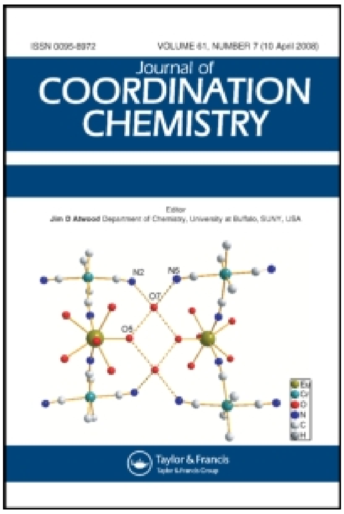

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A SMALL JAHN-TELLER DISTORTION AROUND A Cu(II) ATOM CRYSTAL STRUCTURE OF BIS(*N,N'*-DIMETHYL-FORMAMIDE)BIS(1,1,1,5,5,5-HEXAFLUORO-2,4-PENTANEDIONATO)COPPER(II)

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A SMALL JAHN–TELLER DISTORTION AROUND A Cu(II) ATOM CRYSTAL STRUCTURE OF BIS(*N*,*N*′-DIMETHYLFORMAMIDE)BIS(1,1,1,5,5,5-HEXAFLUORO-2,4-PENTANEDIONATO)COPPER(II)

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The complex Cu(hfac)$_2$(DMF)$_2$ (where hfac = the anion of hexafluoropentanedione and DMF = dimethylformamide) has been prepared and its crystal structure has been determined by X-ray diffraction methods. The complex molecule locates around an inversion centre in the crystal state. Two DMF ligands coordinate to the Cu(II) atom in the axial direction while two hfac ligands chelate to the Cu(II) atom in the equatorial plane. The remarkable feature of this structure is that the difference of 0.032(3) Å in coordination bond distances between the axial direction and the equatorial plane shows a very small Jahn–Teller distortion around the Cu(II) atom.

Keywords: Cu(II) complex; crystal structure; Jahn–Teller distortion

INTRODUCTION

It is well known that the molecular structures of the six coordinate Cu(II) complexes usually display Jahn–Teller distortion[1] with the coordination bonds in the axial direction being longer (the elongated distortion) or shorter (the compressed distortion) than those in the equatorial plane. A few X-ray structures of Cu(II) complexes, in which the Cu(II) atom is located on a higher crystallographic symmetrical position of D_3 or T_d symmetry, are in

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* Corresponding author.

apparent violation of the Jahn–Teller theorem, six coordination bonds being exactly identical in length owing to symmetry restrictions.[2–4] During studies of properties of Cu(II) complexes in solution we obtained the title complex and determined its crystal structure by X-ray diffraction. It is notable that a very small Jahn–Teller distortion exists in the present Cu(II) complex but without any symmetrical restriction.

EXPERIMENTAL

Synthesis

$Cu(hfac)_2 \cdot H_2O$ prepared in a manner similar to that in the literature[5] was dissolved in a mixed EtOH and DMF (9 : 1 volume ratio), then the solution was refluxed for 1 h. After one week, light green crystals were obtained. C, H and N were analysed using a Carlo-Erba 1160 instrument. *Anal.* Calcd. for $C_{16}H_{16}N_2O_6F_{12}Cu$ (%): C, 30.78; H, 2.56; N, 4.49; Found: C, 31.02; H, 2.63; N, 4.38.

Crystal Structure Determination

Intensity data were measured on a Nonius CAD4 diffractometer with MoKα radiation up to $2\theta_{\max}$ of 50°. A total of 2039 independent reflections was measured with the $\omega/2\theta$ scan technique, among which 1836 observed reflections with $I > 3\sigma(I)$ were used for structure refinement. Lp and empirical absorption corrections were applied. The structure was solved by the Patterson method followed by Fourier synthesis and refined anisotropically for all non-H atoms using the TEXSAN program.[6] H atoms were located in a difference Fourier map and fixed during refinement. The final refinement converged R and R_w to 0.049 and 0.061, respectively, where $w = 1$.

RESULTS AND DISCUSSION

Crystal data $C_{16}H_{16}N_2O_6F_{12}Cu$, $M = 623.84$, triclinic, space group $P\bar{1}$, $a = 6.508(2)$, $b = 9.327(2)$, $c = 10.581(1)$ Å, $\alpha = 110.35(1)°$, $\beta = 81.54(2)°$, $\gamma = 104.85(2)°$, $V = 580.9(5)$ Å^3, $Z = 1$, $D_x = 1.78$ g cm^{-3}, $\mu = 1.068$ mm^{-1}, $F(000) = 311$, $(\delta/\sigma)_{\max} = 0.03$, $S = 1.81$.

