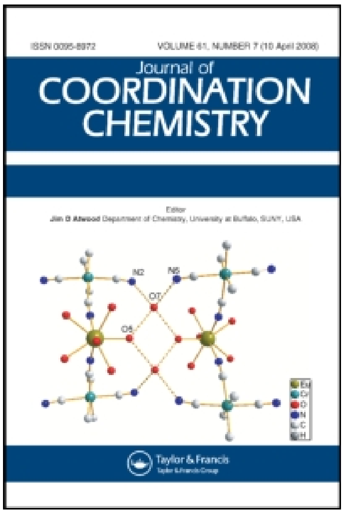

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COPPER(II) PROPIONATES Crystal and Molecular Structure of Bis(propionato)copper(II) Di(methyl-3-pyridylcarbamate)

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COPPER(II) PROPIONATES

Crystal and Molecular Structure of Bis(propionato)copper(II) Di(methyl-3-pyridylcarbamate)

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New copper(II) propionate compounds of composition Cu(prop)$_2$L (L =methyl-3-pyridylcarbamate or N,N-diethylnikotinamide) andau(prop)$_2$L$_2$ (L = methyl-3-pyridylcarbamate or2,6-pyridinemethanole) have been prepared. The crystal and molecular structure of thetetrakis(μ-propionato)di(methyl-3-pyridinecarbamate) dicopper(II),Cu$_2$(prop)$_4$(mpc)$_2$, was determined by direct method and Fouriertechniques. The compound crystallizes in the orthorhombic space group Pcab with four dimeric units in a cell withdimensions a = 19.350(4), b = 15.390(3), c = 10.725(2)Å. The structure was refined byfull-matrix least-squares methods to a R factor of 0.031, based on 3666 independent reflections. Thecompound is dimeric, with square-pyramidal geometry at each copper centre. The two copper atoms are bridgedby four carboxylate groups, while the apical ligands are methyl-3-pyridylcarbamate. The structural dataare compared with those found in similar copper(II) propionates. Spectral data of Cu(prop)$_2$L aretypical for dimeric copper(II) compounds. Both Cu(prop)$_2$L$_2$ compounds seem to possessoctahedral copper(II) stereochemistry with differing tetragonal distortion.

Keywords: Cu(II), propionates, carbomates, structure determinations

TABLE I Crystal data and structure refinement for [Cu2(prop)4(mpc)2]

Empiricalformula	$C_{26}H_{36}Cu_2N_4O_{12}$
Formula weight	726.66
Temperature	293(2) K
Wavelength	0.71069 Å
Crystal system	orthorhombic
Space group	Pbca
Unit cell dimensions	a = 19.350(4) Å b = 15.390(3) Å c = 10.725(2) Å
Volume	3193.9(11) $Å^3$
Z	4
Density (measured)	1.5 Mg/m^3
Density (calculated)	1.505 Mg/m^3
Absorption coefficient	1.396 mm^{-1}
$F(000)$	1496
Crystal size	0.30 × 0.30 × 0.28 mm
ϑ range for data collection	2.49 to 26.07°
Index ranges	0\h\13, 0\k\19,0\l\23
Reflections collected	3156
Independent reflections	3156
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3156/0/199
Goodness-of-fit on F^2	1.038
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0305$, $wR2 = 0.0812$
R indices (all data)	$R1 = 0.0804$, $wR2 = 0.0971$
Largest diff. peak and hole	0.455 and $-0.393 e Å^{-3}$

INTRODUCTION

Solvated copper(II) carboxylates have been the subject of numerous investigations[1]. The effects of the carboxylate substituents and of the axial donorligands on the exchange coupling constant ($-2J$)[2], and also onthe Cu-Cu distances[1], have attracted great interest.

Compounds of general formula $Cu(prop)_2L$ (L = methyl-3-pyridylcarbamate (mpc)or N,N-diethylnicotinamide (Et_2nia)) and $Cu(prop)_2L_2$ (L =methyl-3-pyridylcarbamate or 2,6-pyridinemethanolate (2,6-pyme)) were prepared andstudied by thermal and spectral methods. The derivative $Cu(prop)_2(mpc)$ was also characterized byX-ray crystallography.

