

# Influence of the Bridging Group of Cross-Conjugated Nitrogenous Bases on the Spectra and Structure of Solvatochromic Mixed-Ligand Copper(II) Chelates Containing $\beta$ -Ketoenols

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Received December 12, 1996

The concomitant reaction of copper(II) with a heterocyclic nitrogenous cross-conjugated Lewis base (2,2'-dipyridyl ketone, dpk, or 2,2'-dipyridylamine, dpamH) and the anion of a 2-substituted 1,3-dione,  $\beta^-$ , e.g. X-acac<sup>-</sup> (X = H, Me, Cl, CN, NO<sub>2</sub>) affords mixed-ligand chelates. The composition and structure of the chelates depend on the group linking the pyridyl rings. Chelation renders the 2,2'-dipyridyl ketone susceptible to nucleophilic attack by protic molecules. It also depends on the group attached to the  $\beta$ -dionato moiety since electron attracting substituents facilitate ligation of a water molecule when the 2,2'-dipyridylamine is present. Spectroscopic observations indicated square pyramidal or distorted tetragonal stereochemistries of the ensuing mixed-ligand chelates with the carbonyl oxygens and the pyridyl nitrogens forming the basal plane. Confirmation was acquired by X-ray structure determination of representative chelates. The compound [Cu(NC-acac)dpamH(H<sub>2</sub>O) OClO<sub>3</sub>] crystallizes in the *Pnma* space group with *Z* = 8 (i.e. four molecules per cell), *a* = 17.996(1) Å, *b* = 13.972(1) Å, *c* = 7.801(1) Å. The copper atom is 2.401(3) Å from the oxygen of the water molecule and 2.60(2) Å from an oxygen atom of the ClO<sub>4</sub><sup>-</sup> group. The chelate [Cu(NC-acac)dpC(OH)OCH<sub>3</sub>(OClO<sub>3</sub>), resulting from the addition of methanol to the carbon atom bridging the pyridyl rings, crystallizes in the *P2<sub>1</sub>/n* space group with *a* = 10.661(1) Å, *b* = 14.987(2) Å, *c* = 13.963(1) Å,  $\beta$  = 110.57(3)°, *Z* = 4. An oxygen of the ClO<sub>4</sub><sup>-</sup> group is in apical position, and it is 2.634(8) Å from the copper atom. The etheric oxygen is distanced 2.615(2) Å from the copper atom, and the O–Cu–O angle of these weak bonds is only 154.4(2)°. In these chelates the nitrogenous bases adopt the boat conformation with the pyridyl rings forming dihedral angles of approximately 33°.

## Introduction

There has been considerable interest in the relationship of the spectroscopic, magnetic and structural properties of bidentate nitrogenous bases, enR, and their chelates with transition metal ions that are biologically important, such as copper(II).<sup>1</sup> Studies aimed at elucidating the factors dictating the coordination geometry revealed that the morphology of the ligand, stereo-electronic effects engendered by substituents and the hybridization of the nitrogen donor atoms influence the symmetry about the central metal ion.<sup>2</sup> Among the bidentate nitrogenous bases, those containing the pyridyl ring were found to endow the metal chelates with exceptional spectroscopic, photophysical, and photochemical properties.<sup>3–7</sup> Groups bridging pyridyl rings induce structural changes, affect spectroscopic properties, and instigate ligand reactivity. While much effort has been directed on the effect of the size of the chain linked to the pyridyl ring,<sup>8</sup> the influence of functional groups that induce cross-conjugation have attracted limited attention. For instance, in 2,2'-dipyridyl ketone (pyCOp<sub>y</sub> = dpk) and in 2,2'-dipyridylamine (pyNHp<sub>y</sub> = dpamH) the bridging groups not only induce cross-conjuga-

tion but also render the ligands reactive.<sup>9,10</sup> The ligand reactivity, in conjunction with the tendency of copper(II) to achieve coordination numbers exceeding 4, may occasionally lead to misinterpretation of the spectra. The effects of ligand reactivity on the spectra of coordination compounds are better understood when a series of similarly structured compounds become available and this is accomplished by employing coligands differing in substituents far away from the coordination site. The  $\beta$ -diones,  $\beta$ H, and their chelates have been the focus of many spectroscopic and structural investigations,<sup>11–13</sup> and for this reason their employment as coligands is justified.

In view of the limited information available regarding the spectroscopic properties and the structural features of mixed-ligand copper(II) chelates containing cross-conjugated pyridyl ligands, the present study was undertaken in order to investigate (a) the affinity of cross-conjugated nitrogenous bases toward copper(II) in the presence of anions of  $\beta$ -diones, (b) the reactivity of the cross-conjugated nitrogenous bases toward compounds bearing the hydroxyl group, (c) the structure of the resulting chelates, (d) the effect of the group bridging pyridyl rings on the energy levels of the copper(II) chelate, and (e) the influence of substituents on group vibration. For this purpose 2,2'-dipyridyl ketone (dpk) and 2,2'-dipyridylamine (dpamH) were selected and were reacted with copper(II) perchlorate in

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**Table 1.** Elemental Analyses and Physicochemical Data of Some [Cu(X-acac)PyZpy]ClO<sub>4</sub> (Z = >NH, >C(OH)OCH<sub>3</sub>, >C(OH)<sub>2</sub>)

compound	yield %	mp (°C)	%C	%H	%N	$\Lambda_M^a$			$\mu_{\text{eff}}/m_B$
						a	b	c	
1 [Cu(acac)dpamH(OClO <sub>3</sub> )]	80	245–247	41.6 (41.65)	3.80 (3.72)	9.51 (9.68)	113	33	27	1.77
2 [Cu(Me-acac)dpamH(OClO <sub>3</sub> )]	75	209–212	42.8 (42.96)	4.18 (4.06)	9.20 (9.39)	103	27	26	1.76
3 [Cu(Cl-acac)dpamH(H <sub>2</sub> O)OClO <sub>3</sub> ]	67	248–251	37.0 (37.09)	3.62 (3.53)	8.56 (8.65)	111	37	28	1.72
4 [Cu(NC-acac)dpamH(H <sub>2</sub> O)OClO <sub>3</sub> ]	91	256–257	40.5 (40.35)	3.76 (3.60)	11.5 (11.76)	123	28	24	1.82
5 [Cu(O <sub>2</sub> N-acac)dpamH(H <sub>2</sub> O)OClO <sub>3</sub> ]	84	216–219	36.0 (36.36)	3.40 (3.45)	11.3 (11.27)	184	23	24	1.76
6 [Cu(acac)dpC(OH) <sub>2</sub> OClO <sub>3</sub> ]	78	228–230	41.1 (41.46)	3.60 (3.69)	5.93 (6.02)	141	i	33	1.79
7 [Cu(acac)dpC(OH)OCH <sub>3</sub> (OClO <sub>3</sub> )]	81	226–227	42.6 (42.69)	3.93 (4.00)	5.90 (5.85)	108	i	25	1.71
8 [Cu(Me-acac)dpC(OH)OCH <sub>3</sub> (OClO <sub>3</sub> )]	77	245–247	44.0 (43.91)	4.44 (4.30)	5.54 (5.69)	83	i	23	1.71
9 [Cu(Cl-acac)dpC(OH)OCH <sub>3</sub> (OClO <sub>3</sub> )]	72	225–227	40.1 (39.82)	3.71 (3.54)	5.62 (5.46)	110	31	26	1.73
10 [Cu(NC-acac)dpC(OH) <sub>2</sub> (OClO <sub>3</sub> )]	91	227–228	41.9 (41.72)	3.38 (3.30)	8.41 (8.58)	156	43	30	1.79
11 [Cu(NC-acac)dpC(OH)OCH <sub>3</sub> (OClO <sub>3</sub> )]	79	222–224	43.1 (42.95)	3.57 (3.60)	8.29 (8.34)	102	i	24	1.74
12 [Cu(O <sub>2</sub> N-acac)dpC(OH)OCH <sub>3</sub> (OClO <sub>3</sub> )]	83	203–206	38.7 (39.02)	3.54 (3.47)	7.85 (8.03)	95	i	23	1.72

