The Crystal Structure and Magnetic Property of Di-μ-propionato-*O,O'*-bis[*N*-*p*-tolylsalicylideneaminatocopper(II)]

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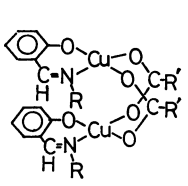
The crystal structure of di-μ-propionato-*O,O'*-bis[*N*-*p*-tolylsalicylideneaminatocopper(II)] was determined by X-ray diffraction method using the data collected by counter diffractometer techniques. The space group is $P\bar{1}$ and the cell constants are $a=12.565(2)$, $b=13.040(2)$, $c=12.230(2)$ Å, $\alpha=107.73(1)$, $\beta=115.72(1)$, $\gamma=100.18(1)°$, and $Z=2$. The structure was solved by the heavy atom method and refined by the block-diagonal least-squares method to an R factor of 0.029. The crystal is composed of one-dimensional chains extended along the c axis, where the two copper atoms coordinated by the Schiff bases are bridged by two propionate groups. The magnetic property was discussed on the basis of the crystal structure.

Recently, Tokii *et al.*[1] found that bis(*N*-R-salicylideneaminato)copper(II), Cu(Sal·*N*-R)$_2$ reacts with copper(II) carboxylates, Cu(R'COO)$_2$, to form a series of the complexes with the formula, [Cu(Sal·*N*-R)R'-COO], where R=phenyl and *p*-tolyl and R'=ethyl. These complexes show antiferromagnetic behavior and the temperature dependence of the magnetic susceptibility (80—300 K) is well expressed by the Bleaney-Bowers equation 1[2]

$$\chi_A = \frac{Ng^2\beta^2}{3kT}\left[1+\frac{1}{3}\exp\left(\frac{-2J}{kT}\right)\right]^{-1} + N\alpha, \qquad (1)$$

where $-2J$ is equal to the energy separation between the lowest singlet and triplet levels, which gives the degree of the magnetic interaction. By the best fit of the observed cryomagnetic data to Eq. 1, assuming $N\alpha=60\times10^{-6}$ emu/mol, they evaluated the values of $-2J=101$ cm^{-1} and $g=2.14$ for [Cu(Sal·*N*-*p*-tolyl)C_2H_5-COO]. On the basis of the magnetic properties and the IR spectral data, they concluded that the complexes possess the binuclear structure shown in **1**.[3]



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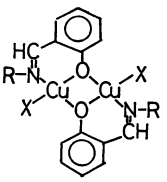

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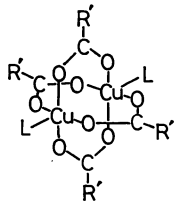

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Binuclear copper(II) complexes with monatomic bridges and with triatomic bridges as shown in **2** and **3** have been studied extensively. However, the binuclear structure consisting of only two triatomic bridges as shown in **1** is rare so far. Only one example of the copper complex of this structure has been reported.[4] Hence, in this study, the crystal structure of [Cu(Sal·*N*-*p*-tolyl)C_2H_5COO], was determined by the single-crystal X-ray diffraction method, in order to clarify the structure and to discuss the magnetic property in more detail in relation to the structure.

Experimental

Dark green crystals of the title complex were prepared according to Ref. 1. Most of the crystals were twins, and accordingly a crystal which had been confirmed to be a single-crystal by the Weissenberg photographs was used for the measurement of the cell parameters and intensities. Preliminary Weissenberg photographs revealed no systematic absences and showed the triclinic symmetry. The cell parameters and intensities were measured on a Syntex $P\bar{1}$ automated diffractometer with monochromated Mo $K\alpha$ radiation ($\lambda=0.71073$ Å). The crystal used was ground to a sphere of radius 0.225 mm. The cell parameters were determined by the least-squares refinement from 15 reflections within a range of $24<2\theta<35°$. The values are $a=12.565(2)$, $b=13.040(2)$, $c=12.230(2)$ Å, $\alpha=107.73(1)$, $\beta=115.72(1)$, $\gamma=100.18(1)°$, and $V=1604.3(4)$ Å^3. The density $D_m=1.43(1)$ g/cm^3 obtained by floatation in hexane-carbon tetrachloride solutions agrees well with the density $D_c=1.435$ g/cm^3 calculated for two dimer units per cell. Of the two possible triclinic space groups, the centrosymmetric space group $P\bar{1}$ was assumed on the basis of its more frequent occurrence. Successful solution and refinement in this space group support this choice.

