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Molecular Modelling Analysis of the Axial Distortion of the Coordination Geometry around Copper(II) in Octahedral Ligand Fields

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Molecular modelling analysis using molecular mechanics, semi-empirical DFT calculations was carried out to investigate Jahn-Teller effect in Cu^{2+} placed in octahedral ligand fields. The results show that both semi-empirical and DFT calculations can predict the axial distortion in octahedral Cu(II) complexes. However, the agreement between observed and calculated Cu(II) ligand distances are found to be much greater with DFT calculations than with semi-empirical calculations.

Key Words: Copper(II), Jahn-Teller effect, Distortion, PM3, DFT.

INTRODUCTION

Six-coordinated copper(II) generally display octahedral geometry with a tetragonal elongation along a four-fold axis[1] so that there is a planar array of four shorter Cu-L (where L stands for a ligand) bonds and two *trans* long ones. For example, in $Cu(H_2O)_2(NH_3)_4^{2+}$ it is found that 4Cu-N distances are all equal to 2.05 Å whereas the Cu-O distances[2] are 2.59 and 3.37 Å. There are also numerous cases in which apparently octahedral Cu(II) complexes exhibit a pulsating Jahn-Teller effect[3].

The d^9 configuration makes Cu(II) subject to Jahn-Teller distortion. The theorem may be stated as follows: Any non-linear molecular system in a degenerate electronic state will be unstable and will undergo some kind of distortion that lowers its symmetry and split the degenerate state. Although the theorem tells us that a regular octahedral complex may be unstable with respect to a distortion, it does not tell us anything about the magnitude of distortion. A very small distortion (small enough to escape detection by most techniques), could in principle satisfy Jahn-Teller requirement[4]. The aim of the present study was to investigate how well molecular modelling analyses based on semi-empirical and DFT calculations could predict the Jahn-Teller distortion in Cu(II) when placed in an octahedral ligand field. Specifically, the structures of the complex ions: $Cu(NH_3)_4(H_2O)_2^{2+}$, $CuCl_2{\cdot}2H_2O$, $Cu(H_2O)_6^{2+}$, $Cu(NH_3)_6^{2+}$, $CuCl_4(H_2O)^{2-}$ and $CuSO_4{\cdot}5H_2O$ were optimized based on PM3 and DFT calculations using the molecular modelling program Spartan'02[5].

EXPERIMENTAL

The structures of $Cu(NH_3)_4(H_2O)_2^{2+}$, $CuCl_2{\cdot}2H_2O$, $Cu(H_2O)_6^{2+}$, $Cu(NH_3)_6^{2+}$, $CuCl_4(H_2O)^{2-}$ and $CuSO_4{\cdot}5H_2O$ were optimized based on molecular mechanics, semi-empirical and DFT calculations using the program Spartan'02. The calculated Cu(II) ligand distances were then compared with the reported values to find out the success of the calculations in predicting the Jahn-Teller distortions in the complexes.

Spartan'02 calculations

The structures were first optimized based on molecular mechanics calculations based on MMFF94 force field. The structures were then optimized based on semi-empirical calculations using the routine PM3. Finally, the structures were optimized based on DFT calculations using the basis set 6-31G*. The six Cu(II) ligand bond distances (two axial and four equatorial) for each structure optimized by semi-empirical and DFT calculations were then recorded and compared with the experimentally observed values. The spin multiplicity of Cu(II) was set at two.

RESULTS AND DISCUSSION

Table-1 gives the observed and calculated Cu(II) ligand bond distances for the complexes: $Cu(NH_3)_4(H_2O)_2^{2+}$, $CuCl_2{\cdot}2H_2O$, $Cu(H_2O)_6^{2+}$, $Cu(NH_3)_6^{2+}$ and $CuCl_4(H_2O)^{2-}$. It can be seen that for $Cu(NH_3)_4(H_2O)_2^{2+}$, the observed axial Cu-O bond lengths are 2.59 and 3.37 Å and the four equatorial Cu-N bond lengths are each equal to 2.05 Å. The corresponding values from PM3 calculations are axial: Cu-O: 2.043 and 2.041 Å and the equatorial 4Cu-N: 1.937, 1.942, 1.937 and 1.942 Å. The values from DFT calculations are axial: Cu-O bond distances: 2.202 and 3.710 Å and equatorial 4Cu-N bond distances: 2.022, 2.044, 2.066 and 2.099 Å. It can be seen that although both PM3 and DFT calculations have been able to predict axial elongation, the results obtained from DFT calculations agree much more closely with the experimentally observed values. When we compare the results for $CuCl_2{\cdot}2H_2O$, it is found that both PM3 and DFT calculations underestimate the extent of elongation of the two axial Cu-Cl bond lengths (the observed values being 2.98 and 2.98 Å whereas the predicted values are from PM3: 2.129 and 2.129 Å and from DFT: 2.261 and 2.261 Å). However, once again the agreement is found to be better for DFT calculations than for PM3 calculations. The same conclusion can be made for $Cu(H_2O)_6^{2+}$, $Cu(NH_3)_6^{2+}$, $CuCl_4(H_2O)^{2-}$ and $CuSO_4{\cdot}5H_2O$.