<sup>a</sup>  $\Lambda_M$  is expressed in S cm<sup>2</sup> mol<sup>-1</sup>; a, b, and c denote acetonitrile, ethanol, and DMSO, respectively; i = sparingly soluble.

the presence of anions of 2,4-pentanedione, acacH, and some of its  $\alpha$ -substituted derivatives, and the products were isolated and characterized. Furthermore the structure of the compounds [aquo(2,2'-dipyridylamine)(3-cyano-2,4-pentanedionato)copper(II)] perchlorate, [Cu(CN-acac)dpyamH(H<sub>2</sub>O)]ClO<sub>4</sub>, and [methoxy(di(2-pyridyl)methanol)(3-cyano-2,4-pentanedionato)copper(II)] perchlorate, [Cu(CN-acac)dpC(OH)OCH<sub>3</sub>]ClO<sub>4</sub>, were resolved by X-ray diffraction analysis. In this report the results are presented and discussed.

## Experimental Section

**Reagents and Preparation of the Cationic Chelates.** The copper(II) perchlorate hexahydrate was procured from Fluka. Acetylacetonone (2,4-pentanedione, acacH), 3-methylacetylacetonone (3-methyl-2,4-pentanedione, Me-acacH), 3-chloroacetylacetonone (3-chloro-2,4-pentanedione, Cl-acacH), 2,2'-dipyridylamine, dpamH, and 2,2'-dipyridyl ketone, dpk, were purchased from Aldrich. The synthesis of 3-cyano-2,4-pentanedione (Taube's acetylacetonone, NC-acacH) was performed by reacting acetylacetonone with cyanogen according to the procedure described by Fackler.<sup>14</sup> The bis(3-nitro-2,4-pentanedionato)copper(II), Cu(NO<sub>2</sub>-acac)<sub>2</sub>, was prepared by Collman's method.<sup>15</sup> The new mixed-ligand copper(II) chelates [Cu(pyZpy) $\beta$ ]ClO<sub>4</sub> (Z = >NH, >C(OH)<sub>2</sub>, >C(OH)OCH<sub>3</sub>) that were prepared by established procedures,<sup>16,17</sup> are deeply colored crystals or crystalline powders. In Table 1 are listed the chelates prepared, their elemental analyses, and some physicochemical quantities and constants. The compounds [Cu( $\beta$ )dpamH]ClO<sub>4</sub> were recrystallized from wet ethanol while recrystallization of the [Cu( $\beta$ )dpC(OH)OCH<sub>3</sub>]ClO<sub>4</sub> chelates was effected from methanol.

**Caution!** Perchlorate compounds are explosive. Use extreme care in handling.

**Physical Measurements and Determinations.** The stoichiometry of the new compounds was determined as reported before.<sup>17</sup> The equipment and the methods employed for the determination of melting points, molar conductivities, and magnetic susceptibilities have been detailed elsewhere.<sup>17</sup> The spectrophotometers and the techniques used for recording of the infrared and the electronic excitation spectra in solution and in the solid state have been described in a previous paper.<sup>18</sup>

**X-ray Crystallographic Analysis of [Cu(NC-acac)dpamH(H<sub>2</sub>O)]ClO<sub>4</sub> and of [Cu(NC-acac)dpC(OH)OCH<sub>3</sub>]ClO<sub>4</sub>.** Intensities of X-ray

reflections within two octants of the reciprocal sphere were collected by means of a four-circle CAD4-F automatic X-ray diffractometer employing graphite-filtered Mo K $\alpha$  radiation. Cell constants and orientation matrixes were obtained by least-squares refinement of the setting angles of 25 randomly selected reflections of high intensity. Accurate unit cell dimensions of the crystals of [Cu(NC-acac)dpC(OH)OCH<sub>3</sub>]ClO<sub>4</sub> and of [Cu(NC-acac)dpamH(H<sub>2</sub>O)OClO<sub>3</sub>] and improved orientation matrixes were obtained from the least-squares refinement of the setting angles of the 25 strongest independent reflections found between 12.0 and 15.0° in  $\theta$ . Intensities for the derivation of structural parameters were collected at ambient temperature ( $T \approx 298$  K) by employing the  $\omega/2\theta$  technique. Three standard reflections were monitored periodically to detect intensity changes during the course of the data acquisition. The scale factor determined by these standard reflections was essentially constant, with only an insignificant random variation due primarily to equipment instability.

The unique reflections obtained using the [Cu(NC-acac)dpC(OH)OCH<sub>3</sub>]ClO<sub>4</sub> crystal were 3642 and in the analysis were employed only reflections that were in compliance with the acceptance criterion  $I_o \geq 2\sigma(I_o)$ . The systematic absences led to space group  $P2_1/n$ . Fewer reflections were collected in the case of [Cu(NC-acac)dpamH(H<sub>2</sub>O)]ClO<sub>4</sub>, and the systematic absences led to space group  $Pnma$ . All intensities were corrected as usual for Lorentz and polarization effects.

The copper position in both compounds was deduced by direct methods employing the SHELXS-86 program<sup>19</sup> and used to compute a first-approximation electron-density synthesis, which revealed the position of all remaining atoms except the hydrogens. After least-squares refinements with the non-hydrogen atoms, the hydrogen atoms were also located in the difference Fourier map and those of the aromatic carbon atoms were in their expected position after each refinement cycle. The positions of the hydrogen atoms of the methyl and the hydroxyl groups were deduced by difference Fourier maps, and their coordinates were refined using slack constraints, C–H = 1.09–(2) Å, and angles around the carbon atom, 109(3)°.