Intensity data were collected by the θ-2θ scan technique with a variable scan rate of 4.0 to 24.0 °/min. Three standard reflections were monitored every 50 reflections, and their intensities showed a good stability. A total of 4154 independent reflections with $2\theta<45°$ were collected. 3421 reflections with I greater than $3\sigma(I)$ were considered as "observed" and were used for the structure analysis, where $\sigma(I)$ was calculated for each reflection on the basis of counting statistics. The Lorentz and polarization corrections were applied, but no absorption correction was made on account of $\mu r=0.33$.

Solution and Refinement of the Structure

The structure was solved by the heavy atom method. The positions of the copper atoms were obtained from a three-dimensional Patterson synthesis. Successive Fourier syntheses and difference Fourier syntheses revealed all the nonhydrogen atoms. Refinement was carried out by the block-diagonal least-squares method. In the course of refinement, it became apparent that the carbon atom C(6) of the ethyl group was subjected to disorder. A difference Fourier map revealed two largest chemically reasonable peaks in the vicinity of C(6). Thus, in further refiements two partial atoms, C(6A) and C(6B), were used. The occupancy factors, 0.4 and 0.6 for C(6A) and C(6B) respectively, were based on the peak heights. The bolckdiagonal least-squares refinement introducing anisotropic thermal pa-

TABLE 1. FRACTIONAL POSITIONAL PARAMETERS AND ANISOTROPIC TEMPERATURE FACTORS ($\times 10^5$) OF NON-HYDROGEN ATOMS WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Temperature factors are of the from: $\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2hkB_{12}+2hkB_{12}+2hlB_{13}+2klB_{23})]$.