EXPERIMENTAL

Preparation

Light green $Cu(prop)_2(mpc)$ was prepared by treating methyl-3-pyridylcarbamate (1.50g, 0.01 mol) with copper(II) propionate monohydrate (2.30 g, 0.01 mol) in

TABLE II Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters[$Å^2 \times 10^3$] for [Cu2(prop)4(mpc)2]. U(eq) is defined asone third of the trace of the orthogonalized U_{ij} tensor

	x	y	*z*	U(eq)
Cu	1124(1)	5338(1)	4933(1)	36(1)
O(1)	4763(2)	4789(2)	3117(1)	74(1)
O(2)	6855(2)	4811(2)	3084(1)	65(1)
O(11)	1260(2)	4561(2)	4137(1)	54(1)
O(12)	−635(2)	3984(2)	4251(1)	52(1)
O(21)	1583(2)	4348(1)	5547(1)	46(1)
O(22)	−306(2)	3800(2)	5674(1)	52(1)
N(1)	2990(2)	5870(2)	4858(1)	42(1)
N(7)	5935(2)	5489(2)	3929(1)	50(1)
C(2)	3802(2)	5567(2)	4388(1)	39(1)
C(3)	5038(2)	5817(2)	4390(2)	40(1)
C(4)	5431(3)	6405(2)	4878(2)	56(1)
C(5)	4598(3)	6722(3)	5352(2)	65(1)
C(6)	3376(3)	6440(2)	5321(2)	55(1)
C(8)	5747(3)	5009(2)	3356(2)	50(1)
C(9)	6862(4)	4271(3)	2485(2)	76(1)
C(11)	397(3)	4071(2)	3948(1)	45(1)
C(12)	567(4)	3560(3)	3291(2)	66(1)
C(13)	1919(4)	3314(3)	3147(2)	92(2)
C(21)	829(3)	3806(2)	5795(1)	45(1)
C(22)	1376(3)	3102(3)	6246(2)	71(1)
C(23)	516(3)	2673(2)	6725(2)	79(1)

hot methanol solution. The solution was left tostand at room temperature. The fine microcrystals that precipitated were filtered off (ca 70% yield), washed withcold methanol and dried at room temperature. The crude product was recrystallized from methanol with a yield of50%. Calc. for Cu(prop)$_2$(mpc): Cu, 17.56; C, 43.15; H, 5.02; N, 7.74%. Found: Cu, 17.43; C, 43.3;H, 5.02; N, 7.68%.

Light green Cu(prop)$_2$(Et$_2$nia) was prepared similarly with an equimolar ratio (3.82 gof Et$_2$nia and 2.60 g of Cu(prop)$_2$H$_2$O) in hot methanol. Calc. forCu(prop)$_2$(Et$_2$nia): Cu, 16.37; C, 48.53, H, 6.23; N, 7.22%. Found: Cu, 16.3; C, 48.0; H,6.0; N, 7.0%.

Compounds of composition Cu(prop)$_2$L$_2$ were prepared by adding L to a methanolsolution of Cu(prop)$_2$H$_2$O (at the molar ratio 1:2). The fine microcrystals producedon standing were separated, washed and dried at room temperature. Calc. forCu(prop)$_2$(mpc)$_2$: Cu, 12.36; C, 46.73; H, 5.09; N, 10.9%. Found: Cu, 12.17; C, 46.37; H,5.14; N, 10.66%. Calc. for Cu(prop)$_2$(2,6-pyme)$_2$: Cu, 13.02; C, 49.22; H, 5.78;N, 5.74%. Found: Cu, 13.8; C, 48.43; H, 5.6; N, 6.0%.

TABLE III Selected bond lengths [Å] and angles [°] for [Cu2(prop)4(mpc)2]

