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Structure and vibrational assignment of bis(4-amino-3-penten-2-onato)nickel(II). A density functional theoretical study

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ABSTRACT

Bis(4-amino-3-penten-2-onato) nickel(II), (Ni(APO)$_2$), and its NH deuterated analog, Ni(DAPO)$_2$, were synthesized and their molecular structure and vibrational assignments were investigated by means of density functional theory (DFT) calculations. The molecular stability was investigated by applying the NBO and geometry calculations. The harmonic vibrational frequencies of Ni(APO)$_2$ and Ni(DAPO)$_2$ were obtained at the B3LYP level using 6-311G* basis set. The calculated geometrical parameters and vibrational frequencies were compared with the experimental results. The measured vibrational band frequencies were interpreted in terms of the calculated vibrational normal modes. The scaled theoretical frequencies and the structural parameters were found to be in good agreement with the experimental data.

1. Introduction

In recent years, the use of amine and imine complexes based on late transition metals as active and selective catalysts for the polymerization of α-olefins has received a great deal of attention [1–7]. The late transition metal complexes, because of their less oxophilic nature relative to early transition metal complexes, are generally considered to be more tolerant toward polar media and polar functional groups and thus make them possible targets for the development of catalysts for polar monomer polymerizations [5,8].

Ni is known to be an excellent catalyst for many processes. He and Wu [9] synthesized and characterized a series of bis(β-ketoamino)nickel(II) complexes and investigated the effects of catalyst structure and polymerization conditions on the polymerization activity of methyl methacrylate using bis(β-ketoamino)nickel(II)/methylaluminoxane (MAO) as catalytic systems [10].

According to Gurr's study [11], the unit cell of bis(4-amino-3-penten-2-onato) nickel(II) [hereafter abbreviated as Ni(APO)$_2$], is orthorhombic, space group Ccca, and the unit cell dimensions are $a = 16.7$, $b = 15.1$, $c = 13.5$ Å. In this research, the complex was prepared in high purity and experimental data were compared with the theoretical calculation results.

2. Experimental

The APO ligand was synthesized according to Lacey [12]. This ligand was added to an aqueous solution of nickel (II) acetate and Ni(APO)$_2$ was obtained as a precipitate. This precipitate was purified by crystallization from a chloroform solution. Anal. Found: C, 47.52; H, 6.42; N, 10.66; Ni, 23.19 Calc.: $NiC_{10}H_{16}O_2N_2$: C, 47.11; H, 6.33; N, 10.99; Ni, 23.02%. M.p. 245 °C, ^1H NMR ($CDCl_3$, 100 MHz, reference: solvent residual peak, δ 7.24 ppm): δ 9.66(b, 2H, NH), δ 4.83(s, 2H, CH), δ 1.84(s, 6H, CH_3CO), δ 1.58(s, 6H, CH_3CN).

The NH deuterated analog of Ni(APO)$_2$, referred to as Ni(DAPO)$_2$, was prepared according to the literature [13].

The infrared spectra in the region 500–4000 cm^{-1} were recorded on a Bomem MB-154 Fourier transform spectrophotometer using KBr pellets and $CHCl_3$ and CH_2Cl_2 solutions. The spectra were collected with a resolution of 2 cm^{-1} by signal averaging the results of 15 scans.

The Far-IR spectra of CsBr pellets of Ni(APO)$_2$ in the 600–150 cm^{-1} region were obtained by using a ThermoNicolet NEXUS 870 FT-IR spectrometer equipped with a DTGS/polyethylene detector and a solid substrate beam splitter. The spectra were collected with a resolution of 2 cm^{-1} by averaging the results of 64 scans.

The FT-Raman spectra in the region 3200–200 cm^{-1} were recorded employing a 180° back-scattering geometry and a Bomem MB-154 Fourier transform Raman spectrometer operating

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at the 1064 nm excitation line of a Nd:YAG laser. It was equipped with a ZnSe beam splitter and a TE cooled InGaAs detector. Rayleigh filtration was afforded by a set of two holographic technology filters. The spectra were accumulated for 2500 scans with a resolution of 2 cm^{-1}. The laser power at the sample was 500 mW.

3. Method of analysis

All the computations in the present study were performed using GAUSSIAN 03 software package [14] and NBO 5.0 [15] programs. The geometry optimization and vibrational frequencies are performed at the B3LYP level using 6-311G* basis set.

Raman activities were computed by numerical differentiation of dipole derivatives with respect to the electric field, using standard GAUSSIAN 03 procedures (Freq = Raman) and default options.

Vibrational assignments are based on comparison of calculated and observed Raman and IR frequencies and activities. The proposed assignments are further corroborated by noting the deuterium isotopic shifts of different bands and their predicted shifts by the same theoretical methods. The assignment of the calculated wavenumbers is aided by the animation option of the GaussView 3.0 graphical interface for Gaussian programs [14,16], which gives a visual representation of the shape of the vibrational modes.