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu(1)	−2205(3)	−3830(3)	10253(4)	566(4)	604(3)	784(5)	181(3)	375(4)	303(3)
Cu(2)	3755(4)	1228(3)	39354(4)	712(4)	592(3)	842(5)	162(3)	483(4)	244(3)
O(1)	15664(21)	−2176(22)	19502(25)	612(22)	1058(25)	1090(30)	328(19)	457(22)	592(23)
O(2)	17973(22)	−1832(23)	38653(25)	818(25)	1053(25)	1035(30)	388(21)	550(24)	413(23)
O(3)	−6813(22)	−19116(19)	9595(23)	937(25)	584(19)	941(27)	232(18)	508(23)	287(19)
O(4)	−6477(23)	−15168(19)	28806(24)	1106(28)	589(20)	1081(31)	166(19)	710(26)	258(20)
O(5)	3318(20)	11031(18)	10656(23)	700(22)	582(19)	1012(28)	200(16)	514(21)	284(19)
O(6)	−10535(21)	2992(19)	40361(24)	758(23)	613(19)	1214(32)	229(17)	609(23)	297(20)
N(1)	−19399(24)	−3518(23)	4914(27)	598(26)	689(24)	839(32)	156(20)	385(25)	309(23)
N(2)	12871(27)	18010(24)	48051(28)	855(30)	657(24)	836(33)	118(22)	483(27)	264(23)
C(1)	21566(31)	−2432(30)	30510(35)	707(34)	825(32)	967(41)	310(27)	489(32)	394(30)
C(2)	34374(40)	−3255(48)	34817(46)	959(44)	1985(64)	1314(56)	808(44)	625(43)	930(50)
C(3)	38428(51)	−4961(66)	25085(66)	1303(59)	2948(97)	2448(95)	1383(65)	1256(65)	1627(83)
C(4)	−8377(33)	−21887(29)	17949(36)	864(36)	592(28)	1032(43)	211(26)	503(34)	316(29)
C(5)	−12797(55)	−34516(35)	14585(55)	2330(81)	534(33)	1923(73)	271(41)	1200(66)	386(41)
C(6A)	−7845(200)	−40896(104)	6862(180)	4650(391)	713(104)	3286(306)	1300(170)	2974(313)	1087(153)
C(6B)	−18559(114)	−43248(75)	1472(97)	3101(188)	912(78)	1620(126)	46(95)	1153(130)	357(81)
C(7)	−1091(32)	19306(28)	13495(32)	841(34)	599(27)	694(36)	217(25)	389(30)	230(26)
C(8)	6231(36)	30694(31)	17601(40)	944(39)	700(31)	1329(50)	211(28)	710(38)	335(33)
C(9)	2100(41)	39605(32)	20949(46)	1259(47)	622(31)	1621(59)	246(31)	863(45)	368(35)
C(10)	−9379(43)	37636(34)	20159(48)	1471(52)	756(34)	1815(64)	575(35)	1104(51)	547(39)
C(11)	−16837(37)	26646(34)	15827(42)	1000(41)	891(35)	1391(52)	425(31)	774(40)	503(35)
C(12)	−12930(30)	17250(28)	12589(33)	737(33)	698(29)	887(39)	291(26)	495(31)	370(28)
C(13)	−21587(31)	5961(30)	7549(34)	659(32)	782(30)	913(40)	275(26)	460(31)	369(29)
C(14)	−30045(29)	−14068(28)	−1106(34)	579(30)	654(28)	916(39)	155(24)	379(30)	306(28)
C(15)	−36143(40)	−15884(36)	5412(42)	1137(46)	957(39)	1166(50)	−49(34)	720(41)	155(35)
C(16)	−46277(43)	−25934(39)	−583(49)	1228(51)	1092(44)	1679(65)	−71(37)	977(51)	403(43)
C(17)	−50253(36)	−34376(34)	−12942(44)	776(38)	798(35)	1491(57)	87(29)	455(39)	319(37)
C(18)	−43928(38)	−32357(34)	−19150(42)	997(43)	800(35)	1153(50)	137(31)	448(39)	86(34)
C(19)	−33862(34)	−22318(33)	−13428(38)	817(37)	866(34)	1066(45)	164(29)	563(35)	300(32)
C(20)	−61146(47)	−45585(41)	−19236(60)	1230(55)	902(43)	2394(89)	−186(39)	876(59)	269(50)
C(21)	−13764(34)	12144(31)	41647(34)	935(37)	809(31)	815(39)	346(28)	521(33)	337(29)
C(22)	−26165(39)	11051(37)	38452(45)	1043(44)	1083(41)	1487(58)	485(35)	749(43)	501(40)
C(23)	−29955(46)	20375(47)	39691(54)	1356(55)	1624(58)	1875(73)	966(48)	966(55)	805(54)
C(24)	−21634(54)	31160(44)	44336(55)	2191(77)	1331(52)	1987(76)	1189(54)	1385(67)	904(53)
C(25)	−9644(48)	32598(37)	47445(49)	1756(61)	880(38)	1631(62)	601(40)	1038(53)	611(40)
C(26)	−5368(37)	23150(31)	46042(37)	1184(43)	687(30)	965(43)	376(29)	637(36)	366(30)
C(27)	7540(38)	25482(30)	49502(36)	1231(44)	574(29)	893(42)	112(28)	561(36)	230(29)
C(28)	26216(35)	22848(31)	52944(36)	904(38)	723(32)	882(41)	−6(27)	481(34)	153(29)
C(29)	34752(41)	22697(41)	64320(47)	1071(47)	1208(45)	1449(60)	224(37)	644(45)	575(43)
C(30)	47732(41)	27712(46)	69325(51)	888(45)	1507(55)	1571(65)	173(39)	530(46)	504(48)
C(31)	51929(42)	32385(45)	62850(50)	926(46)	1447(55)	1466(63)	−155(39)	666(46)	−85(46)
C(32)	43280(52)	32327(59)	51574(57)	1463(65)	2262(81)	1683(75)	−310(57)	948(60)	701(63)
C(33)	30250(46)	27432(52)	46217(49)	1197(53)	2053(71)	1223(58)	−199(49)	528(47)	774(53)
C(34)	66016(53)	37655(65)	68357(71)	1122(62)	2438(94)	2502(107)	−173(59)	1088(71)	172(79)