Cu-O(11)	1.956(2)	Cu-O(12)#1	1.963(2)
Cu-O(22)#1	1.977(2)	Cu-O(21)	1.993(2)
Cu-N(1)	2.167(2)	Cu-Cu#1	2.6396(8)
O(11)-C(11)	1.249(4)	O(12)-C(11)	1.261(4)
O(21)-C(21)	1.258(4)	O(22)-C(21)	1.240(3)
O(1)-C(8)	1.201(4)	O(2)-C(8)	1.335(4)
O(2)-C(9)	1.427(4)	N(1)-C(6)	1.321(4)
N(1)-C(2)	1.344(3)	N(7)-C(8)	1.346(4)
N(7)-C(3)	1.405(4)	C(11)-C(12)	1.506(4)
C(12)-C(13)	1.524(6)	C(21)-C(22)	1.510(4)
C(22)-C(23)	1.463(4)	C(2)-C(3)	1.381(4)
C(3)-C(4)	1.375(4)	C(4)-C(5)	1.371(5)
C(5)-C(6)	1.381(5)		
O(11)-Cu-O(12)#1	167.97(9)	O(11)-Cu-O(22)#1	88.60(10)
O(11)-Cu-O(21)	89.02(10)	O(12)#1-Cu-O(21)	89.62(9)
O(22)#1-Cu-O(21)	167.47(8)	O(11)-Cu-N(1)	96.30(9)
O(12)#1-Cu-N(1)	95.72(9)	O(22)#1-Cu-N(1)	96.71(9)
O(21)-Cu-N(1)	95.78(9)	O(11)-Cu-Cu#1	84.48(7)
O(12)#1-Cu-Cu#1	83.49(7)	O(22)#1-Cu-Cu#1	85.25(6)
O(21)-Cu-Cu#1	82.28(6)	N(1)-Cu-Cu#1	177.90(6)
C(11)-O(11)-Cu	123.0(2)	C(11)-O(12)-Cu#1	123.6(2)
C(21)-O(21)-Cu	125.2(2)	C(21)-O(22)-Cu#1	122.9(2)
C(8)-O(2)-C(9)	117.2(3)	C(6)-N(1)-C(2)	119.2(3)
C(6)-N(1)-Cu	119.7(2)	C(2)-N(1)-Cu	120.8(2)
C(8)-N(7)-C(3)	128.1(3)	O(11)-C(11)-O(12)	125.3(3)
O(11)-C(11)-C(12)	118.2(3)	O(12)-C(11)-C(12)	116.4(3)
C(11)-C(12)-C(13)	113.5(3)	O(22)-C(21)-O(21)	124.3(3)
O(22)-C(21)-C(22)	119.1(3)	O(21)-C(21)-C(22)	116.6(3)
C(23)-C(22)-C(21)	116.4(3)	N(1)-C(2)-C(3)	121.6(3)
C(4)-C(3)-C(2)	118.7(3)	C(4)-C(3)-N(7)	117.6(3)
C(2)-C(3)-N(7)	123.7(3)	C(5)-C(4)-C(3)	119.7(3)
C(4)-C(5)-C(6)	118.5(3)	N(1)-C(6)-C(5)	122.4(3)
O(1)-C(8)-O(2)	124.5(3)	O(1)-C(8)-N(7)	127.1(3)
O(2)-C(8)-N(7)	108.4(3)		

Spectral Studies

Electronic spectra in the region 10-28 KK were measured with a Perkin-Elmer 450 spectrometer usingnujol suspensions. EPR spectra of powdered samples were obtained using a Varian E4 spectrometer at roomtemperature.

Crystallography

Data collection and cell refinement were carried out using Syntex $P2_1$ software. Intensity data werecorrected to Lorenz and polarization factors using $XP2_1$[3]. The structure was solved by the heavy atom method with SHELX86[4], and subsequent Fourier synthesis using SHELXL93[5]. Anisotropic thermal parame-

TABLE IV Hydrogen coordinates (×10^4) and isotropic displacement parameters (Å^2× 10^3) for [Cu2(prop)4(mpc)2]

	x	*y*	*z*	U(eq)
H(2)	3524(3)	5179(2)	4053(1)	47
H(4)	6258(3)	6586(2)	4887(2)	67
H(5)	4850(3)	7118(3)	5688(2)	78
H(6)	2805(3)	6661(2)	5638(2)	66
H(7)	6699(2)	5610(2)	4024(1)	60
H(9A)	7702(5)	4206(16)	2322(9)	114
H(9B)	6361(23)	4533(10)	2130(6)	114
H(9C)	6527(26)	3711(7)	2600(4)	114
H(12A)	255(4)	3901(3)	2906(2)	80
H(12B)	72(4)	3034(3)	3318(2)	80
H(13A)	2405(7)	3831(3)	3084(17)	138
H(13B)	1960(6)	2966(18)	2736(10)	138
H(13C)	2244(11)	2989(19)	3530(8)	138
H(22A)	1737(3)	2662(3)	5949(2)	85
H(22B)	2050(3)	3353(3)	6514(2)	85
H(23A)	294(3)	3069(3)	7088(1)	118
H(23B)	913(4)	2170(3)	6920(3)	118
H(23C)	−221(4)	2499(2)	6480(1)	118

