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Stabilization of a Hydrated Ketone by Metal Complexation. The Crystal and Molecular Structures of Bis-2,2′,N,N′-bipyridyl Ketone-hydrate Nickel(II) Sulfate, Copper(II) Chloride and Copper(II) Nitrate

SUE-LEIN WANG, JAMES W. RICHARDSON Jr., SHELLEY J. BRIGGS, ROBERT A. JACOBSON*
Ames Laboratory-USDOE and Department of Chemistry, Iowa State University, Ames, Iowa 50011, U.S.A.
and WILLIAM P. JENSEN
Department of Chemistry, South Dakota State University, Brookings, S.D. 57007, U.S.A.

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Abstract

The crystal structure of the complexes (I) $Ni[C_{11}N_8N_2(OH)_2]_2SO_4$, (II) $Cu[C_{11}H_8N_2(OH)_2]_2Cl_2\cdot 4H_2O$ and (III) $Cu[C_{11}H_8N_2(OH)_2]_2(NO_3)_2\cdot 2H_2O$ have been determined by three-dimensional X-ray analysis methods. Crystal data are: (I), monoclinic, space group $C2/c$, $Z = 4$, $a = 19.666(4)$, $b = 7.994(2)$, $c = 16.045(6)$ Å, $\beta = 111.231(9)°$, (II), monoclinic, space group $C2/c$, $Z = 4$, $a = 14.504(4)$, $b = 12.333(8)$, $c = 14.630(3)$ Å, $\beta = 90.92°$; and (III), monoclinic, space group $P2_1/n$, $Z = 2$, $a = 7.601(5)$, $b = 11.977(4)$, $c = 14.463(6)$ Å, $\beta = 93.10(8)°$. These structural investigations clearly demonstrate that in each case hydration occurs across the ketone double bond in the ligand and that the resulting hydroxyl group coordinates to the metal. Two di-2-pyridyl ketone ligands are thus bonded to the metal atom in a tridentate fashion. In the nickel complex (I), all six coordination interactions appear to have approximately the same strength. However, in the copper complexes (II) and (III), the pyridyl nitrogens are strongly coordinating to the metal in the equatorial plane, while the hydroxyl groups are more weakly coordinating in the axial direction. The metal to ligand bond distances are: (I) $d_{Ni-O} = 2.098(4)$, $d_{Ni-N} = 2.062(4)$, 2.087(4) Å, (II) $d_{Cu-O} = 2.465(5)$, $d_{Cu-N} = 1.994(5)$, 2.006(5) Å, (III) $d_{Cu-O} = 2.464(5)$, $d_{Cu-N} = 1.990(5)$, 2.036(5) Å. The neutral diol that results from hydrolysis of di-2-pyridyl ketone is stabilized by coordination to the metal and such coordination is little affected by changes in the metal, the anion or the extent of hydration.

Introduction

The structure of complexes of di-2-pyridyl ketone (hereafter called DPK) have been studied primarily using spectroscopic and magnetic methods during the past few decades [1–5]. The first report of DPK complexes (exclusively with Cu(II)) appeared in 1967 [1], in which metal–ligand chelation was suggested via nitrogen and oxygen atoms from the pyridyl rings and the keto (C=O) groups, respectively. However, DPK was also reported to exist either as a ketone-hydrate, *i.e.*, $(C_5H_4N)_2C(OH)_2$, abbreviated $DPK\cdot H_2O$, or as a derived anion ($DPK\cdot OH^-$) in several transition metal complexes [2–4]. Therefore although much work has been done in studying these structures using chemical [5] and spectral methods, the exact chelation mode in copper complexes and the form of the hydrated DPK in other metal complexes have remained uncertain. In this paper, we present evidence from single crystal X-ray studies of three such compounds to show that in each case the keto group has undergone a hydrolysis reaction and the neutral hydrated DPK bonds with the metal atoms to form a complex which contains an octahedral trans N_4O_2 ligand.

