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Structural, IR, and EPR studies of the bis(methoxyacetato) diaquo-copper(II) complex

Z. Alimohammadi · H. Rahemi · M. Golzan · S. F. Tayyari · M. J. Riley

Abstract The structure, stability, and the IR, and EPR spectroscopic properties of bis(methoxyacetato)diaquo-copper(II) were studied both experimentally using FT-IR and theoretically using B3LYP/6-31G**, B3LYP/6-311G, BWP91/6-31G** methods. The same approaches were used to calculate the harmonic frequencies and to compare them to the experimental solid state values. The g-tensors are calculated using the NMR/GIAO computational method.

Keywords Bis(methoxyacetato)diaquo-copper(II) · DFT · EPR · IR

Introduction

The crystal structure of *trans*-bis(methoxyacetato)diaquo-copper(II), $C_6H_{14}O_8Cu$, has been determined by neutron diffraction at 4.2 K (monoclinic, $P2_1/n$, $a=6.88(1)$, $b=7.19(1)$, $c=9.77(2)$ Å, $\gamma=95.7(1)$, ($Z=2$)) and by X-ray diffraction at 125, 165, 205, 240, 265, 295, and 325 K, [1]. The copper (II) coordination at 4.2 K is a tetragonally distorted elongated rhombic octahedron (Cu-OOC 1.955(1), Cu-OMe 2.209(1), and Cu-OH₂ 2.031(2) Å). There is no phase change in the temperature range 4.2–325 K, however, as the temperature is increased to 325 K, the Cu-OOC bonds shorten slightly to 1.934(5) Å, the Cu-O-Me bonds shorten more markedly to 2.137(4) Å, and Cu-OH₂ lengthens to 2.155(6) Å to give an apparent tetragonally distorted compressed rhombic octahedron [1]. In the crystal structure there are six hydrogen bonds per complex and ignoring them may cause major structural deviations from crystalline structure. An interesting point is that the double bonded oxygen atom of the methoxyacetate participates in the formation of two hydrogen bonds.

In the present study one of our aims is to analyze the FTIR spectrum of the bis(methoxyacetato)diaquo-copper (II) crystal and to compare the vibrations to those theoretically computed for the free complex to determine the effect of the hydrogen bonding.

EPR spectroscopy represents one of the most powerful experimental methods for investigating electronic and structural features of systems containing unpaired electrons, such as radicals, coordination compounds and paramagnetic sites in solids [2, 3]. Since, the bis(methoxyacetato)diaquo-copper(II) complex has the d⁹ configuration, it possesses an unpaired electron, and can interact with an applied magnetic field, making it EPR active. Therefore, our other principal goal will be studying changes of the EPR g tensor parameters in the 4.2–325K temperature range using the available solid state bond lengths and bond angles of the complex.

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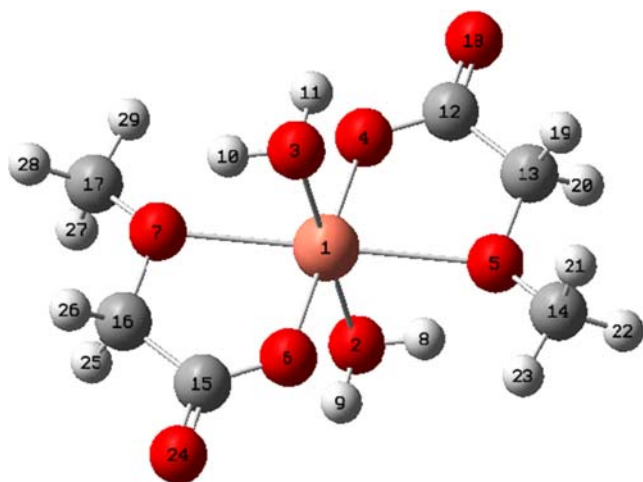Brisbane, Qld 4072, Australia

Experimental section

The complex is prepared according to the procedure given in the literature [1]. Basic copper carbonate was prepared

Fig. 1 The B3LYP/6-31G** optimized structure of the bis(methoxyacetato) diaquo-copper (II)

by using 6M nitric acid and copper wire. Sodium hydroxide is then added to neutralize the excess nitric acid. A saturated sodium carbonate solution is then added and the sediment filtered off from solution. The copper carbonate is dissolved in the aqueous methoxyacetic acid. The excess carbonate was filtered off from solution until pH<5 then left to crystallize by evaporation of its aqueous solution, [1]. The FTIR spectrum in the 400–4000 cm^{-1} region was acquired using a FT-IR Thermonicolet, Nexus – 670 Spectrophotometer.