The oxygen atoms of the perchlorate groups of both compounds were found disordered over three positions, and the occupation factors in the case of [Cu(CN-acac)dpC(OH)OCH<sub>3</sub>]ClO<sub>4</sub> were  $2/5$ ,  $2/5$ , and  $1/5$  while those for the ClO<sub>4</sub><sup>-</sup> group in [Cu(CN-acac)dpamH(H<sub>2</sub>O)]ClO<sub>4</sub> were  $1/2$ ,  $1/4$ , and  $1/4$ . The coordinates of the ClO<sub>4</sub><sup>-</sup> group were also refined using slack constraints Cl–O = 1.40(2) Å and O<sub>1</sub>–Cl–O<sub>2</sub>(angle) = 109(3)°. All calculations were performed using the CRYSTALS program.<sup>20</sup> The figures of the clinographic projections were produced with the ORTEP II programs.<sup>21</sup> Refinement was carried out by full-matrix least-squares, and in the final stage of the refinement a Chebyshev weighing scheme was introduced. The function minimized in the least-squares refinement was  $\sum w(|F_o| - |F_c|)^2$  where  $|F_o|$  and

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**Table 2.** Crystal Data and Experimental Details for the Structural Study of  $[\text{Cu}(\text{NC-acac})\text{Dp}(\text{OH})\text{OCH}_3(\text{OClO}_3)]$  and  $[\text{Cu}(\text{NC-acac})\text{DpyamH}(\text{H}_2\text{O})\text{OClO}_3]^a$ 

empirical formula	$\text{C}_{16}\text{H}_{17}\text{N}_4\text{O}_3\text{CuClO}_4$	$\text{C}_{18}\text{H}_{18}\text{N}_3\text{O}_4\text{CuClO}_4$
molecular mass, $M_r$	476.33	503.35
space group	<i>Pnma</i>	<i>P2<sub>1</sub>/n</i>
<i>a</i> (Å)	17.996(1)	10.661(1)
<i>b</i> (Å)	13.972(1)	14.987(2)
<i>c</i> (Å)	7.801(1)	13.963(1)
$\alpha$ (deg) = $\gamma$ (deg)	90.00	90.00
$\beta$ (deg)	90.00	110.57(3)
$V_c$ (Å <sup>3</sup> )	1961.5(1)	2088.7(4)
molecules per cell, <i>Z</i>	4 (8 asymmetric units)	4
$D_x$ (Mg m <sup>-3</sup> )	1.61 (calcd)	1.60 (calcd)
$\lambda$ (Mo K $\alpha$ ) (Å)		0.716 09
<i>T</i> (°C)		25(2)
$\mu$ (cm <sup>-1</sup> )	12.97	12.24
<i>R</i> ( <i>F</i> ) <sup>a</sup>	0.0369	0.0393
$R_w = (F^2)^b$	0.0428	0.0418

$$^a R = \sum(|F_o| - |F_c|)/\sum|F_o|. \quad ^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}.$$

$|F_c|$  are the observed and calculated structure factor amplitudes, respectively. Agreement factors are defined and given in Table 2. Further experimental details have been deposited with the Cambridge Crystallographical Data Center. Structure factors and thermal parameters have been deposited with the British Library as Supplementary Publication No. SUP90480 (48 pages) and are available on request from the Document Supply Center at Boston Spa, Wetherby, West Yorkshire LS23 7BY, U.K.

## Results and Discussion

The simultaneous presence of di-2-pyridine nitrogenous bases, pyZpy ( $Z = >\text{CO}, >\text{NH}$ ), and anions of  $\beta$ -diones ( $\beta^-$ ) in solutions containing copper(II) ions leads to formation of mixed-ligand chelates that are stabilized by mononuclear polyatomic counteranions such as the perchlorate group,  $\text{ClO}_4^-$ . The reaction proceeds in a stepwise fashion, apparently following an Eigen–Wilkins pathway. The same products are obtained when bis( $\beta$ -dionato)copper(II) chelates,  $\text{Cu}\beta_2$ , are reacted with stoichiometric quantities of the nitrogenous bases in the presence of the required amount of copper(II) cations. The isolation of the mixed-ligand chelates asserts that the  $[\text{Cu}(\text{pyZpy})_2]^{2+}$  and the  $[\text{Cu}\beta]^+$  species possess discriminating qualities. Conductivity measurements in nitromethane, ethanol ( $\Lambda_M \approx 22 \text{ S cm}^2 \text{ M}^{-1}$ ), and acetonitrile solutions ( $\Lambda_M \approx 100 \text{ S cm}^2 \text{ M}^{-1}$ ) indicated that in these chelates the interactions of perchlorate group with copper(II) probably are not purely electrostatic and depend on the solvent. Analyses indicated that solvent molecules and moisture influence the composition of the resulting chelates just as much as the nitrogenous base and the  $\beta$ -dione. While compounds corresponding to the general formula  $[\text{Cu}(\beta)\text{pyZpy}]\text{ClO}_4 \cdot \text{H}_2\text{O}$  were obtained when quantities of water were present in the reaction mixture or nonprotic solvents were employed, in the case of dpk use of anhydrous alcohols as solvents afforded chelates having composition corresponding to the general formula  $[\text{Cu}(\beta)\text{dpk}]\text{ClO}_4 \cdot \text{ROH}$ . The composition of these compounds was converted to  $[\text{Cu}(\beta)\text{dpk}]\text{ClO}_4 \cdot \text{H}_2\text{O}$  when recrystallization was effected employing solvents with even small water content. Recrystallization from dry  $\text{CH}_3\text{CN}$  or  $\text{CH}_2\text{Cl}_2$  did not alter the composition of the compounds. It is known that dpk (pyCOpy) upon chelation becomes susceptible to nucleophilic attack by protic molecules,<sup>9</sup> and, as recent investigations confirmed, the coordinated ketone reacts with alcohols to yield the corresponding semiacetals.<sup>22</sup> Thus the

formulas  $[\text{Cu}(\beta)\text{dpC}(\text{OH})\text{OR}]\text{ClO}_4$  and  $[\text{Cu}(\beta)\text{dpC}(\text{OH})_2]\text{ClO}_4$  are more appropriate (Table 1). The predominant reaction of chelated 2,2'-dipyridylamine is deprotonation.<sup>23</sup> Therefore, the interactions of the water molecule with the copper center are distinctly different, and in the compounds  $[\text{Cu}(\beta)\text{dpamH}(\text{H}_2\text{O})]\text{ClO}_4$  it acts as coligand. Further information on the reactivity and on the mode of interaction of the ligands and the counterbalancing anion was gathered from the spectra of the new compounds.