Final atomic fractional coordinates and equivalent isotropic thermal parameters for non-H atoms are listed in Table I. Selected bond distances and angles are presented in Table II. The molecular structure of the title

TABLE I Atomic fractional coordinates and thermal parameters for non-H atoms with e.s.d.'s in parentheses

Atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq} (Å^2)
Cu	1	1	1	0.0330(3)
F(1)	1.0972(5)	0.4957(3)	0.6828(3)	0.070(1)
F(2)	1.3998(4)	0.6540(3)	0.7204(3)	0.060(1)
F(3)	1.2504(5)	0.6092(3)	0.5403(2)	0.060(1)
F(4)	0.7152(5)	0.8435(4)	0.5148(2)	0.069(1)
F(5)	0.5347(4)	0.9638(3)	0.6854(2)	0.054(1)
F(6)	0.8318(5)	1.0853(4)	0.6195(3)	0.067(1)
O(1)	1.1229(4)	0.8180(3)	0.8701(2)	0.041(1)
O(2)	0.8195(4)	0.9869(3)	0.8527(2)	0.038(1)
O(3)	0.7704(4)	0.8435(3)	1.0734(3)	0.046(1)
N	0.4485(5)	0.6953(4)	1.1068(3)	0.040(1)
C(1)	1.0988(5)	0.7637(4)	0.7467(3)	0.034(1)
C(2)	0.9777(6)	0.8048(5)	0.7630(3)	0.038(1)
C(3)	0.8497(5)	0.9118(4)	0.7311(3)	0.033(1)
C(4)	1.2128(7)	0.6309(5)	0.6712(4)	0.043(2)
C(5)	0.7298(6)	0.9495(5)	0.6361(4)	0.040(1)
C(6)	0.5818(6)	0.7907(4)	1.0495(3)	0.039(1)
C(7)	0.519(1)	0.6520(7)	1.2100(6)	0.058(2)
C(8)	0.2280(8)	0.6343(6)	1.0742(6)	0.054(2)

TABLE II Selected bond distances (Å) and angles (°)

Cu–O(1)	2.040(3)	Cu–O(2)	2.039(2)
Cu–O(3)	2.072(3)	F(1)–C(4)	1.329(5)
F(2)–C(4)	1.331(5)	F(3)–C(4)	1.323(4)
F(4)–C(5)	1.319(5)	F(5)–C(5)	1.321(5)
F(6)–C(5)	1.329(5)	O(1)–C(1)	1.243(4)
O(2)–C(3)	1.247(4)	O(3)–C(6)	1.228(5)
N–C(6)	1.318(5)	N–C(7)	1.455(5)
N–C(8)	1.447(6)	C(1)–C(2)	1.386(5)
C(1)–C(4)	1.527(6)	C(2)–C(3)	1.385(5)
C(3)–C(5)	1.536(5)		
O(1)–Cu–O(2)	90.0(1)	O(1)–Cu–O(3)	89.7(1)
O(2)–Cu–O(3)	94.2(1)	C(1)–O(1)–Cu	124.3(2)
C(3)–O(2)–Cu	123.4(2)	C(6)–O(3)–Cu	129.8(2)
C(6)–N–C(8)	122.2(3)	C(6)–N–C(7)	120.1(4)
C(7)–N–C(8)	117.6(4)	O(3)–C(6)–N	124.2(3)
O(2)–C(3)–C(2)	128.8(3)	O(2)–C(3)–C(5)	113.6(3)
C(2)–C(3)–C(5)	117.6(3)	O(1)–C(1)–C(2)	128.3(3)
C(1)–C(2)–C(3)	123.4(3)	F(1)–C(4)–F(3)	106.5(3)
F(1)–C(4)–F(2)	106.6(3)	F(1)–C(4)–C(1)	110.5(3)
F(2)–C(4)–F(3)	106.7(3)	F(2)–C(4)–C(1)	112.0(3)
F(3)–C(4)–C(1)	114.0(3)	F(4)–C(50)–F(5)	107.6(3)
F(4)–C(5)–F(6)	106.8(3)	F(4)–C(5)–C(3)	113.3(3)
F(5)–C(5)–F(6)	107.0(4)	F(5)–C(5)–C(3)	112.2(3)
F(6)–C(5)–C(3)	109.6(3)		