X-ray Analysis

Data Collection and Reduction

Reaction of DPK with nickel(II) sulfate, copper(II) chloride or nitrate in 2:1 stoichiometric amounts in aqueous solution yields the complexes (I) $Ni[C_{11}H_8N_2(OH)_2]_2SO_4$, (II) $Cu[C_{11}H_8N_2(OH)_2]_2Cl_2\cdot 4H_2O$, and (III) $Cu[C_{11}H_8N_2(OH)_2]_2(NO_3)_2\cdot 2H_2O$. Crystals suitable for data collection, approximately 0.20–0.30 mm on a side, were selected from the reaction mixtures, attached to glass fibers and mounted on standard goniometers. All intensity data were collected at room temperature. The unit cell parameters were initially calculated using the automatic indexing procedure BLIND [7]. The observed systematic absence of (I) and (II) *hkl*: $h + k = 2n + 1$ and *h*0*l*: $l = 2n + 1$, (III) *h*0*l*: $h + l = 2n + 1$ and 0*k*0: $k = 2n + 1$, coupled with positive tests for a

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*Author to whom correspondence should be addressed.

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TABLE I. Crystal Data for $Ni[C_{11}H_8N_2(OH)_2]_2SO_4$ (I), $Cu[C_{11}H_8N_2(OH)_2]_2Cl_2 \cdot 4H_2O$ (II) and $Cu[C_{11}H_8N_2(OH)_2]_2NO_3 \cdot 2H_2O$ (III)

	I	II	III
Empirical formula	$NiC_{22}H_{20}N_4O_8S$	$CuC_{22}H_{28}N_4O_8Cl_2$	$CuC_{22}H_{24}N_6O_{11}$
Formula weight	599.19	608.7	611.8
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$C2/c$	$C2/c$	$P2_1/n$
a (Å)	19.666(4)	14.504(4)	7.601(5)
b (Å)	7.994(2)	12.244(8)	11.977(4)
c (Å)	16.045(6)	14.630(3)	14.463(6)
β (deg)	111.231(9)	90.92(4)	93.10(8)
V (Å^3)	2351.2(2)	2597.8	1314.7
Z	4	4	2
$\mu(MoK_\alpha)$ (cm^{-1})	5.43[a]	11.30[a]	9.42[a]
ρ_{calc} (g cm^{-3})	1.58	1.49	1.53
T (°C)	25	25	25
Diffractometer	AL[6]	AL	AL
Monochromator	oriented graphite crystal	oriented graphite crystal	oriented graphite crystal
Reflections measured (4 octants)	$hkl, \bar{h}\bar{k}l, \bar{h}k\bar{l}, h\bar{k}\bar{l}$	$hkl, \bar{h}\bar{k}l, \bar{h}k\bar{l}, h\bar{k}\bar{l}$	$hkl, \bar{h}k\bar{l}, \bar{h}\bar{k}l, h\bar{k}\bar{l}$
Radiation	MoK_α (λ = 0.71034 Å)	MoK_α (λ = 0.71034 Å)	MoK_α (λ = 0.71034 Å)
Scan type	ω-scan	ω-scan	ω-scan
Standard reflections	3 (measured every 75)[b]	3 (measured every 75)	3 (measured every 75)
Reflections collected	5572 collected, 3360 observed ($I > 3\sigma(I)$)	3996 collected, 3347 observed ($I > 3\sigma(I)$)	3996 collected, 3347 observed, ($I > 3\sigma(I)$)
Max. 2θ (deg)	50	50	50
Min. 2θ (deg)	2	0	0
Number of unique reflections	1636	1717	1800
Max. number of parameters refined	205	169	181
R[c]	0.042	0.054	0.063
R_w[c]	0.055	0.069	0.055

[a] A phi scan showed insignificant intensity variations; no absorption correction applied. [b] No decay correction was applied. [c] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$. $w = 1/\sigma^2(F)$.

center of symmetry [8], indicated that the correct space groups were $C2/c$, $C2/c$ and $P2_1/n$, respectively. Final lattice constants were determined by a least squares fit to the 2θ values of higher angle reflections. The intensities were corrected for Lorentz and polarization effects and equivalent reflections were averaged. No absorption corrections were made as the absorption coefficients are all relatively low. Table I contains tabulation of the pertinent information relevant to the data collection and reduction.

Structure Solutions and Refinement

In all three structures the metal atom is constrained to lie on a center of symmetry. Analysis of the three-dimensional Patterson maps revealed the appropriate positions for these atoms and electron density maps [9] generated from the structure factors phased by the metal atom yielded the probable locations for all of the other non-hydrogen atoms. These positions and the associated anisotropic thermal parameters were refined by a combination of block matrix/full matrix least-squares calculations [10]. The atomic scattering factors used were those found in the International Tables [11], with those for nickel, copper, chlorine, and sulfur being corrected for anomalous dispersion effects [12]. Positions for hydrogen atoms were either located from a difference electron density map or calculated assuming a C–H distance of 1.05 Å.