**Infrared Spectra.** In the infrared spectra of the newly obtained chelates appears a plethora of discrete bands. The bands may be classified in those originating from the  $\beta$ -dione, in those emanating from the pyridine base, in those emerging from the perchlorate anion and in those due to bonds formed between copper(II) and donor atom. Disregarding minor shifts, comparison with the spectra of model compounds, e.g. the homoleptic  $\text{Cu}\beta_2$  and the  $[\text{Cu}(\text{pyZpy})_2]^{2+}$  chelates, facilitates the deduction of the origin of the bands. For instance, the intense broad band that exhibits a maximum at  $\sim 1095 \text{ cm}^{-1}$  is associated with the  $\text{ClO}_4^-$  group<sup>24</sup> while the split band at  $\sim 3350 \text{ cm}^{-1}$  in the spectra of certain  $[\text{Cu}(\text{dpamH})\beta(\text{H}_2\text{O})]\text{ClO}_4$  compounds indicated the presence of coordinated water molecules (Table 3).

**Spectra of the Bidentate Ligands.** The anions of  $\beta$ -ketoenols are capable of attaining diverse conformations and coordinate in a variety of modes. The presence of certain substituents in the 3-position adds new coordination sites<sup>25–27</sup> and renders the  $\beta$ -dionato anions capable of attaining the rarely encountered *S(E,Z)* conformation. The band pattern of the chelates prepared and the intense absorption at about  $1600 \text{ cm}^{-1}$  originating from the bands attributed to perturbed  $\text{C}=\text{O}$  and conjugated  $\text{C}=\text{C}$  bonds as well as the other changes in the frequencies of the vibrational modes of the free ligands<sup>13</sup> suggest bonding through the carbonyl oxygens and formation of a six-membered chelate ring comprising the copper(II) and the anion of the  $\beta$ -dione,  $\beta^-$ .

The nitrogenous bases may be regarded as 2-substituted pyridines and extensive infrared correlations have been made for compounds of this type.<sup>28</sup> The vibrations of interest are those due to the  $\text{C}=\text{N}$  and  $\text{C}=\text{C}$  bonds, the pyridine ring breathing and the skeletal modes, and the groups inducing cross conjugation. Ligation renders some bands spectroscopically silent while the concurrent alteration in the electron distribution induces changes in band frequencies. Regarding the  $[\text{Cu}(\text{dpamH})\beta]^+$  species, the frequency and the intensity of the N–H stretching vibration suggest that the nitrogen atom connecting the pyridyl rings is not involved in bond formation with copper(II) (Table 4). In contrast, the appreciable increase in frequency of the first band in the region  $1640\text{--}1400 \text{ cm}^{-1}$  in which the skeletal  $\text{C}=\text{N}$  and  $\text{C}=\text{C}$  vibrations occur, indicate involvement of the heteroatom in copper–nitrogen bonding. Further, the appearance of five bands in this region, as it happens in the structurally characterized tetrahedral  $\text{Cu}(\text{dpamH})_2(\text{ClO}_4)_2$ , suggest that the heteroaromatic residues are chemically equivalent. The pyridine ring breathing mode that in dpamH is observed at

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**Table 3.** Wavenumber of the Main Absorptions in the Infrared Spectra of Some [Cu(X-acac)PyZpy]ClO<sub>4</sub> Chelates

	compound	X	C=O	C=C	OH	N-H		
1	[Cu(acac)dpamH(OClO <sub>3</sub> )]		1583	1532	1380	3346	3250	3210
2	[Cu(Me-acac)dpamH(OClO <sub>3</sub> )]		1585	1526	1372	3337	3250	3210
3	[Cu(Cl-acac)dpamH(H <sub>2</sub> O)OClO <sub>3</sub> ]		1581	1523	1373	3531	3358	3220
4	[Cu(CN-acac)dpamH(H <sub>2</sub> O)OClO <sub>3</sub> ]	2207	1615	1523	1392	3552	3330	3240
5	[Cu(NO <sub>2</sub> -acac)dpamH(H <sub>2</sub> O)OClO <sub>3</sub> ]	1327	1600	1512	1380	3593	3330	3240
6	[Cu(acac)dpC(OH) <sub>2</sub> OClO <sub>3</sub> ]		1583	1520	1377	3340		
7	[Cu(acac)dpC(OH)OCH <sub>3</sub> (OClO <sub>3</sub> )]		1580	1520	1377	3337		
8	[Cu(Me-acac)dpC(OH)OCH <sub>3</sub> (OClO <sub>3</sub> )]		1575		1359	3414		
9	[Cu(Cl-acac)dpC(OH)OCH(OClO <sub>3</sub> )]		1583		1367	3438		
10	[Cu(CN-acac)dpC(OH) <sub>2</sub> (OClO <sub>3</sub> )]	2205	1610	1580	1384	3578		
11	[Cu(CN-acac)dpC(OH)OCH <sub>3</sub> (OClO <sub>3</sub> )]	2218	1613	1598	1390	3462		
12	[Cu(NO <sub>2</sub> -acac)dpC(OH)OCH <sub>3</sub> (OClO <sub>3</sub> )]	1339	1596	1518	1379	3521		

**Table 4.** Selected Interatomic Distances (Å) and Bond Angles (deg) of [Cu(CN-acac)dpamH(H<sub>2</sub>O)OClO<sub>3</sub>] and of [Cu(CN-acac)dpC(OH)OCH<sub>3</sub>(OClO<sub>3</sub>)]

