Structure of bis(3-amino-1-phenyl-2-buten-1-onato) copper(II) and prediction of its formation constant

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Introduction

β-Enaminones are versatile synthetic intermediates and have been extensively used for the preparation of a variety of heterocyclic systems [1,2]. Therefore, their transition metal complexes can act as possible alternatives for olefin polymerization catalysts [3,4]. A series of copper(II) complexes based on *β*-ketoamine ligands are investigated and used for the polymerization of norbornene and styrene in the presence of methylaluminoxane, as well.

The main purpose of the present paper is to investigate the structure of bis(3-amino-1-phenyl-2-buten-1-onato) copper(II) ($Cu(APBO)_2$) and to determine its **kf** by means of density functional theory (DFT). The calculated geometrical parameters for this complex will be compared with corresponding X-ray results.

Theoretical methods

The molecular equilibrium geometry and thermodynamic properties of this compoundwere computed with the GAUSSIAN 09 software [5] by using B3LYP hybrid density functional [6,7] and 6-311G* basis set.

Results and discussion

The geometry of $Cu(APBO)_2$, calculated at B3LYP/6-311G*, is given in Fig. 1. The full optimized geometrical parameters of this compound along with the experimental structural parameters are compared in Table 1. According to this table, the bond length difference of C-O and C-N in $Cu(APBO)_2$ is less than that of APBO which indicates more stability of this compound due to more electron π-delocalization. Theagreement between the geometrical parameters calculated at the B3LYP level and the experimental X-ray data is excellent.

The formation constant of $Cu(APBO)_2$ has been obtained by the calculation of the thermodynamic properties of all species in the following reaction and using $\Delta G^\circ = - RT \ln K_f$,

$$Cu^{2+}(sol) + 2CH_3COO^-(sol) + 2APBO(sol) \rightarrow Cu(APBO)_2(s) + 2CH_3COOH(sol)$$

The value of calculated formation constant of $Cu(APBO)_2$ is 6.93×10^{17}.

Fig 1. The optimized structure of $Cu(APBO)_2$.

Table 1. The calculated and experimental geometrical parameters for $Cu(APBO)_2$

		Calculated	
Bond lengths (Å)	**X-ray**	**$Cu(APBO)_2$**	**APBO**
Cu – O	1.954	1.956	
Cu – N	1.919	1.918	
O – C	1.298	1.282	1.245 [a]
N – C	1.312	1.311	1.346
C – N	1.318	1.346	1.346

[a]data from ref [9]

Conclusions

The structural parameters of $Cu(APBO)_2$ were calculated at B3LYP level using the 6-311G* basis set. Comparison of these parameters implies that the stability of $Cu(APBO)_2$ is more than APBO ligand. The structure of this complex was confirmed by X-ray diffraction method. There is a good agreement between the calculated geometries and the X-ray crystallographic results. The formation constant of $Cu(APBO)_2$ was obtained by DFT calculation and its value is 6.93×10^{17}.

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