Conclusion

Although both semi-empirical and DFT calculations can predict qualitatively the axial elongation in Cu(II) ligand distances in octahedral ligand field, the agreement between observed and calculated Cu(II) ligand distances is much greater with DFT calculations.

TABLE-1
OBSERVED AND CALCULATED Cu(II) LIGAND BOND DISTANCES FOR THE COMPLEXES: $Cu(NH_3)_4(H_2O)_2^{2+}$, $CuCl_2 \cdot 2H_2O$, $Cu(H_2O)_6^{2+}$, $Cu(NH_3)_6^{2+}$, $CuCl_4(H_2O)^{2-}$ AND $CuSO_4 \cdot 5H_2O$

Complex ion or molecule	Calculation type	Routine used	Axial bond distances (Å)	Equatorial bond distances (Å)
$Cu(NH_3)_4(H_2O)_2^{2+}$	Observed[2, 6, 7]	N/A	1 Cu-O: 2.59, 1 Cu-O: 3.37	4 Cu-N: 2.05, 2.05, 2.05, 2.05
	Semi-empirical	PM3	1 Cu-O: 2.043, 1 Cu-O: 2.041	4 Cu-N: 1.937, 1.942, 1.948, 1.937
	DFT	B3LYP with basis set 6-31G*	1 Cu-O: 2.202, 1 Cu-O: 3.710	4 Cu-N: 2.044, 2.066, 2.022, 2.099
$CuCl_2 \cdot 2H_2O$	Observed[2, 6, 7]	N/A	2 Cu-Cl: 2.98, 2.98	2 Cu-Cl: 2.31, 2.31; 2 Cu-O: 2.01, 2.01
	Semi-empirical	PM3	2 Cu-O: 2.129, 2.129	2 Cu-O: 2.129, 2.129; 2 Cu-Cl: 2.140, 2.140
	DFT	B3LYP with basis set 6-31G*	2 Cu-O: 2.261, 2.261	2 Cu-O: 2.261, 2.261; 2 Cu-Cl: 2.252, 2.252
$Cu(H_2O)_6^{2+}$	Observed[2, 6, 7]	N/A	2 Cu-O: 2.46, 2.46	4 Cu-O: 1.96, 1.96, 1.96, 1.96
	Semi-empirical	PM3	2 Cu-O: 1.909, 1.909	4 Cu-O: 1.898, 1.898, 1.983, 1.983
	DFT	B3LYP with basis set 6-31G*	2 Cu-O: 2.206, 2.206	4 Cu-O: 2.068, 2.068, 2.141, 2.141
$Cu(NH_3)_6^{2+}$	Observed[2, 6, 7]	N/A	2 Cu-N: 2.62, 2.62	4 Cu-N: 2.07, 2.07, 2.07, 2.07
	Semi-empirical	PM3	2 Cu-N: 2.053, 2.062	4 Cu-N: 1.963, 1.963, 1.962, 1.962
	DFT	B3LYP with basis set 6-31G*	2 Cu-N: 2.202, 3.710	4 Cu-N: 2.022, 2.044, 2.066, 2.099
$CuCl_4(H_2O)_2^{2-}$	Observed[2, 6, 7]	N/A	2 Cu-Cl: 2.98, 2.98	2 Cu-O: 2.01, 2.01; 2 Cu-Cl: 2.31, 2.31
	Semi-empirical	PM3	2 Cu-O: 2.112, 2.112	4 Cu-Cl: 2.251, 2.251, 2.249, 2.249
	DFT	B3LYP with basis set 6-31G*	2 Cu-Cl: 3.096, 3.096	2 Cu-Cl: 2.368, 2.368; 2 Cu-O: 1.966, 1.966
$CuSO_4 \cdot 5H_2O$	Observed[2, 6, 7]	N/A	2 Cu-OSO_3: 2.40, 2.40	4 Cu-OH_2: 1.96, 1.96, 1.98, 1.99
	Semi-empirical	PM3	2 Cu-O: 1.909, 1.909	4 Cu-O: 1.898, 1.898, 1.983, 1.983
	DFT	B3LYP with basis set 6-31G*	2.206, 2.206	4 Cu-O: 2.068, 2.068, 2.141, 2.141

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