(a) [Cu(CN-acac)dpamH(H <sub>2</sub> O)OClO <sub>3</sub> ]							
Cu(1)–O(1)	1.940(2)	C(1)–C(2)	1.496(4)	N(2)–C(9)	1.329(3)	C(8)–C(9)	1.400(4)
Cu(1)–N(2)	1.985(2)	C(2)–C(3)	1.419(3)	C(5)–C(6)	1.356(4)	C(9)–N(3)	1.375(3)
Cu(1)–O(2)	2.401(3)	C(3)–C(4)	1.411(5)	C(6)–C(7)	1.386(5)	Cl(1)–O(3)	1.41(1)
Cu(1)–O(3)	2.63(1)	C(4)–N(1)	1.145(6)	C(7)–C(8)	1.361(5)	Cl(1)–O(4)	1.43(1)
O(1)–C(2)	1.248(3)	N(2)–C(5)	1.355(3)				
O(1)–Cu(1)–O(1a)	90.3(1)	O(1a)–Cu(1)–O(3)	80.3(3)	C(3)–C(2)–C(1)	119.6(2)	C(6)–C(5)–N(2)	122.8(3)
N(2)–Cu(1)–O(1)	177.93(9)	N(2)–Cu(1)–O(3)	79.5(3)	C(2)–C(3)–C(2)	123.2(3)	C(5)–C(6)–C(7)	118.7(3)
N(2)–Cu(1)–O(1a)	90.56(8)	N(2a)–Cu(1)–O(3)	97.7(3)	C(4)–C(3)–C(2)	118.2(2)	C(8)–C(9)–N(2)	121.4(2)
N(2)–Cu(1)–N(2a)	88.6(1)	O(2)–Cu(1)–O(3)	166.9(3)	N(1)–C(4)–C(3)	179.5(5)	N(3)–C(9)–N(2)	119.7(2)
O(2)–Cu(1)–O(1)	89.62(8)	C(2)–O(1)–Cu(1)	128.7(2)	C(5)–N(2)–Cu(1)	120.3(2)	C(9)–N(3)–C(9)	127.3(3)
O(2)–Cu(1)–N(2)	92.29(9)	C(1)–C(2)–O(1)	116.3(2)	C(9)–N(2)–C(5)	118.3(2)	O(4)–Cl(1)–O(3)	111.2(7)
O(1)–Cu(1)–O(3)	98.8(3)	C(3)–C(2)–O(1)	124.1(2)				
(b) [Cu(CN-acac)dpC(OH)OCH <sub>3</sub> (OClO <sub>3</sub> )]							
Cu(1)–O(1)	1.919(2)	C(3)–C(6)	1.436(5)	C(12)–O(3)	1.380(4)	Cl(1)–O(7)	1.386(9)
Cu(1)–O(2)	1.911(2)	C(4)–C(5)	1.488(5)	C(12)–O(4)	1.421(4)	Cl(1)–O(8)	1.51(2)
Cu(1)–N(2)	2.005(2)	C(6)–N(1)	1.143(5)	C(13)–C(14)	1.364(4)	Cl(1)–O(9)	1.26(2)
Cu(1)–N(3)	1.989(2)	N(2)–C(7)	1.338(4)	C(13)–N(3)	1.344(4)	Cl(1)–O(10)	1.45(1)
Cu(1)–O(4)	2.613(2)	N(2)–C(11)	1.338(4)	C(14)–C(15)	1.388(5)	Cl(1)–O(11)	1.62(2)
Cu(1)–O(5)	2.634(8)	C(7)–C(8)	1.376(5)	C(15)–C(16)	1.363(5)	Cl(1)–O(12)	1.41(1)
O(1)–C(2)	1.260(4)	C(8)–C(9)	1.375(5)	C(16)–C(17)	1.373(5)	Cl(1)–O(13)	1.433(8)
O(2)–C(4)	1.256(4)	C(9)–C(10)	1.376(5)	C(17)–N(3)	1.335(4)	Cl(1)–O(14)	1.45(1)
C(1)–C(2)	1.499(5)	C(10)–C(11)	1.386(4)	O(4)–C(18)	1.432(4)	Cl(1)–O(15)	1.452(8)
C(2)–C(3)	1.403(5)	C(11)–C(12)	1.524(4)	Cl(1)–O(5)	1.424(7)	Cl(1)–O(16)	1.35(1)
C(3)–C(4)	1.404(5)	C(12)–C(13)	1.537(4)	Cl(1)–O(6)	1.538(9)		
O(2)–Cu(1)–O(1)	92.5(1)	C(3)–C(2)–C(1)	120.3(4)	O(3)–C(12)–C(11)	107.8(2)	O(6)–Cl(1)–O(5)	111.1(5)
N(2)–Cu(1)–O(1)	177.5(1)	C(4)–C(3)–C(2)	124.6(3)	O(3)–C(12)–C(13)	113.2(2)	O(7)–Cl(1)–O(5)	108.1(5)
N(2)–Cu(1)–O(2)	89.03(9)	C(6)–C(3)–C(2)	118.2(3)	O(4)–C(12)–C(11)	110.6(2)	O(7)–Cl(1)–O(6)	115.6(5)
N(3)–Cu(1)–O(1)	89.4(1)	C(6)–C(3)–C(4)	117.2(3)	O(4)–C(12)–C(13)	103.5(2)	O(8)–Cl(1)–O(5)	110.2(7)
N(3)–Cu(1)–O(2)	177.9(1)	C(3)–C(4)–O(2)	124.2(3)	O(4)–C(12)–O(3)	113.4(2)	O(8)–Cl(1)–O(6)	108.8(7)
N(3)–Cu(1)–N(2)	89.08(9)	C(5)–C(4)–O(2)	115.5(3)	C(14)–C(13)–C(12)	122.7(3)	O(8)–Cl(1)–O(7)	102.8(7)
O(1)–Cu(1)–O(4)	104.7(1)	C(5)–C(4)–C(3)	120.3(3)	N(3)–C(13)–C(12)	115.0(2)	O(10)–Cl(1)–O(9)	111.0(10)
O(1)–Cu(1)–O(5)	88.0(2)	N(1)–C(6)–C(3)	178.9(4)	N(3)–C(13)–C(14)	122.3(3)	O(11)–Cl(1)–O(9)	106.5(11)
O(2)–Cu(1)–O(4)	110.43(9)	C(7)–N(2)–Cu(1)	121.6(2)	C(15)–C(14)–C(13)	118.0(3)	O(11)–Cl(1)–O(10)	107.5(8)
O(2)–Cu(1)–O(5)	90.7(2)	C(11)–N(2)–Cu(1)	119.0(2)	C(16)–C(15)–C(14)	119.9(3)	O(12)–Cl(1)–O(9)	117.8(10)
N(2)–Cu(1)–O(4)	72.83(8)	C(11)–N(2)–C(7)	119.4(2)	C(17)–C(16)–C(15)	119.0(3)	O(12)–Cl(1)–O(10)	108.7(8)
N(2)–Cu(1)–O(5)	94.0(2)	C(8)–C(7)–N(2)	122.0(3)	N(3)–C(17)–C(16)	121.7(3)	O(12)–Cl(1)–O(11)	104.7(8)
N(3)–Cu(1)–O(4)	69.87(8)	C(9)–C(8)–C(7)	118.4(3)	C(13)–N(3)–Cu(1)	118.6(2)	O(14)–Cl(1)–O(13)	112.3(7)
N(3)–Cu(1)–O(5)	88.5(2)	C(10)–C(9)–C(8)	120.2(3)	C(17)–N(3)–Cu(1)	122.3(2)	O(15)–Cl(1)–O(13)	112.6(5)
O(4)–Cu(1)–O(5)	154.4(2)	C(11)–C(10)–C(9)	118.2(3)	C(17)–N(3)–C(13)	119.0(3)	O(15)–Cl(1)–O(14)	110.7(6)
C(2)–O(1)–Cu(1)	127.2(2)	C(10)–C(11)–N(2)	121.7(3)	C(18)–O(4)–C(12)	114.9(3)	O(16)–Cl(1)–O(13)	107.0(6)
C(4)–O(2)–Cu(1)	127.3(2)	C(12)–C(11)–N(2)	114.7(2)	C(18)–O(4)–Cu(1)	119.1(2)	O(16)–Cl(1)–O(14)	103.0(6)
C(1)–C(2)–O(1)	115.7(4)	C(12)–C(11)–C(10)	123.6(3)	Cl(1)–O(5)–Cu(1)	137.8(5)	O(16)–Cl(1)–O(15)	110.8(6)
C(3)–C(2)–O(1)	123.9(3)	C(13)–C(12)–C(11)	108.1(2)				

990 cm<sup>-1</sup> is affected by the copper–nitrogen bond formation, and the shift to ~1020 cm<sup>-1</sup> is accompanied by loss of intensity. The bands at 734 and 768 cm<sup>-1</sup>, probably due to the (C–H) and (C–C ring) out-of-plane deformation vibrations, respectively, virtually merge and appear at ~770 cm<sup>-1</sup>. The water molecule occurs in certain chelates in which dpamH participates may only be linked to copper.