rameters yielded discrepancy factors $R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|=0.045$ and $R_2=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}=0.067$. At this stage, a difference Fourier map revealed all the hydrogen atoms except for those bound to the disordered carbon atom C(6). Further refinement including the hydrogen atoms yielded final values of 0.029 and 0.042 for R_1, and R_2, respectively. The final shift in the atomic parameters of the nonhydrogen atoms averaged 0.05σ with a maximum of 0.42σ, with the exception of several parameters of the disordered carbon atom C(6) which were undergoing poorly damped oscillations of $0.05—2.15\sigma$. A final difference Fourier map showed no important features, the highest peak being 0.25 e/Å^3 except for some peaks of 0.26—0.29 e/Å^3 corresponding to the hydrogen atoms bound to C(6).

In the least-squares refinement the function minimized was $\Sigma w(|F_o|-k|F_c|)^2$, and the weighting scheme was

Table 2. Fractional positional parameters ($\times 10^4$) and isotropic temperature factors of hydrogen atoms

The average of estimated standard deviations of the isotropic temperature factors is 1.2 Å.

Atom	x	y	z	B Å^2
H(C2)	3477(49)	−856(44)	3849(55)	9.6
H(C2)′	4092(50)	247(47)	4387(59)	10.6
H(C3)	4736(53)	−493(49)	2903(61)	11.0
H(C3)′	3885(61)	141(53)	2284(69)	13.4
H(C3)″	3191(71)	−1240(63)	1719(82)	17.0
H(C5)	−1881(48)	−3666(43)	1678(54)	9.3
H(C5)′	−346(57)	−3595(52)	1950(64)	12.0
H(C8)	1436(33)	3210(31)	1720(37)	5.0
H(C9)	746(32)	4769(29)	2369(35)	4.5
H(C10)	−1164(36)	4426(33)	2263(41)	5.7
H(C11)	−2504(34)	2489(31)	1510(38)	5.2
H(C13)	−3009(31)	552(28)	642(33)	3.9
H(C15)	−3411(36)	−998(33)	1351(41)	5.9
H(C16)	−5016(54)	−2774(49)	414(62)	11.2
H(C18)	−4573(41)	−3800(38)	−2707(46)	7.4
H(C19)	−2935(28)	−2115(25)	−1683(30)	3.0
H(C20)	−6738(55)	−4683(48)	−2712(62)	11.5
H(C20)′	−6372(51)	−4597(47)	−1420(59)	11.0
H(C20)″	−5886(50)	−5204(45)	−2009(54)	9.8
H(C22)	−3114(38)	378(34)	3601(41)	6.1
H(C23)	−3877(37)	1869(33)	3699(40)	5.8
H(C24)	−2446(45)	3759(41)	4540(50)	8.6
H(C25)	−298(37)	4011(34)	5126(42)	6.3
H(C27)	1280(35)	3416(32)	5412(39)	5.5
H(C29)	3183(40)	1854(36)	6833(45)	7.0
H(C30)	5304(54)	2686(50)	7743(62)	11.5
H(C32)	4544(71)	3642(67)	4753(84)	17.5
H(C33)	2362(51)	2749(46)	3799(58)	10.1
H(C34)	6463(55)	4188(50)	6448(63)	12.4
H(C34)′	7016(72)	3370(65)	6942(82)	16.9
H(C34)″	6956(61)	4192(55)	7808(69)	13.5

$w=(6.0+|F_o|+0.01|F_o|^2)^{-1}$.[5] Atomic scattering factors for Cu, O, N, C_{val}, and H, and the anomalous dispersion corrections, $\Delta f'$ and $\Delta f''$ for Cu, were taken from International Tables for X-ray Crystallography.[6]

The final positional and thermal parameters with their estimated standard deviations are given in Tables 1 and 2.***

The calculations were carried out at the Computer Center of Kyushu University, with the UNICS-II program system.

Description of the Structure and Discussion

The molecular structure obtained is shown in Fig. 1. The bond distances and angles with their estimated standard deviations are listed in Tables 3 and 4, respectively. Some least-squares planes with the deviations of atoms from the planes are given in Table 5.