Computational details

Geometry optimizations were performed at the gradient corrected DFT level using a combination of Becke's three-parameter adiabatic connection exchange functional [4, 5] with the Lee-Yang-Parr correlation [6], all together B3LYP. All structures were fully optimized with the Gaussian 03W program at the B3LYP/6-311G, 6-31G**, BWP91/6-31G** levels, [7]. After the optimization, IR absorption spectra and g values were calculated using the GIAO method [8–12].

Results and discussion

A   The structure

This complex is a rather large cation, containing 29 atoms with several heavy atoms and it is rather difficult to handle with a PC. The only symmetry element the complex has is the center of inversion, therefore the complex is a centro- symmetric species. Using Gaussian 03 software, the z-matrix is written by keeping C_i symmetry in the input file then the optimization was carried out by DFT level theory.

The optimized structural parameters are saved for the next step of calculations. The g-tensor calculation was performed by using of NMR/GIAO option.

Geometry optimization of the bis(methoxyacetato)diaquo-copper(II) is carried out at B3LYP/6-31G**, 6-311G and BPW91/6-31G** levels of calculations, which provide a chance to compare two basic methods B3LYP/6-31G** and BPW91/6-31G** with inclusion of polarization in the basis sets. The optimized structure of the molecule is displayed using GaussView, shown in Fig. 1. Bond lengths and bond angles are compared to experiment in Table 1 [13]. Bond angles and bond lengths were calculated in the gas phase; therefore it is expected that there will be a difference between experimental and calculated values. The B3LYP/6-31G** level of calculation provides a better agreement to corresponding experimental values. When hydrogen bonds are neglected, bond lengths in which oxygen involved in H-bonds O_2-Cu and O_4-Cu (2.0779 and 1.8787 Å) are shorten, but bond length in which oxygen is involved in H-bonds O_5-Cu (2.4245 Å) is longer than the corresponding solid state bond lengths (2.1392,

Table 1 Optimized bond lengths and bond angles with different levels of theory

Bond length	B3LYP/6-31G**	BPW91/6-31G**	Expt. [14]
O2-Cu	2.0779	2.0399	2.031
O4-Cu	1.8787	1.8737	1.955
O5-Cu	2.4245	2.6107	2.209
H8-O2	0.9737	0.9915	
H9-O2	0.9724	0.9807	
C12-O4	1.3063	1.3143	
C13-O5	1.4328	1.4436	
C14-O5	1.4283	1.4365	
C12-O18	1.2190	1.2307	
H19-C13	1.0986	1.1053	
H20-C13	1.0961	1.1041	
H21-C14	1.0968	1.1036	
H22-C14	1.0973	1.1046	
H23-C14	1.0914	1.0980	
O2-Cu-O5	89.84	73.06	87.45
O4-Cu-O5	77.89	76.07	77.91
O2-Cu-O4	94.01	68.81	89.09
H8-O2-Cu	95.25	93.37	
H9-O2-Cu	95.33	97.33	
C12-O4-Cu	119.54	130.19	
C13-O5-Cu	119.64	103.52	
C14-O5-Cu	133.03	137.55	
O18-C12-O4	124.00	124.95	
H19-C13-O5	111.45	109.31	
H20-C13-O5	113.71	110.53	
H21-C14-O5	109.71	110.58	
H22-C14-O5	98.04	111.33	
H23-C14-O5	116.73	106.95	

Fig. 2 Theoretical fit of the experimental FTIR spectrum of the complex
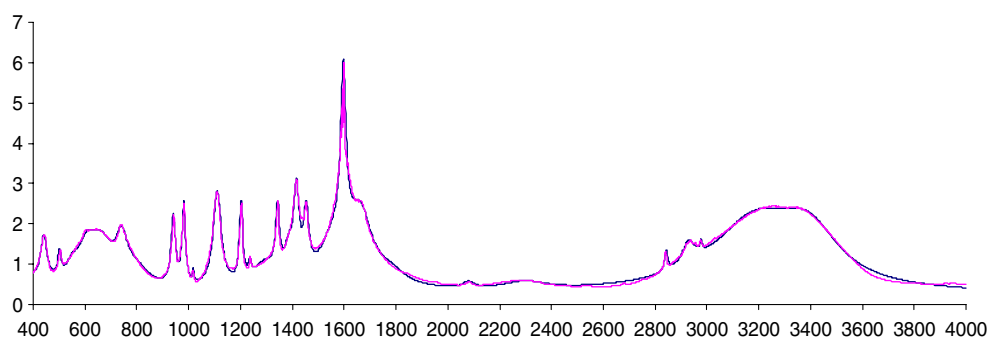
19.9331 and 2.1441 Å respectively), Table 1. Calculated H_8O_2Cu bond angle, 95.25°, is rather far from the expected value, which can be explained due to single molecule calculation; solid state hydrogen bond network is neglected. However, generally we expect by increasing the size of basis sets to approach the experimental values, but the level of calculation has a major effect in calculation.