The electron-poor nature of the pyridines in dpk reduces the carbonyl bond order and the stretching vibration of this group

is observed at 1683 cm<sup>-1</sup>. Changes in the frequency are indicative of the extent of  $\pi$  delocalization of the heteroaromatic system and possible loss of cross conjugation.<sup>3,29</sup> In the case of N,N-chelated dpk, the formation of a planar six-membered metallocyclic ring incites strain that renders the carbonyl group susceptible to nucleophilic addition with subsequent destruction

(29) (a) Newkome, G. R.; Taylor, H. C. R.; Fronczek, F. R.; Gupta, V. K. *Inorg. Chem.* **1991**, *30*, 1943 (b) Ortego, J. D.; Seymour, S. *Polyhedron* **1982**, *1*, 21.

of the cross-conjugation. When the  $sp^2$  hybridization of the carbon atom of the keto group changes to  $sp^3$  and the cross-conjugation is eliminated, the strain is eased. In the IR spectra of  $[\text{Cu}(\beta)\text{dpk}]\text{ClO}_4 \cdot \text{H}_2\text{O}$  and  $[\text{Cu}(\beta)\text{dpk}]\text{ClO}_4 \cdot \text{CH}_3\text{OH}$  compounds, the absence of bands in the region  $1720\text{--}1670\text{ cm}^{-1}$  indicate conversion of the carbonyl group. Further, the band that appears at  $\sim 1042\text{ cm}^{-1}$  and is attributed to the stretching vibration of the C–O bond is enhanced, becoming very intense and clearly discernible even though it occurs in a frequency at which the  $\text{ClO}_4^-$  group absorbs strongly. These imply that for the chelates of dpk the formulas  $[\text{Cu}(\beta)\text{dpC}(\text{OH})\text{OCH}_3]\text{ClO}_4$  and  $[\text{Cu}(\beta)\text{dpC}(\text{OH})_2]\text{ClO}_4$  are more appropriate. The skeletal C–N and C–C vibrations are observable even though in the same region bands appear that originate from the  $\beta$ -dionato moiety. The pyridine ring breathing mode that occurs at  $993\text{ cm}^{-1}$  is affected by the copper–nitrogen bond formation and the shift to  $\sim 1020\text{ cm}^{-1}$  is accompanied by loss of intensity. Confirmation of the ligand reactivity was obtained from the determination of the structure of  $[\text{Cu}(\text{CN-acac})(\text{dpC}(\text{OH})\text{OCH}_3)]\text{ClO}_4$  by X-ray diffraction.

**Electronic Excitation Spectra.** The electronic absorption spectra of the chelates were studied in the visible and the near-infrared region, in solution and in the solid state by reflectance. Attempts were made to obtain transmission spectra of Nujol mulls but the intensities of the absorption bands were generally too low for reliable determinations of band positions. Inert solvents such as dichloroethane were employed to evade nucleophilic attack on the chelates of dpk, to avoid exchange reactions and, in conjunction with the spectra in polar solvents, to provide information on donor–acceptor interactions. While in the ligand field electronic excitation spectra of the homoleptic  $\text{Cu}\beta_2$  chelates ( $B_{1g}$  ground state) three to four bands assignable to the transitions  $d_{xy} \leftarrow d_z^2$ ,  $d_{xy} \leftarrow d_{x^2-y^2}$ ,  $d_{xy} \leftarrow d_{yz}$ ,  $d_{xz}$  ( $\sim 1.45\text{ }\mu\text{m}^{-1}$ ,  $\sim 1.56\text{ }\mu\text{m}^{-1}$ , and  $\sim 1.80\text{ }\mu\text{m}^{-1}$ ) are discernible,<sup>30</sup> in the spectra of the compounds under consideration only one broad envelope appears at  $\sim 1.6\text{ }\mu\text{m}^{-1}$ , reminiscent of the solution spectra of the  $[\text{Cu}(\text{enR})_2]^{2+}$  chelates<sup>31</sup> (enR denotes 1,2-diamine). The low-energy envelope of the  $[\text{Cu}(\text{enR})_2]^{2+}$  chelates was resolved<sup>31</sup> in three Gaussian components with maxima at  $\sim 1.45\text{ }\mu\text{m}^{-1}$  ( $d_{x^2-y^2} \leftarrow d_z^2$ ),  $\sim 1.70\text{ }\mu\text{m}^{-1}$  ( $d_{x^2-y^2} \leftarrow d_{xy}$ ),  $\sim 1.90\text{ }\mu\text{m}^{-1}$  ( $d_{x^2-y^2} \leftarrow d_{yz}$ ,  $d_{xz}$ ). Attempts to resolve the observed envelopes into Gaussian components did not produce unique sets of values. The frequency of the maximum of the envelope is affected mainly by the substituents attached to the  $\beta$ -dionato moiety and, in solution, by the nature of the solvent. This and the constitution of the chelates under consideration suggest<sup>16,32</sup> a tetragonal  $\text{CuN}_2\text{O}_2\text{O}'$  or a square-based pyramidal  $\text{CuN}_2\text{O}_2\text{O}'$  chromophore.