The asymmetric unit contains two crystallographi-

*** A list of structure factors has been deposited with the Chemical Society of Japan as a Document No. 7716.

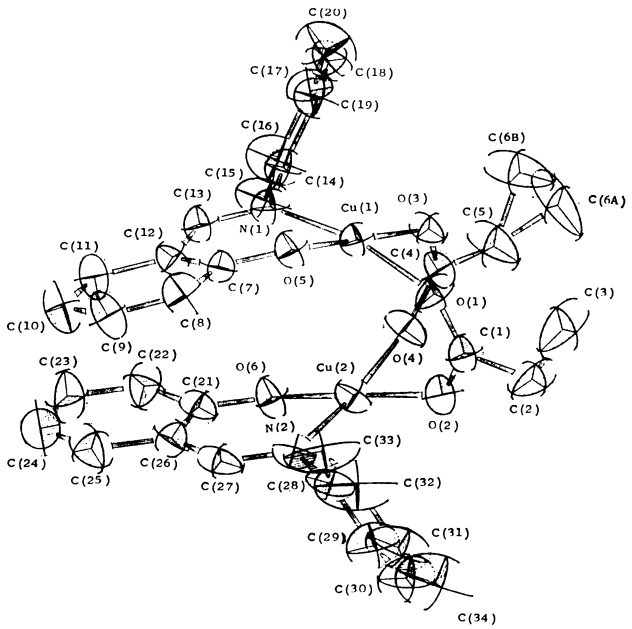

Fig. 1. A perspective view of the molecule.

Table 3. Interatomic distances (l/Å) with their estimated standard deviations in parentheses

Copper coordination spheres			
Cu(1)-O(1)	1.960(2)	Cu(2)-O(2)	1.929(3)
Cu(1)-O(3)	1.941(3)	Cu(2)-O(4)	1.949(2)
Cu(1)-O(5)	1.917(3)	Cu(2)-O(6)	1.901(3)
Cu(1)-N(1)	1.979(3)	Cu(2)-N(2)	1.968(3)
Cu(1)-O(5)^{II}	2.371(3)	Cu(2)-O(6)^{II}	2.519(3)
Propionate groups			
O(1)-C(1)	1.238(5)	O(3)-C(4)	1.260(6)
O(2)-C(1)	1.248(6)	O(4)-C(4)	1.237(5)
C(1)-C(2)	1.496(7)	C(4)-C(5)	1.502(6)
C(2)-C(3)	1.460(11)	C(5)-C(6A)	1.478(26)
		C(5)-C(6B)	1.408(10)
N-p-tolylsalicylideneamine moieties			
O(5)-C(7)	1.320(5)	O(6)-C(21)	1.314(5)
C(7)-C(8)	1.402(5)	C(21)-C(22)	1.400(7)
C(8)-C(9)	1.377(7)	C(22)-C(23)	1.372(8)
C(9)-C(10)	1.374(8)	C(23)-C(24)	1.368(8)
C(10)-C(11)	1.358(6)	C(24)-C(25)	1.345(9)
C(11)-C(12)	1.409(6)	C(25)-C(26)	1.422(7)
C(12)-C(7)	1.412(6)	C(21)-C(26)	1.402(5)
C(12)-C(13)	1.425(5)	C(26)-C(27)	1.433(7)
C(13)-N(1)	1.289(5)	C(27)-N(2)	1.288(6)
N(1)-C(14)	1.450(4)	N(2)-C(28)	1.447(5)
C(14)-C(15)	1.364(8)	C(28)-C(29)	1.347(6)
C(15)-C(16)	1.375(6)	C(29)-C(30)	1.405(7)
C(16)-C(17)	1.372(7)	C(30)-C(31)	1.349(10)
C(17)-C(18)	1.360(8)	C(31)-C(32)	1.331(8)
C(18)-C(19)	1.375(5)	C(32)-C(33)	1.401(8)
C(19)-C(14)	1.364(5)	C(33)-C(28)	1.358(9)
C(17)-C(20)	1.515(6)	C(31)-C(34)	1.521(8)
Nonbonded contacts			
Cu(1)-Cu(1)^{I}	3.1828(12)	O(5)-O(5)^{I}	2.9093(44)
Cu(2)-Cu(2)^{II}	3.2106(13)	O(6)-O(6)^{II}	3.1000(52)
Cu(1)-Cu(2)	3.1217(9)		

I) $-x, -y, -z$. II) $-x, -y, 1-z$.