The X-ray data in the temperature range of 4.2–325 K is available, therefore there is a chance to use solid state experimental geometry data to calculate g values and inspect for possible phase transitions. We have used the low temperature (4.2 K) experimental values in Table 1, as the higher temperature values are a thermal average of a number of structural isomers (see below).

B IR spectrum analysis

Using a Lorentzian line shape the bis(methoxyacetato) diaquo-copper (II) FTIR spectrum is fitted as shown in Fig. 2. The details of the fitting and band assignment are summarized in Table 2. Animation of the theoretically obtained frequencies by using GaussView had a major role in band assignment. When a scaling factor of 0.97 is used to correct for anharmonicity; the calculated frequencies are in better correlation with the experimental values. The hydrogen bonding network in the crystal causes the C = O stretching mode to appear at 1597.6 cm^{-1}; about 100 cm^{-1} lower than its normal value. This drastic shift can be explained due to involvement of this oxygen in two hydrogen bonds. CH_3 and CH_2 stretching frequencies are shifted about 10 cm^{-1} downwards while bending modes of the fragments participating in hydrogen bonds are elevated in the same order. Traces of free water were also detected.

C The g tensor calculation

Jakob and Reinen [14] performed EPR single-crystal and powder measurements between 4.2 and 350 K using a Varian E 15 spectrometer at X-and Q-band frequencies. DPPH was used as internal standard. The Cu-O bond lengths in the pseudo octahedral bis(methoxyacetato)dia-quo-copper(II) complex are determined by the bonding

properties of the three different oxygen ligator atoms [14]. The intention of the following investigation is to correlate the temperature dependence of the g-values with corresponding calculated values using the neutron diffraction and X-Ray measured Cartesian coordinates of all atoms, [1], which were available at the temperatures 4.2,

Table 2 Frequencies are obtained by decomposing the absorption spectra

No	Frequency	Intensity, Rel.	Band width, cm^{-1}	Assignment
1	3395	1.2	280	OH Asym. Str.
2	3185.5	1.7	410	OH Sym. Str
3	2977.9	0.25	10	CH_3 Asym. Str.
4	2929.4	0.55	60	CH_2 Asym. Str.
5	2844	0.5	15	CH_3, CH_2 Sym. Str.
6	2298.9	0.2	200	Water
7	2080.6	0.15	50	
8	1661.6	1.75	115	Water
9	1597.6	4.25	25	C=O Str.
10	1556.8	1	120	HOH Defor.
11	1454	1.5	25	CH_2 Sciss.
12	1416.2	2.05	25	CH_2 Defor.
13	1387.1	0.65	40	CH_3 Umbrella
14	1343.5	1.6	18	
15	1295	0.55	120	CH_2 Wag.
16	1236.8	0.35	12	O-C=O Defor.
17	1202.8	1.9	15	CH_2 Twist
18	1110.6	2.37	37	CH_3 Twist
19	1018.5	0.3	5	CH_2 Rock
20	981.6	2	15	CH_3 Rock
21	941	1.7	20	CH_3 ,CH_2 bend
22	795.4	0.43	125	C=O out of plane bend
23	742	0.96	55	Ring Defor.
24	662.5	1	110	H_2O Defor.
25	607.2	0.8	80	H_2O Defor.
26	552.9	0.35	60	Ring Defor.
27	501.5	0.6	15	Ring Defor.
28	441.4	1.1	30	Ring Defor.