Final positional parameters for the atoms in the three structures are listed in Table II, along with averaged thermal parameters. Anisotropic thermal parameters, hydrogen positional parameters and tables of observed and calculated structure factors are available in the supplementary material.

Discussion

In these complexes (see Figs. 1 and 2) ORTEP drawings of the molecular cations show that the two ligand groups are bonded to the metal atom in a tridentate fashion. The geometry of the ligands about the metal can be described as a distorted octahedron. In the nickel complex all six of the metal–ligand distances are very similar (d_{Ni-O} = 2.098(4), d_{Ni-N} =

TABLE II. Atomic Coordinates (×10^4) and Average Temperature Factors ($Å^2 \times 10^3$) for $Ni[C_{11}H_8N_2(OH)_2]_2SO_4$ (I), $Cu[C_{11}H_8N_2(OH)_2]_2Cl_2\cdot 4H_2O$ (II). Refined Atomic Positional Parameters (×10^4) for $Cu(C_{11}H_8N_2(OH)_2)_2(NO_3)_2\cdot 2H_2O$ (**III**)

Atom	*x*	*y*	*z*	U_{ave}
(a) I				
Ni	2500	2500	0	25
S1	5000	2764(2)[a]	2500	37
O2	1917(1)	2732(3)	8623(2)	27
O3	4440(1)	1683(4)	1875(2)	38
O4	4664(2)	3810(5)	3003(2)	66
N2	1763(2)	3268(4)	587(2)	29
N3	2012(2)	181(4)	9717(2)	30
C1	1029(2)	3145(6)	278(3)	35
C2	636(2)	3704(6)	782(3)	44
C3	987(2)	4451(6)	1597(3)	48
C4	1749(2)	4573(5)	1925(3)	39
C5	2114(2)	3914(5)	1399(2)	29
O5	1751(2)	939(4)	7406(2)	39
C10	3534(3)	7365(6)	63(3)	46
C11	3162(2)	5876(5)	9743(3)	37
C12	3179(2)	5207(5)	1153(3)	29
C13	3551(2)	6647(6)	1511(3)	42
C14	2938(2)	3873(5)	1676(2)	28
C15	3729(3)	7731(6)	954(4)	50
(b)**II**				
Cu	0	5000	5000	34
Cl	1176(1)	964(1)	6317(1)	63
N1	737(3)	4785(3)	6157(3)	34
N2	−505(3)	6360(3)	5552(3)	35
O1	1250(2)	6363(3)	4930(2)	38
O2	1745(2)	7447(3)	6161(2)	44
O3	947(3)	8890(4)	3474(3)	73
O4	3075(2)	5769(3)	4951(2)	44
C1	1230(3)	5648(4)	6452(3)	32
C2	1796(4)	5584(5)	7211(4)	42
C3	1856(4)	4607(5)	7681(4)	47
C4	1347(4)	3721(5)	7379(4)	48
C5	794(4)	3842(4)	6626(4)	40
C6	119(3)	7055(4)	5904(3)	32
C7	−129(4)	8043(4)	6302(4)	45
C8	−1066(4)	8285(5)	6343(4)	50
C9	−1703(4)	7566(5)	5995(4)	47
C10	−1403(3)	6617(4)	5599(4)	40
C11	1115(3)	6664(4)	5862(3)	33
(c) **III**				
Cu	5000	5000	5000	40
O1	5644(5)	4133(3)	6526(3)	42
O2	3788(6)	2897(3)	7257(3)	63
N1	2867(6)	5219(4)	5715(3)	42
N2	4283(6)	3373(4)	4854(3)	41
C1	2590(8)	4482(4)	6381(4)	51
C2	1125(10)	4516(6)	6922(5)	57
C3	−69(10)	5375(7)	6734(5)	69
C4	235(10)	6144(6)	6048(6)	58
C5	1695(8)	6045(6)	5575(6)	41
C6	3872(7)	2838(4)	5624(4)	40
C7	3375(8)	1730(5)	5622(4)	51