TABLE 4. BOND ANGLES (φ/°) WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Copper coordination spheres			
O(1)-Cu(1)-O(3)	89.3(1)	O(2)-Cu(2)-O(4)	90.1(1)
O(1)-Cu(1)-O(5)	87.3(1)	O(2)-Cu(2)-O(6)	174.6(1)
O(1)-Cu(1)-N(1)	167.5(1)	O(2)-Cu(2)-N(2)	91.9(1)
O(3)-Cu(1)-O(5)	175.7(1)	O(4)-Cu(2)-O(6)	85.9(1)
O(3)-Cu(1)-N(1)	92.5(1)	O(4)-Cu(2)-N(2)	173.1(1)
O(5)-Cu(1)-N(1)	91.4(1)	O(6)-Cu(2)-N(2)	92.5(1)
O(1)-Cu(1)-O(5)$^{I)}$	89.7(1)	O(2)-Cu(2)-O(6)$^{II)}$	88.1(1)
O(3)-Cu(1)-O(5)$^{I)}$	92.6(1)	O(4)-Cu(2)-O(6)$^{II)}$	86.1(1)
O(5)-Cu(1)-O(5)$^{I)}$	84.7(1)	O(6)-Cu(2)-O(6)$^{II)}$	87.9(1)
N(1)-Cu(1)-O(5)$^{I)}$	102.5(1)	N(2)-Cu(2)-O(6)$^{II)}$	100.6(1)
Propionate groups			
Cu(1)-O(1)-C(1)	125.6(3)	Cu(2)-O(2)-C(1)	133.1(3)
Cu(1)-O(3)-C(4)	128.0(2)	Cu(2)-O(4)-C(4)	129.1(3)
O(1)-C(1)-O(2)	126.2(4)	O(3)-C(4)-O(4)	126.2(3)
O(1)-C(1)-C(2)	118.0(5)	O(3)-C(4)-C(5)	117.4(4)
O(2)-C(1)-C(2)	115.8(4)	O(4)-C(4)-C(5)	116.5(5)
C(1)-C(2)-C(3)	117.3(5)	C(4)-C(5)-C(6A)	111.6(9)
		C(4)-C(5)-C(6B)	123.0(7)
N-*p*-tolylsalicylideneamine moieties			
Cu(1)-O(5)-C(7)	125.4(3)	Cu(2)-O(6)-C(21)	127.1(3)
Cu(1)-O(5)-Cu(1)$^{I)}$	95.3(1)	Cu(2)-O(6)-Cu(2)$^{II)}$	92.1(1)
C(7)-O(5)-Cu(1)$^{I)}$	119.5(2)	C(21)-O(6)-Cu(2)$^{II)}$	113.7(3)
Cu(1)-N(1)-C(13)	122.6(2)	Cu(2)-N(2)-C(27)	123.6(3)
Cu(1)-N(1)-C(14)	120.7(2)	Cu(2)-N(2)-C(28)	121.5(3)
C(13)-N(1)-C(14)	116.5(3)	C(27)-N(2)-C(28)	114.9(3)
O(5)-C(7)-C(8)	119.0(4)	O(6)-C(21)-C(22)	119.5(4)
O(5)-C(7)-C(12)	123.0(3)	O(6)-C(21)-C(26)	123.2(4)
C(8)-C(7)-C(12)	118.0(4)	C(22)-C(21)-C(26)	117.3(4)
C(7)-C(8)-C(9)	120.8(5)	C(21)-C(22)-C(23)	121.6(4)
C(8)-C(9)-C(10)	121.3(4)	C(22)-C(23)-C(24)	120.9(6)
C(9)-C(10)-C(11)	119.1(5)	C(23)-C(24)-C(25)	119.5(6)
C(10)-C(11)-C(12)	121.8(5)	C(24)-C(25)-C(26)	121.5(4)
C(7)-C(12)-C(11)	118.9(3)	C(21)-C(26)-C(25)	119.1(4)
C(7)-C(12)-C(13)	122.9(4)	C(21)-C(26)-C(27)	123.2(4)
C(11)-C(12)-C(13)	118.0(4)	C(25)-C(26)-C(27)	117.6(4)
N(1)-C(13)-C(12)	126.7(4)	N(2)-C(27)-C(26)	126.7(3)
N(1)-C(14)-C(15)	121.1(3)	N(2)-C(28)-C(29)	119.2(5)
N(1)-C(14)-C(19)	119.0(4)	N(2)-C(28)-C(33)	121.2(4)
C(15)-C(14)-C(19)	119.9(3)	C(29)-C(28)-C(33)	119.7(4)
C(14)-C(15)-C(16)	119.8(4)	C(28)-C(29)-C(30)	119.3(6)
C(15)-C(16)-C(17)	121.3(6)	C(29)-C(30)-C(31)	121.9(5)
C(16)-C(17)-C(18)	117.5(4)	C(30)-C(31)-C(32)	117.5(5)
C(16)-C(17)-C(20)	120.8(6)	C(30)-C(31)-C(34)	121.1(5)
C(18)-C(17)-C(20)	121.6(4)	C(32)-C(31)-C(34)	121.4(7)
C(17)-C(18)-C(19)	122.2(4)	C(31)-C(32)-C(33)	122.6(7)
C(14)-C(19)-C(18)	119.2(5)	C(28)-C(33)-C(32)	119.0(5)