Rel. = Relative, Asym. = Asymmetry, Sym. = Symmetry, Str. = Stretching, Defor. = Deformation, Sciss. = Scissoring, Wag. = Wagging

Fig. 3 The temperature dependence of the g-values of bis (methoxyacetato)diaquo-copper (II)
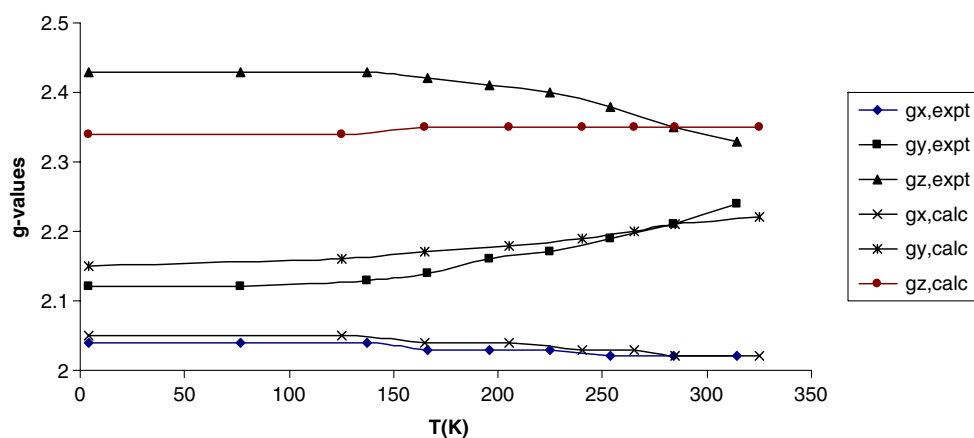
125, 165, 205, 240, 265, 295, and 325 K. The g-tensor values have been calculated using GIAO/ B3LYP/6-31G** as implemented in Gaussian 03.

In a series of calculations covering the temperature range 4.2–325 K the g tensor components are computed and diagonalized g_x, g_y, and g_z are represented in Fig. 3 and Table 3. The temperature dependent behavior of computed values compared to experiment is close for g_x (within 0.5%) following the experimental values and by increasing temperature the correspondence becomes closer. The g_y and g_z components show a greater deviation, as apparent from the Fig. 3 However as temperature increases the deviations in all three components getting smaller and in the temperature 285 K the calculated values are the same as experimental ones. The reason for this behavior is because the bonds associated with g_y and g_z, the $Cu\text{-}OH_2$ and the $Cu\text{-}OCH_3$ bonds respectively, are apparent rather than actual bond lengths. The crystallographically determined bond lengths are likely an average of two or more Jahn-Teller levels that are in thermal equilibrium and are structural isomers. This mechanism is known to be responsible, for example, for the temperature dependent bond lengths and g-values that occurs in a number of copper Tuttons salts [15]. The unit cell dimensions show large changes with temperature; **a** from 6.88 to 6.972, **b** from 7.19 to 7.244 and **c** from 9.77 to 10.166 Å in the range 4.2–325 K [1]. Changes in unit cell dimensions in the temperature range 4.2–120 K were not significant and therefore calculated and experimental g values stay almost unaltered in this region. Beyond this region, the unit cell dimensions, bond lengths, and the experimental g values all change significantly.

Conclusion

The structural optimization of the bis(methoxyacetato) diaquo-copper(II) has been carried out using B3LYP/6-

31G** and BPW91/6-31G level of calculations and then the IR frequencies calculated with the same approaches. Reasonable correlations between calculated and experimental determined values are obtained.

The structure of the bis(methoxyacetato)diaquo-copper (II) consists of three different pairs of oxygen ligators, two of which are part of chelate rings Cu-OOC, Cu-OMe and the third from water molecules. The crystallographically determined copper (II) coordination sphere varies with temperature, but when the g tensor components are calculated using these geometries with a B3LYP/6-31G** approach, a good correlation between the experimental and calculated values is only obtained for the lowest g-value. This demonstrates that the temperature dependent structure and g-values of this complex are more complicated and we are pursuing additional structural and EPR measurements on this system [16].

Table 3 Experimental and calculated of g-tensor values

T	$g_{x(expt)}$	$g_{y(expt)}$	$g_{z(expt)}$	g_x	g_y	g_z
4.2	2.04	2.12	2.43			
77	2.04	2.12	2.43			
137	2.04	2.13	2.43			
166	2.03	2.14	2.42			
196	2.03	2.16	2.41			
225	2.03	2.17	2.4			
254	2.02	2.19	2.38			
284	2.02	2.21	2.35			
314	2.02	2.24	2.33			
4.2				2.05	2.15	2.34
125				2.05	2.16	2.34
165				2.04	2.17	2.35
205				2.04	2.18	2.35
240				2.03	2.19	2.35
265				2.03	2.2	2.35
285				2.02	2.21	2.35
325				2.02	2.22	2.35

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