efficient local DFT, coupled with large basis sets, enables successful modeling of (classical) transition metal complexes of the type discussed above. Further, the results of the previous MM investigations of the relative stabilities of the isomers of [Ni(cyclam)]$^{2+}$ are confirmed.

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(17) Summary comparison between nonlocal functional p86/6-311g* calculated and observed (X-ray)[10] parameters (H atoms not included) for the *trans-III* isomer, root-mean-square differences: for bonds 0.065 Å; for adjacent angles 1.91°; for 38 torsional angles (excluding angles above 170° which are subject to high uncertainty)[5] 3.07°; for all interatomic distances 0.139 Å.

(18) Summary comparison between local functional SVWN5/6-311g* calculated and observed (X-ray)[10] parameters (H atoms not included) for the *trans-III* isomer, root-mean-square differences: for bonds 0.024 Å; for adjacent angles 1.04°; for 38 torsional angles (excluding angles above 170° which are subject to high uncertainty)[5] 1.54°; for all interatomic distances 0.036 Å.

(19) Summary comparison between calculated and observed (X-ray)[13] parameters (H atoms not included) for the *trans-V* isomer, root-mean-square differences: for bonds 0.096 Å; for adjacent angles 2.63°; for 38 torsional angles (excluding angles above 170° which are subject to high uncertainty)[5] 5.18°; for all interatomic distances 0.092 Å.