4. Results and discussion

4.1. Molecular geometry

According to the theoretical DFT calculations, two configurations are possible for Ni(APO)$_2$. These are recognized as trans and cis configurations and are shown in Fig. 1. The optimized geometrical parameters of trans Ni(APO)$_2$ are summarized in Table 1. The theoretical calculations in the gas phase indicate that the trans configuration is considerably more stable than the cis configuration (about 27.45 kJ mol^{-1}), which is not in agreement with the X-ray result of Gurr [11]. According to the X-ray crystallography, the cis configuration is prominent. This is most likely due to the neglect of solvent effects in our theoretical calculations, which is certainly important (but not easily incorporated) for Ni(APO)$_2$ complex systems [17,18]. However, Bradbury et al. [19] have shown that Ni(APO)$_2$ is predominantly trans in solution with the cis and trans isomers in rapid equilibrium at room temperature, therefore both vibrational frequencies and molecular geometry is dependent on the chemical environment. This isomerization probably occurs by twisting to produce a pseudo-tetrahedral intermediate of the type discussed by Holm and O'Connor [20]. Calculations in solution phase show that the energy difference between the cis and trans isomers decreases considerably (about 14.4 kJ mol^{-1}), compared to that in the gas phase. Unfortunately there is no way to predict the energy difference in the solid state. However, this large energy shift may be consistence with the lower energy of the cis form in the solid state.

Table 1
Selected experimental (X-ray) and calculated geometrical parameters for Bis-(4-amino-3-penten-2-ono)nickel(II) (bond lengths in Å, bond angles in °).

Parameter	Ni(APO)$_2$		X-ray	Ni(acac)$_2$[a]	APO[b]
Bond lengths	Cis	Trans			
Ni—O	1.865	1.853	1.845	1.876	
Ni—N	1.859	1.857	1.843		
O—C	1.274	1.287	1.337	1.273	1.238
N—C	1.318	1.306	1.299		1.348
C9—C10	1.406	1.420	1.405	1.401	1.445
C7—C10	1.395	1.385	1.342		1.375
C6—C14	1.511	1.510	1.475	1.504	1.522
C8—C16	1.513	1.512	1.536		1.505
N—H	1.014	1.014	0.796		1.005
C14—H	1.091	1.091	0.960		
C11—H13	1.081	1.083	0.961		1.083
Bond angles					
O2—Ni—O3	84.66	179.58	85.30	93.6	
O2—Ni—N5	176.8	93.37	178.0		
O2—NI—N4	92.17	86.63	94.33		
N4—Ni—N5	90.99	179.83	86.11		
O2—C6—C11	124.99	125.56	123.87		123.5
O2—C6—C14	114.71	114.03	116.05		119.5
N4—C8—C11	122.83	121.83	123.76		122.4
N4—C8—C16	118.45	120.07	116.97		116.0
C16—C8—C11	120.30	120.41	120.03		121.6
C6—C11—C8	122.33	123.01	124.37		123.1
Ni—N—H	118.52	114.86	121.45		
C—N—H	112.62	116.12	111.39		
C8—C11—H13	118.62	118.77	118.20		118.2
H4—N4—Ni—N5	0.72		2.74		
O2—Ni—N5—H5		0.5			
H17—C17—C9—N5	158.022	2.752	129.43		
H—C14—C6—O2	179.020	179.729	156.37		
[c]ΔEgas	27.45				
ΔEsolution	13.07				

[a] Data from [21].

[b] Calculated at B3LYP/6-311G*.

[c] $\Delta E = E_{cis} - E_{Trans}$ in kJ mol^{-1}.

As it is shown in Table 2, the calculated bond lengths of C—O and C_7—C_{10} are longer and C—N and C_9—C_{10} are shorter than the corresponding values in APO. This results show that the resonance in Ni(APO)$_2$ has increased relative to APO. The calculated Ni—O distance in Ni(APO)$_2$ is 1.882 Å that is shorter and, therefore, stronger than the similar bond in bis (acetylacetonato) nickel(II) (Ni(acac)$_2$) [21].

As Table 1 shows, the geometrical parameters are close to the previously determined structural X-ray parameters [11]. The

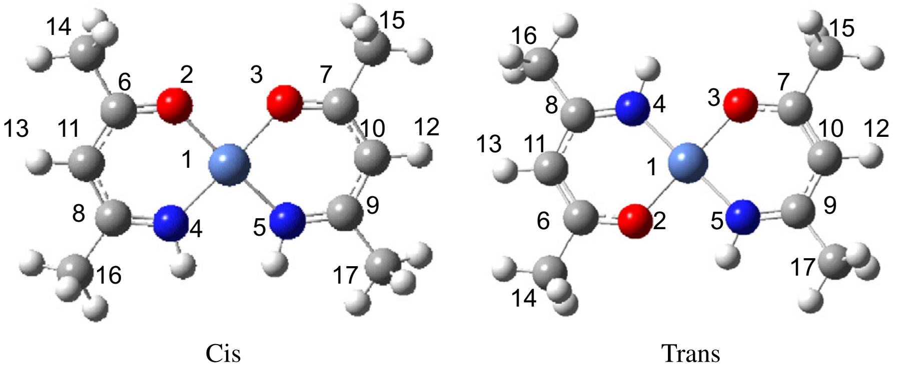

Fig. 1. Cis and Trans configurations and atom numbering of Ni(APO)$_2$.