I) $-x, -y, -z$. II) $-x, -y, 1-z$.

cally independent copper(II) atoms, two *N*-*p*-tolylsalicylideneamine ligands, and two propionate groups. The structure essentially agrees with that proposed by Tokii *et al.* The copper atoms Cu(1) and Cu(2) are bridged by two propionate groups in a "*syn-syn*" configuration, and each copper atom is coordinated by the amino nitrogen and the phenolic oxygen atoms of *N*-*p*-tolylsalicylideneamine and by the two oxygen atoms of propionate groups with the distances of the normal Cu–O and Cu–N in-plane coordination. These four coordinating atoms slightly deviate from the least-squares plane (plane A and A′ in Table 5). Such a slight distortion from a plane toward the tetrahedron has been reported for a number of copper complexes. In addition to these coordinations, the phenolic oxygen atoms coordinate to neighbouring copper atoms from the apical direction with the bond distances of 2.371(3) and 2.519(3) Å, respectively.

Table 5. Deviations of the atoms from least-squares (l/Å) and dihedral angles between them (φ/°)

(A)	Plane through O(1), O(3), O(5), and N(1) (plane A)										
	O(1)	0.130	O(3)	−0.123	O(5)	−0.128	N(1)	0.120	Cu(1)	−0.087	
(A′)	Plane through O(2), O(4), O(6), and N(2) (plane A′)										
	O(2)	0.083	O(4)	−0.089	O(6)	0.087	N(2)	−0.082	Cu(2)	0.028	
(B)	Plane through C(7), C(8), C(9), C(10), C(11), and C(12) (plane B)										
	C(7)	0.007	C(8)	−0.011	C(9)	0.003	C(10)	0.010	C(11)	−0.013	C(12) 0.005
(B′)	Plane through C(21), C(22), C(23), C(24), C(25), and C(26) (plane B′)										
	C(21)	0.009	C(22)	0.002	C(23)	−0.010	C(24)	0.007	C(25)	0.005	C(26) −0.012
(C)	Plane through C(14), C(15), C(16), C(17), C(18), C(19), and C(20) (plane C)										
	C(14)	0.004	C(15)	0.009	C(16)	−0.013	C(17)	−0.010	C(18)	−0.005	
	C(19)	0.002	C(20)	0.013	N(1)	0.016					
(C′)	Plane through C(28), C(29), C(30), C(31), C(32), C(33), and C(34) (plane C′)										
	C(28)	0.010	C(29)	−0.009	C(30)	0.006	C(31)	−0.002	C(32)	0.005	
	C(33)	−0.009	C(34)	−0.001	N(2)	0.038					
(D)	Plane through O(5), N(1), C(7), C(8), C(9), C(10), C(11), C(12), and C(13) (plane D)										
	O(5)	0.012	N(1)	0.029	C(7)	0.002	C(8)	−0.025	C(9)	−0.005	
	C(10)	0.020	C(11)	0.007	C(12)	0.018	C(13)	−0.058	Cu(1)	0.584	