The homoleptic  $\text{Cu}\beta_2$  and the  $[\text{Cu}(\text{enR})_2]^{2+}$  chelates exhibit solvatochromism attributable to donor–acceptor interactions and so do the mixed-ligand  $[\text{Cu}(\text{enR})\beta]\text{ClO}_4$  chelates.<sup>33</sup> In the compounds investigated the envelope of the ligand field transitions was shifted to longer wavelengths as the ability of a solvent to act as an electron-pair donor was enhanced. For instance, the band maximum of  $[\text{Cu}(\text{CN-acac})\text{dpamH}(\text{H}_2\text{O})\text{OCIO}_3]$  in  $\text{C}_2\text{H}_4\text{Cl}_2$  is observed at  $1.65\text{ }\mu\text{m}^{-1}$ . Increase in the solvent parameter  $D_s$ <sup>33</sup> diminishes the wavenumber of the band maximum; in  $\text{CH}_3\text{CN}$  solutions it occurs at  $1.63\text{ }\mu\text{m}^{-1}$ ,

and in DMSO solutions it is observed at  $1.53\text{ }\mu\text{m}^{-1}$ . The spectral shift accompanying the increase in the donating ability of the solvent suggests that the approach of polar or polarizable solvent molecules enhances the donor–acceptor interactions and culminates in gradual change of the environment in which copper(II) exists. It is very likely that as the interactions occurring along an axis perpendicular to the basal plane are intensified, solvent molecules replace the  $\text{ClO}_4^-$  group and the coordinated water. The information on donor–acceptor interactions are not extensive nor detailed. Regarding the influence of the –CN group, the data in Table 1 suggest that its insertion in the  $\beta$ -dionato moiety increases the susceptibility of the  $[\text{Cu}(\text{enR})\beta]^+$  entity to covalent interactions. The assessment of the influence of the groups linking the pyridyl rings of the nitrogenous base on the energy levels of the  $[\text{Cu}(\text{pyZpy})\beta]^+$  entity is more difficult because of the simultaneous changes in the symmetry of the ligand field. This, perhaps, becomes clear when the ligand-field band maxima of  $[\text{Cu}(\text{CN-acac})\text{dpamH}(\text{H}_2\text{O})\text{OCIO}_3]$  are compared with those of  $[\text{Cu}(\text{NC-acac})\text{dpC}(\text{OH})\text{OCH}_3(\text{OCIO}_3)]$  that occur at lower wavenumbers ( $\nu_{\text{max}}$ :  $1.642\text{ }\mu\text{m}^{-1}$  in  $\text{CH}_2\text{Cl}_2$ ,  $1.623\text{ }\mu\text{m}^{-1}$  in  $\text{CH}_3\text{CN}$ ,  $1.570\text{ }\mu\text{m}^{-1}$  in  $\text{C}_5\text{H}_2\text{OH}$ , and  $1.486\text{ }\mu\text{m}^{-1}$  in DMSO). Addition of drops of water to solutions of  $[\text{Cu}(\beta)\text{dpC}(\text{OH})\text{OCH}_3(\text{OCIO}_3)]$  in inert solvents did not cause any significant changes in the spectra while small aliquots altered the spectral bands in the ultraviolet region and the resemblance to the spectra of the  $[\text{Cu}(\beta)\text{dpC}(\text{OH})_2(\text{OCIO}_3)]$  chelates was evident, indicating conversion of the hemiacetal to diol. The information regarding the structural features of the newly obtained chelates was augmented by the X-ray structure determination of two representative compounds,  $[\text{Cu}(\text{CN-acac})\text{dpamH}(\text{H}_2\text{O})\text{OCIO}_3]$  and  $[\text{Cu}(\text{CN-acac})\text{dpC}(\text{OH})\text{OCH}_3(\text{OCIO}_3)]$ .

**Description of the Structure of  $[\text{Cu}(\text{CN-acac})\text{dpamH}(\text{H}_2\text{O})\text{OCIO}_3]$ .** In the unit cell of  $[\text{Cu}(\text{CN-acac})\text{dpamH}(\text{H}_2\text{O})\text{OCIO}_3]$  there are four copper atoms. Each copper atom has in its immediate vicinity two carbonyl oxygens and the pyridyl nitrogens in a square-planar arrangement with copper  $0.032(3)\text{ \AA}$  from the basal plane. The interatomic distances suggest that the organic species are bonded as bidentate ligands and chelate ring formation takes place, as expected. At a much longer distance from copper ( $2.401(3)\text{ \AA}$ ) and in apical position exists the oxygen of the water molecule. Both bidentate ligands are symmetrical and are bisected by the plane of symmetry in which lie the copper atom, the oxygen atom of the water molecule, the cyano group, the nitrogen atom linking the pyridyl rings, and an oxygen atom of the  $\text{ClO}_4^-$  group  $2.63(1)\text{ \AA}$  from copper. The last interatomic distance is appreciably longer than the bond lengths of the atoms in basal positions but within a range that weak covalent interactions, termed “semicoordination”, become effective.<sup>34</sup> The bond distances and angles indicate that the coordination geometry about copper is distorted tetragonal. The difference in the axial bond lengths may be regarded as a consequence of the initial  ${}^2E_g$  ground state of copper(II) resulting in a Jahn–Teller stabilization by splitting in  ${}^2A_{1g}$  and  ${}^2B_{1g}$ . The  $\text{ClO}_4^-$  group that counterbalances the charge of the complex cation is oriented in such a way that the chlorine atom is closer to the  $\beta$ -dionato anion. The  $\text{ClO}_4^-$  oxygen atoms were found to be disordered.

The interatomic distances and bond angles within the 3-cyano-2,4-pentanedionato anion (Table 4) are in accord with values reported in the literature for this ligand in the  $U(\text{Z},\text{Z})$  conformation.<sup>25–27</sup> The chelate ring assumes a conformation reminiscent of boat and the plane defined by the carbonyl groups

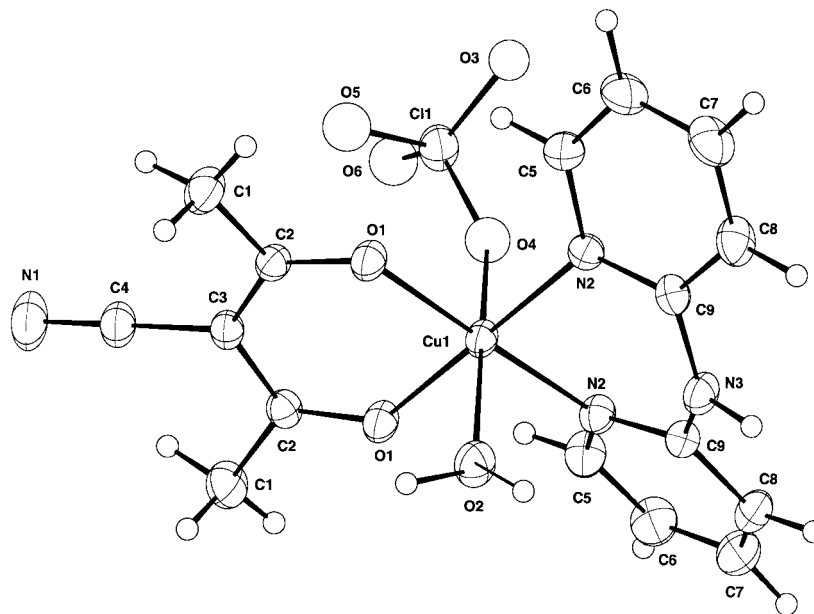
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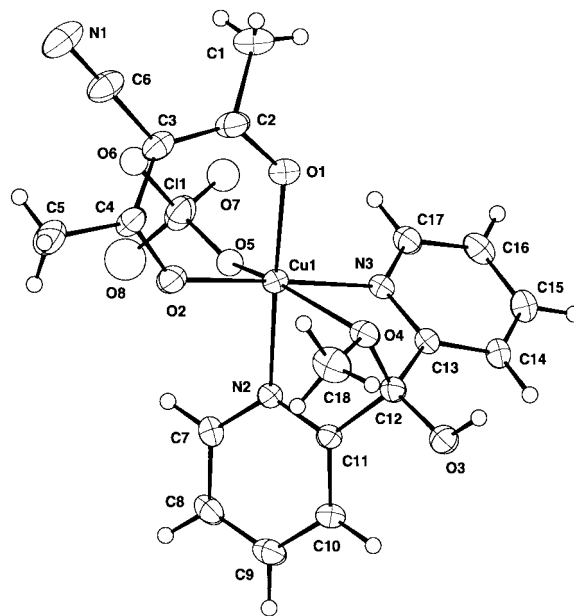
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**Figure 1.** Atom labeling scheme and clinographic projection of  $[\text{Cu}(\text{NC-acac})\text{dpamH}(\text{H}_2\text{O})\text{OClO}_3]$  with thermal ellipsoids at the 50% probability level.