TABLE II *(continued)*

Atom	*x*	*y*	*z*	U_{ave}
C8	3293(9)	1158(5)	4793(5)	58
C9	3705(8)	1710(5)	3993(5)	56
C10	4199(7)	2812(5)	4047(4)	47
C11	3922(8)	3565(4)	6489(4)	44
N3	1466(8)	8297(5)	3610(4)	63
O3	1831(7)	7429(4)	3195(4)	86
O4	1852(13)	8378(5)	4433(4)	85
O5	889(15)	9080(6)	3185(5)	170
O6(H_2O)[b]	8954(8)	836(4)	3783(4)	117

[a] In this and subsequent tables, estimated standard deviations are given in parentheses for the least significant digit.
[b] This oxygen atom is from the water molecule.

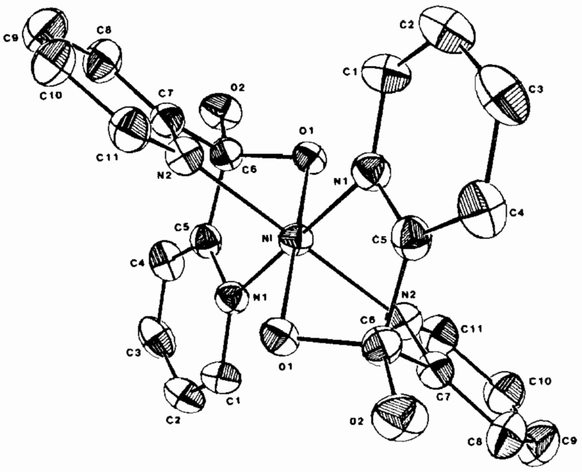

Fig. 1. ORTEP drawing of $Ni[C_{11}H_8N_2(OH)_2]_2^{2+}$.

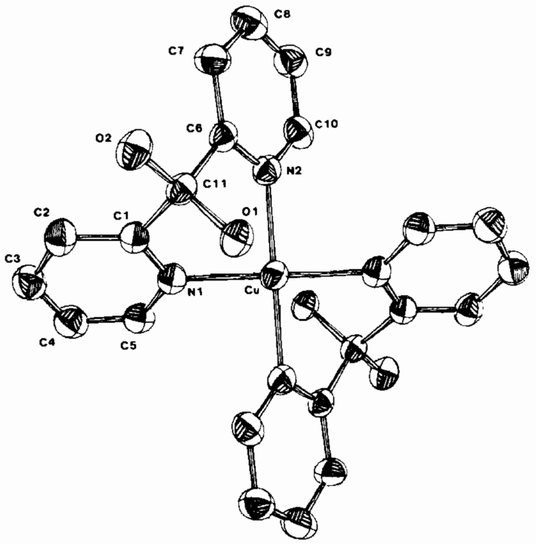

Fig. 2. ORTEP drawing of $Cu[Cu_{11}H_8N_2(OH)_2]_2^{2+}$.

2.062(4), 2.087(4) Å), implying that the coordination interactions have approximately the same bond strength, and the complex is somewhat distorted such that the axial oxygen atoms are bent toward the equitorial plane. In the copper complexes, the pyridyl nitrogens can be viewed as strongly coordinating to the metal in the equatorial plane ($d_{Cu—N}$ = 1.990(5), 2.036(5) Å) (see Table III), while one of the hydroxyl groups on each ligand is weakly coordinating in the axial direction ($d_{Cu—O}$ = 2.464(4), 2.467(4) Å). Here the distortion appears to be due not only to the steric requirements imposed by the ligands but also due to the Jahn–Teller effect which usually inhibits the formation of ideal octahedral configurations in d^9 metal systems. The angle formed between a line from the metal to oxygen and normal to the equatorial plane is ~41° and ~25° in the nickel and copper complexes, respectively.