ters were refined for all nonhydrogen atoms.Geometrical analysis was performed using SHELXL93[5]. The structureswere drawn using ORTEP[6]. The final parameters after refinementare summarised in Table I. Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2 ×10^3) are given in Table II. Selectedinter-atomic distances and bond angles are given in TableIII. Calculated hydrogen coordinates (×10^4) are given in Table IV and anisotropic displacement parameters [Å × 10^3]in Table V.

Supplementary material including the thermal parameters of non-hydrogen atoms has been deposited at theCambridge Crystallographic Data Centre. Observed and calculated structural factors are available on request fromM.M.

RESULTS AND DISCUSSION

The initial temperature of decomposition is 150°C for $Cu(prop)_2(mpc)$ and 160°C$Cu(prop)_2(Et_2nia)$, which are somewhat higher than those of 120 and 130°C found for$Cu(prop)_2(mpc)_2$ and $Cu(prop)_2(2,6\text{-}pyme)_2$,respectively.

The electronic spectra of $Cu(prop)_2L$ (L = mpc or Et_2nia) exhibit a band at 13.8KK (mpc) or 14.2 KK (Et_2nia), which was assigned to *d-d* transitions of copper(II), and ashoulder at 27 KK (mpc) or 26.5 KK (Et_2nia). The shoulder is characteristic of the bridging system withan antiferromagnetic interaction[1].

TABLE V Anisotropic displacement parameters [Å^2 × 10^3] for[Cu2(prop)4(mpc)2] The anisotropic displacement factor exponent takes the form: $-2p^2[(ha^*)^2U_{11} + \ldots + 2hka^*b^*U_{12}]$

	U11	*U22*	*U33*	*U23*	*U13*	*U12*
Cu	31(1)	45(1)	32(1)	0(1)	−1(1)	−6(1)
O(11)	54(1)	70(2)	39(1)	−14(1)	8(1)	−11(1)
O(12)	52(1)	58(1)	47(1)	−13(1)	4(1)	−6(1)
O(21)	31(1)	56(1)	52(1)	12(1)	−5(1)	−3(1)
O(22)	32(1)	63(1)	61(1)	21(1)	−5(1)	−7(1)
O(1)	42(1)	121(2)	58(2)	−21(2)	−2(1)	−9(2)
O(2)	42(1)	92(2)	62(1)	−9(1)	7(1)	2(1)
N(1)	37(1)	46(1)	42(1)	4(1)	−1(1)	−9(1)
N(7)	28(1)	74(2)	49(1)	0(1)	−4(1)	−6(1)
C(11)	58(2)	47(2)	30(1)	1(1)	1(1)	−3(2)
C(12)	95(3)	64(2)	40(2)	−11(2)	13(2)	−18(2)
C(13)	114(4)	85(3)	77(3)	−22(2)	41(3)	2(3)
C(21)	42(2)	55(2)	37(1)	4(1)	−6(1)	−4(2)
C(22)	56(2)	85(3)	73(2)	34(2)	−12(2)	−4(2)
C(23)	91(3)	79(3)	65(2)	26(2)	1(2)	6(2)
C(2)	32(1)	49(2)	37(1)	5(1)	−4(1)	−6(1)
C(3)	26(1)	51(2)	43(2)	12(1)	−2(1)	−3(1)
C(4)	37(2)	66(2)	65(2)	−5(2)	−5(2)	−16(2)
C(5)	56(2)	71(2)	67(2)	−20(2)	−2(2)	−23(2)
C(6)	47(2)	62(2)	55(2)	−10(2)	7(2)	−11(2)
C(8)	39(2)	64(2)	48(2)	9(2)	1(1)	−1(2)
C(9)	71(3)	82(3)	75(3)	−11(2)	12(2)	8(2)