forms a dihedral angle of  $8.1(8)^\circ$  with the basal plane. The linear cyano group is below the basal plane and is directed away from the water molecule. The 2,2'-dipyridylamine, dpamH, upon chelate formation adopts the boat configuration as observed before,<sup>35</sup> even though the electron lone pair of the nitrogen atom that effects cross-conjugation remains intact. Consequently the  $\text{sp}^3$  nitrogen atom is  $1.231(6)$  Å above the basal plane in the direction of the water molecule. The plane defined by the pyridyl atoms participating in the chelate ring forms a dihedral angle of  $32.3(6)^\circ$  with the basal plane and a dihedral angle of  $27.2(6)^\circ$  with the plane defined by the bridging nitrogen atom and the carbon atoms bonded to it. The dihedral angle formed by the pyridyl rings is  $32.9(6)^\circ$ . A clinographic projection of the molecule in thermal ellipsoids is shown in Figure 1.

**Description of the Structure of  $[\text{Cu}(\text{CN-acac})\text{dpC}(\text{OH})\text{OCH}_3(\text{OClO}_3)]$ .** The structure of  $[\text{Cu}(\text{CN-acac})\text{dpC}(\text{OH})\text{OCH}_3(\text{OClO}_3)]$  has no unusual packing features. In the unit cell there are four copper atoms. In the immediate vicinity of each copper atom are the carbonyl oxygens of the  $\beta$ -dionato moiety and the nitrogen atoms of the heterocyclic rings. Disregarding the negligible tetrahedral distortion, the pyridyl nitrogens and the carbonyl oxygens assume a nearly square-planar arrangement, the "center" of which is engaged by the copper atom. Electrical neutrality is conferred by the  $\text{ClO}_4^-$  group, and the Cu–O vector of one oxygen atom at  $2.634(8)$  Å is perpendicular to the basal  $\text{CuN}_2\text{O}_2$  plane. The Cu–O length suggests "semicoordination" and is in accord with the value determined in  $[\text{Cu}(\text{CN-acac})\text{dpamH}(\text{H}_2\text{O})\text{OClO}_3]$  (Table 4). In the other side of the basal plane and at a distance of  $2.613(2)$  Å from copper exists another oxygen atom, O(4). This oxygen atom is simultaneously bonded to a methyl group and to the carbon atom linking the heterocyclic rings, C(12). The nucleophilic addition leads to semiacetal formation with the electrophilic C(12) assuming tetrahedral stereochemistry (Table 4). An  $\text{sp}^3$ -hybridized carbon atom connecting the pyridyl groups and trans to the copper(II) ion accommodates<sup>23</sup> the adoption of the boat conformation by the chelate ring and facilitates the



**Figure 2.** Atom labeling scheme and clinographic projection of  $[\text{Cu}(\text{NC-acac})\text{dpC}(\text{OH})\text{OCH}_3(\text{OClO}_3)]$  with thermal ellipsoids at the 50% probability level.

approach of the etheric oxygen to copper. These indicate that the resulting di(2-pyridyl)methoxymethanol acts as tridentate ligand as in  $\text{Cu}(\text{dpC}(\text{OH})\text{OCH}_3)\text{Cl}_2$ .<sup>22</sup> Incidentally, the interatomic distance of the hydroxyl oxygen from copper is  $4.344(2)$  Å. The disposition of the ligated di(2-pyridyl)methoxymethanol is not symmetrical since the dihedral angles of the pyridyl rings of the N(2) and the N(3) atoms with the basal plane are  $45.3(5)^\circ$  and  $136.0(5)^\circ$ , respectively, while their dihedral angle is  $63.1(6)^\circ$ . Further, the nonbonding distances of the methyl carbon atom from the neighboring C(11) and C(13) atoms are  $2.970(5)$  and  $3.671(5)$  Å, respectively. The plane defined by the pyridyl atoms participating in the chelate ring forms an angle of  $66.0(6)^\circ$  with the basal plane. The microsymmetry around copper is highly irregular tetragonal because the angle of the axial bonds about copper is only  $154.4(2)^\circ$ .

(35) (a) Johnson, J. E.; Beineke, T. A.; Jacobson, R. A. *J. Chem. Soc. A* **1971**, 1371. (b) Ray, N. J.; Hulett, L.; Sheahan, R.; Hathaway, B. J. *J. Chem. Soc., Dalton Trans.* **1981**, 1463.

Regarding the  $\beta$ -dionato metallocyclic ring, the Cu–O bond lengths are shorter than those encountered in the similarly structured [Cu(CN-acac)dpamH(H<sub>2</sub>O)OClO<sub>3</sub>] and the bite angle is more obtuse. However, the bond lengths and bond angles are in accord with the values encountered in the literature for this chelate ring in half-chair conformation.<sup>26,27</sup> The plane defined by the carbonyl groups forms a dihedral angle of 36.7(6)° with the basal plane and the cyano group is away from the basal plane in the direction of the perchlorato group. A clinographic

projection of the molecule with thermal ellipsoids at the 50% probability level is shown in Figure 2.

**Supporting Information Available:** Tables 1s–6s, giving details of crystallographic data and structure refinement, anisotropic thermal parameters of nonhydrogen atoms, fractional coordinates of hydrogen atoms, calculated hydrogen atom coordinates, full listing of bond lengths and angles, and diagrams of the unit cell contents (20 pages). Ordering information is given on any current masthead page.

IC961475N