TABLE III. Intramolecular Bond Distances (Å) for $Ni[C_{11}H_8N_2(OH)_2]_2SO_4$ (**I**), $Cu(C_{11}H_8N_2(OH)_2)_2Cl_2 \cdot 4H_2O$ (**II**) and $Cu(C_{11}H_8N_2(OH)_2)_2(NO_3)_2 \cdot 2H_2O$

Atoms	Distance
(a) **I**	
Ni–N1	2.087(4)
Ni–N2	2.062(4)
Ni–O1	2.098(4)
N1–C1	1.346(5)
N1–C5	1.339(5)
N2–C7	1.343(5)
N2–C11	1.339(6)
C1–C2	1.377(7)
C2–C3	1.379(7)
C3–C4	1.400(7)
C4–C5	1.391(6)
C5–C6	1.518(6)
C6–C7	1.537(6)
S–O3	1.471(3)
S–O4	1.475(4)
O1–H1	0.84(6)
O2–H2	0.83(5)
O1–H1•••O3	2.539(4)
O2–H2•••O4	2.623(5)
(b) **II**	
Cu–N1	2.006(5)
Cu–N2	1.994(5)
Cu–O1	2.465(5)
N1–C1	1.344(7)
N1–C5	1.351(8)
C1–C2	1.379(8)
C2–C3	1.397(10)
C3–C4	1.395(10)
C4–C5	1.369(9)
N2–C6	1.340(7)
N2–C10	1.347(7)
C6–C7	1.395(9)
C7–C8	1.405(9)
C8–C9	1.373(10)
C9–C10	1.388(9)
C1–C11	1.534(8)
C6–C11	1.519(8)
C11–O1	1.422(7)
C11–O2	1.387(7)
(c) **III**	
Cu–N1	1.990(5)
Cu–N2	2.036(5)
Cu–O1	2.464(4)
N1–C1	1.330(8)
N1–C5	1.355(8)
C1–C2	1.392(10)
C2–C3	1.401(11)
C3–C4	1.398(11)
C4–C5	1.394(10)
N2–C6	1.326(8)
N2–C10	1.349(8)
C6–C7	1.384(8)
C7–C8	1.371(10)
C8–C9	1.383(10)
C9–C10	1.383(10)
C1–C11	1.536(8)
C6–C11	1.523(8)
C11–O1	1.417(7)
C11–O2	1.381(7)
N3–O3	1.242(8)
N3–O4	1.211(8)
N3–O5	1.190(10)

These data all indicate that these three complexes are stabilized in the diol form by the interaction of the hydroxyl oxygen with the metal. Furthermore, an FT-IR spectrum of the pure ligand shows that an absorption band appears at ~1690 cm^{-1} which is characteristic of the C=O functional group, and that no absorption band appears above 3200 cm^{-1}. In the metal complexes, however, the IR spectra show that the band at 1690 cm^{-1} has disappeared and a broad hydrogen-bonded O–H absorption band has appeared at ~3400 cm^{-1}.

The distances and angles in the di-2-pyridyl ketone groups in all three structures are quite normal. The average C–C bond distances within the rings are 1.385(7), 1.388(10), and 1.388(9) Å, respectively. All of these values are very close to the accepted value for pyridine, 1.395(1) [16]. Similarly, the average C–N bond distances, 1.342(5), 1.343(8) and 1.346(7) Å, are close to the accepted value of 1.340(1) Å. The average bond angles, 119.8°, 120.0°, and 120.0° (see Tabel IV) are equally representative. Thus, there is no evident strain or distortion in the rings and it seems likely, therefore, that the stabilization is accomplished merely by a twist of the rings

TABLE IV. Intramolecular Bond Angles (°) for $Ni[C_{11}H_8N_2(OH)_2]_2SO_4$ (I), $Cu(C_{11}H_8N_2(OH)_2)_2Cl_2 \cdot 4H_2O$ (II) and $Cu(C_{11}H_8N_2(OH)_2)_2(NO_3)_2 \cdot 2H_2O$ (III)