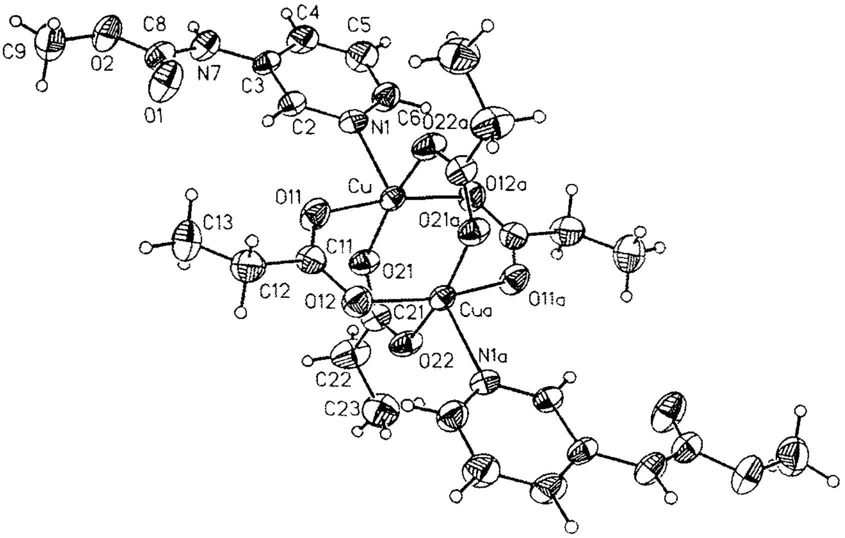

FIGURE 1 The molecular structure of [Cu$_2$(prop)$_4$(mpc)$_2$]

TABLE VI Structural data for copper(II) propionates with the CuO_4N chromophore

Compound	*Cryst.cl. Space gr.Z*	*a/Å b/Å c/Å*	*α/° β/° γ/°*	*Cu-O (basal)/Å*	*Cu-N(apical)/Å*	*Cu-Cu/ÅCu-O-C-O-Cu/Å*	*Cu-O-C/°Cu-Cu-L_{AX}/°*	*Ref.*
*$Cu_2(prop)_4(py)_2$	*tr*	16.209(4)	101.9(1)	1.97(1.,2)	N2.13(1)	2.619(2)	127(1.1)	7
	P-1	8.442(5)	121.0(1)	6.42	175(1)			
	4	11.618(7)	90.4(1)					
				1.96(1.,0)	N 2.17(1)	2.642(2)	126(1.1)	
6.42	173(1)							
$Cu_2(prop)_4(3pic)_2$	*m*	20.702(4)		1.970(2,12)	N 2.167(2)	2.6312(4)	124.2(1.5)	8
	C2/c	7.306(2)	107.8(5)	6.44	175(1)			
	8	18.957(4)						
$Cu_2(prop)_4(nia)_2$	*tr*	9.895(7)	87.36(5)	1.978(6,27)	N2.181(8,5)	2.635(2)	124.1(8,1.8)	9
	P-1	11.204(7)	89.17(5)	6.48	177.5(2,1.5)			
	2	13.509(7)	74.25(5)					
$Cu_2(prop)_4(mpc)_2$	*or*	19.350(4)		1.972(2)	N 2.167(2)	2.6396(8)	123.7(2)	this
	Pbca	15.390(3)	6.45	177.90(6)	work			
	4	10.725(2)						
$Cu_2(prop)_4(3,5lut)_2$	*tr*	8.6652(4)	77.31(8)	1.975(3,4)	N2.168(2)	2.6447(6)	126.0(3,1)	10
	P-1	8.7357(6)	67.67(13)	6.44	177.42(6)			
	1	10.8223(4)	85.69(9)					
$Cu_2(prop)_4(2pic)_2$	*tr*	8.080(7)	111.9(2)	1.97(1,1)	N2.21(2)	2.647(4)	126.5(1,1.5)	11
	P-1	8.290(7)	75.7(1)	6.44	179(1)			
	2	12.444(10)	119.4(1)					
$Cu_2(prop)_4(4pic)_2$	*or*	20.300(3)		1.970(9,3)	N 2.143(9)	2.655(3)	125(1)	12
	Cccm	14.244(3)	6.46	180(1)				
	8	20.479(6)						
				1.972(922)	N 2.148(9)	2.659(3)	124(1)	
6.44	180(1)							
$Cu_2(prop)_4(4Clanl)_2$	*tr*	8.848(1)	102.66(2)	1.9690(4)	N2.215(2)	2.689(2)	126.48(3)	13
	P-1	12.358(4)	100.23(2)	6.44	172.12(8)			
	2	12.844(3)	96.10(2)					

*there are two crystallographically independent molecules tr-triclinic,m-monoclinic, or-othorhombic

The separation between the twobands of 13.2 KK in the former and 12.3 KK in the latter, indicates differing degrees of distortion about the copper(II)atom.