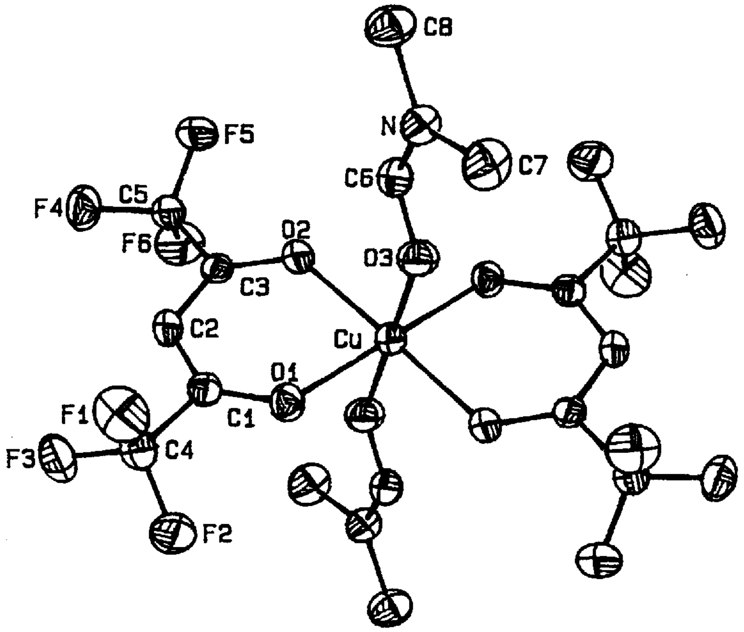

FIGURE 1 Molecular structure of Cu(hfac)$_2$(DMF)$_2$ showing 30% probability displacement ellipsoids. H atoms are omitted for clarity.

complex is illustrated in Figure 1. The complex crystallizes in space group $P\bar{1}$ with one molecule in the unit cell; the Cu(II) atom occupies a crystallographic inversion centre. While two hfac ligands chelate to the Cu(II) atom in the equatorial plane with *trans* configuration, two DMF molecules coordinate to the Cu(II) atom in the axial direction through the amide oxygen atom to complete an elongated octahedral coordination geometry. It is notable that the Cu–O(3) coordination distance of 2.072(3) Å in the axial direction is only 0.032(3) Å longer than those in the equatorial plane [Cu–O(1) = 2.040(3) and Cu–O(2) = 2.039(3) Å].

As is well known, in almost all Cu(II) complexes with an elongated Jahn–Teller distortion the coordination bond distance in the axial direction is about 0.2–0.6 Å longer than those in the equatorial plane.[7] The difference of 0.032(3) Å in the present complex shows an unusually small Jahn–Teller distortion from the regular octahedron. Some coordination bond distances found in relevant Cu(II) complexes are summarized in Table III for comparison. In the equatorial plane the Cu–O distance of 2.040 Å in the present complex is 0.1 Å longer than the average Cu–O distance of 1.940 Å found in hfac complexes of Cu(II) reported previously,[8–11] while in the axial direction

TABLE III Comparison of coordination bond distances (Å)

Complex	*Cu–O in equatorial plane*	*Cu–O in axial direction*	*Ref.*
Cu(hfac)$_2$NITiPr	1.933(6)–1.938(5)		8
Cu(hfac)$_2$(NIT-Me)	1.927(4)–1.956(3)		9
Cu(hfac)$_2$(diprox)	1.926(6)–1.951(6)		10
Cu(hfac)$_2$TMPO	1.943(4)–1.949(5)		11
Cu(Naphac)$_4$(DMF)$_2$		2.131(7)–2.161(7)	12
Cu(hfac)$_2$(DMF)$_2$	2.039(3)–2.040(3)	2.072(3)	This work

the Cu–O distance of 2.072(3) Å in the present complex is 0.074 Å shorter than the average distance of 2.146(7) Å found in a reported DMF complex of Cu(II).[12] We do not know why the Jahn–Teller distortion in the present structure is so unusually small.

Within the hfac ligand the bond distances and angles are normal. The average C–F distance is 1.325(5) Å. Delocalization of the double bond within the enol ring of pentanedione is observed [C(1)–O(1) = 1.243(4) and C(3)–O(2) = 1.247(3) Å] as usually reported for β–diketone complexes. The C(6)–O(3) distance of 1.228(5) Å and C(6)–N distance of 1.318(5) Å in the DMF ligand agrees with those found in [CuCl$_2$(DMF)$_2$]$_2$.[13] A least-squares plane calculation shows good planarity of DMF. The Cu–O(3)–C(6) angle of 129.8(2)° is much larger than 122(1)° reported previously.[12]

The crystal consists of discrete complex molecules. The shortest intermolecular contact of 3.080(4) Å is between F(5) and C(6) $(1-x, 2-y, 2-z)$ atoms.

Acknowledgments

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Supplementary Material

Full lists of H atom positions, anisotropic thermal parameters for non-H atoms and observed and calculated structure factors are available from authors upon request.

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