Atoms	Angle
(a) **I**	
N1–Ni–N2	88.93(14)
N1–Ni–O1	104.26(14)
N2–Ni–O1	79.34(13)
Ni–N1–C5	110.75(27)
Ni–O1–C6	100.01(22)
C1–N1–C5	119.43(37)
N1–C5–C4	122.54(39)
C3–C4–C5	117.74(43)
C2–C3–C4	118.84(46)
C1–C2–C3	120.24(45)
N1–C1–C2	121.03(43)
N1–C5–C6	113.39(35)
O1–C6–C5	103.91(32)
O1–C6–O2	112.77(33)
O1–C6–C7	107.54(32)
O2–C6–C5	108.95(35)
O2–C6–C7	113.63(35)
C5–C6–C7	109.58(34)
N2–C7–C8	122.26(41)
C7–C8–C9	118.49(48)
C8–C9–C10	120.39(49)
C9–C10–C11	118.29(48)
N2–C11–C10	121.47(44)
O3–S–O4	109.46(20)
O3–S–O3′	108.17(29)
O4–S–O4′	110.82(36)
O1–H1–O3	170.20(5)
O1–H2–O2	74.37(4)
O2–H2–O2′	174.37(6)
b (**II**)	
N1–Cu–N2	87.9(2)
N1–Cu–O1	105.0(2)
N2–Cu–O1	74.1(2)
Cu–N1–C1	116.2(4)
Cu–N1–C5	124.3(4)
C1–N1–C5	119.4(5)
N1–C1–C2	122.4(5)
N1–C1–C11	113.9(5)
C1–C2–C3	117.9(6)
C2–C3–C4	119.6(6)
C3–C4–C5	118.9(6)
C4–C5–N1	121.8(6)
Cu–N2–C6	115.8(4)
Cu–N2–C10	124.8(4)
C6–N2–C10	119.4(5)
N2–C6–C7	122.6(5)
N2–C6–C11	114.9(5)
C6–C7–C8	117.4(6)
C7–C8–C9	119.7(6)
C8–C9–C10	119.5(6)
C9–C10–N2	121.4(6)
C1–C11–C6	109.1(4)
C1–C11–O1	108.0(4)
C1–C11–O2	108.3(4)
C6–C11–O1	105.5(4)
C6–C11–O2	113.2(5)
O1–C11–O2	112.6(4)
(c) **III**	
N1–Cu–N2	87.3(2)
N1–Cu–O1	73.5(2)
N2–Cu–O1	74.1(2)
Cu–N1–C1	116.9(4)
Cu–N1–C5	123.0(4)
C1–N1–C5	120.0(5)
N1–C1–C2	122.9(6)
N1–C1–C11	114.4(5)
C1–C2–C3	118.0(7)
C2–C3–C4	118.9(7)
C3–C4–C5	119.6(6)
C4–C5–N1	120.6(6)
Cu–N2–C6	116.6(4)
Cu–N2–C10	123.9(4)
C6–N2–C10	119.6(5)
N2–C6–C7	122.0(6)
N2–C6–C11	114.1(5)
C6–C7–C8	118.9(6)
C7–C8–C9	119.4(6)
C8–C9–C10	119.0(6)
C9–C10–N2	121.1(6)
C1–C11–C6	108.1(5)
C1–C11–O1	105.4(5)
C1–C11–O2	113.0(5)
C6–C11–O1	108.7(5)
C6–C11–O2	108.9(5)
O3–N3–O4	119.8(7)
O3–N3–O5	119.8(7)
O4–N3–O5	120.3(7)

about the C5–C6 and C6–C7 bonds in the nickel complex and the C1–C11 and C6–C11 bonds in the copper complexes. The intra-ligand pyridyl ring dihedral angles are 63°, 65° and 83° for **I**, **II** and **III**, respectively, which are much larger in those found in other bipyridyl type ligands. For example, in the structures of some bipyridylamine metal complexes [13–15] with approximate octahedral coordination geometry, the angles between two pyridine planes are only about 42° [13]. The formation of the additional M–O coordination bond appears to stabilize the $-C(OH)_2$ group even at the expense of greater deviation from planarity in the ligand. Detailed results of least squares plane calculations for all three structures are available as supplementary material.

As one might expect, hydrogen bonding appears to play a role in the packing in these structures. In the nickel complex, (I), hydrogen bonds are formed between the sulfate oxygen and the OH group of the hydrated ketone. Since the sulfur atom lies on the crystallographic 2-fold axis, there are two crystallographically different sulfate oxygen atoms. These two different S—O bonds are equivalent in distances: 1.471(3) Å and 1.475(4) Å, respectively. However, the hydrogen bond lengths involving these oxygens (OH group to sulfate oxygen) exhibit somewhat greater variation (Table IIIa). In the copper complexes, the hydrogen bonds are formed among water molecules, anions and the hydroxyl groups of the hydrated ketone.

Even though the anions interact with the molecular cation through hydrogen bonding, the presence of a different anion in each structure appears to have no appreciable effect on the coordination of the metal atom or the arrangement of the ligand in the complex. Respective bond distances and angles are all within the estimated standard deviations of one another. Additionally, the extent of hydration appears to have no measurable effect on the stability of the diol complex.

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