The solid electronic spectra of $Cu(prop)_2L_2$ (L = mpc or 2,6-pyme)exhibit a broad ligand field band with a maximum at 17.9 KK (mpc) or 13.7 KK (2,6-pyme), with a shoulder at about15.0 KK and 12.5 KK, respectively. This type of *d-d* spectrum is typical for tetragonal arrangementsaround copper(II) and corresponds to electron transfer from the one-electron orbital ground state, $d_{(x^2-y^2)}$.

The EPR spectra obtained for the powdered samples of $Cu(prop)_2L$ at room temperature containedtypical absorption bands of an axially symmetric dimer. The spectrum shows absorptions at low and high fieldsHz_1 and Hz_2, respectively, with an asymmetrical absorption near 4500G(H_T2). One absorption (H_T1) is missing because $|D| > h\nu$ at theX-band frequency used. The spectra can be interpreted using a spin Hamiltonian for axial symmetry:

$$H = g_{\parallel}\beta H_Z S_Z + g_{\perp}(\beta H_x S_x + H_Y S_Y) + D(S_Z^2 + 2/3)$$

where S = 1 for the thermally accessible triplet state, and the other symbols have their usual meanings. Thevalues obtained for the spin Hamiltonian parameters are: $g = 2.08_2$;$g_{\parallel} = 2.38_5$ and $|D| = 0.348$ cm^{-1} for L= mpc; and $g = 2.07_5$, $g_{\parallel} = 2.37_3$ and $|D| = 0.355$ cm^{-1} for L =Et_2nia. The |D| values of about 0.3 cm^{-1} are large compared to themagnetic quantities, but are small compared to vibrational frequencies. The values are comparable to those found indimeric copper(II) carboxylates[1]. A somewhat higher|D| value of $Cu(prop)_2(mpc)$ than for $Cu(prop)_2(Et_2nia)$corresponds to the energy of *d-d* transitions.

The EPR spectra of the powdered $Cu(prop)_2L_2$ samples are the axial types($g_{\parallel} > g_{\perp}$) typical for compounds with tetragonal distortion around thecopper(II) atom. The g-values for the respective compounds are: $g_{\perp} = 2.07_4$ and $g_{\parallel} = 2.26_5$ for L = mpc;$g_{\perp} = 2.06_9$ and $g_{\parallel} = 2.23_6$ for L= 2,6-pyme.

X-ray analysis of $Cu(prop)_2(mpc)$ showed dimeric molecules. The principle structural featuresof $Cu_2(prop)_4(mpc)_2$ are illustrated in Figure 1. The crystal structure consists of the centrosymmetric$Cu_2(prop)_4(mpc)_2$ molecules, where the centre of symmetry lies between thetwo copper(II) atoms. The copper(II) atoms are bridge-bonded by four propionate anions. Each copper(II)atom shows five-coordination in the form of a square pyramid, with four oxygen atoms of the bridgingpropionate anions in the basal plane and one nitrogen atom of a methyl-3-pyridylcarbamate molecule atthe apex. Selected bond lengths and angles are given in Table III. The meancarboxylate Cu-O bond length of 1.972(2) Å and $Cu-N_{apical}$ = 2.167(2)Åare comparable with those found in copper(II) propionates. The Cu-Cu distance is 2.6396(8)Å. Thedisplacement of the copper(II) atoms from the basal plane towards the apical N donors is 0.211(1)Å.

Structural data for dimeric copper(II) propionates with the CuO_4N chromophore are summarized inTable VI. The Cu-Cu distances are in the range from 2.619(2)to 2.689(2) Å. The mean Cu-O and Cu-O-C-O-Cu bond distances of 1.97 and6.44 Å are comparable with those found in the series of dimeric copper(II) carboxylates[1]. The apical Cu-N bond distances range from 2.13 to 2.215(2)Å. There is tendency for the Cu(II) atoms to be pushed out of the basal O_4 plane upon elongationof the Cu-Cu distance.

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