(D′)	Plane through O(6), N(2), C(21), C(22), C(23), C(24), C(25), C(26), and C(27) (plane D′)										
	O(6)	0.037	N(2)	−0.066	C(21)	0.015	C(22)	−0.017	C(23)	−0.036	
	C(24)	−0.000	C(25)	0.023	C(26)	0.014	C(27)	0.030	Cu(2)	−0.389	
(E)	Plane through O(5), N(1), C(7), C(12), and C(13) (plane E)										
	O(5)	−0.010	N(1)	0.027	C(7)	−0.002	C(12)	0.031	C(13)	−0.045	Cu(1) 0.557
	C(8)	−0.029	C(9)	0.010	C(10)	0.051	C(11)	0.037	C(14)	−0.178	
(E′)	Plane through O(6), N(2), C(21), C(26), and C(27) (plane E′)										
	O(6)	0.023	N(2)	−0.030	C(21)	−0.021	C(26)	−0.012	C(27)	0.039	Cu(2) −0.356
	C(22)	−0.088	C(23)	−0.130	C(24)	−0.084	C(25)	−0.028	C(28)	0.106	
(F)	Plane through O(1), O(2), C(1), and C(2) (plane F)										
	O(1)	0.003	O(2)	0.003	C(1)	−0.007	C(2)	0.002	Cu(1)	−0.318	
	Cu(2)	0.219	C(3)	−0.124							
(F′)	Plane through O(3), O(4), C(4), and C(5) (plane F′)										
	O(3)	0.002	O(4)	0.002	C(4)	−0.004	C(5)	0.001	Cu(1)	−0.109	
	Cu(2)	0.529	C(6A)	0.756	C(6B)	−0.362					
(G)	Plane through Cu(1), Cu(1)$^{I)}$, O(5), and O(5)$^{I)}$ (plane G)										
	Cu(1)	0.000	O(5)	0.000	Cu(1)$^{I)}$	0.000	O(5)$^{I)}$	0.000			
(G′)	Plane through Cu(2), Cu(2)$^{II)}$, O(6), and O(6)$^{II)}$ (plane G′)										
	Cu(2)	0.000	O(6)	0.000	Cu(2)$^{II)}$	0.000	O(6)$^{II)}$	0.000			

Dihedral angles between the planes

A and A′	35.9	A and D	28.2	A′ and D′	17.3	B and C	51.5
B and D	0.7	B and E	1.4	B′ and C′	66.3	B′ and D′	1.1
B′ and E′	2.5	C and D	51.9	D and D′	10.9	D and E	0.8
C′ and D′	66.4	D′ and E′	1.4	A and G	83.6	A′ and G′	82.6

Equations of planes[a)]

(A)	$-0.3587X+0.0881Y+0.9293Z=1.2826$	(E)	$-0.0903X-0.3031Y+0.9487Z=0.7441$
(A′)	$-0.1178X-0.4768Y+0.8711Z=4.2711$	(E′)	$-0.2168X-0.2209Y+0.9509Z=4.8016$
(B)	$-0.0657X-0.3095Y+0.9486Z=0.6983$	(F)	$0.2298X+0.8709Y+0.4345Z=-0.1688$
(B′)	$-0.2588X-0.2146Y+0.9418Z=4.9144$	(F′)	$0.8337X-0.3117Y+0.4559Z=0.0875$
(C)	$0.4717X-0.7646Y+0.4393Z=-0.9120$	(G)	$0.8260X-0.3126Y+0.4690Z=0.0000$
(C′)	$-0.2993X+0.7965Y+0.5254Z=3.0862$	(G′)	$0.2455X+0.7629Y+0.5981Z=0.8104$
(D)	$-0.0781X-0.3106Y+0.9473Z=0.7105$		
(D′)	$-0.2402X-0.2121Y+0.9473Z=4.8531$		

I) $-x$, $-y$, $-z$. II) $-x$, $-y$, $1-z$. a) Equations have the from $AX+BY+CZ=D$ where X, Y, and Z are Cartesian axes lying along a$\times c^*$, b, and c*, respectively.

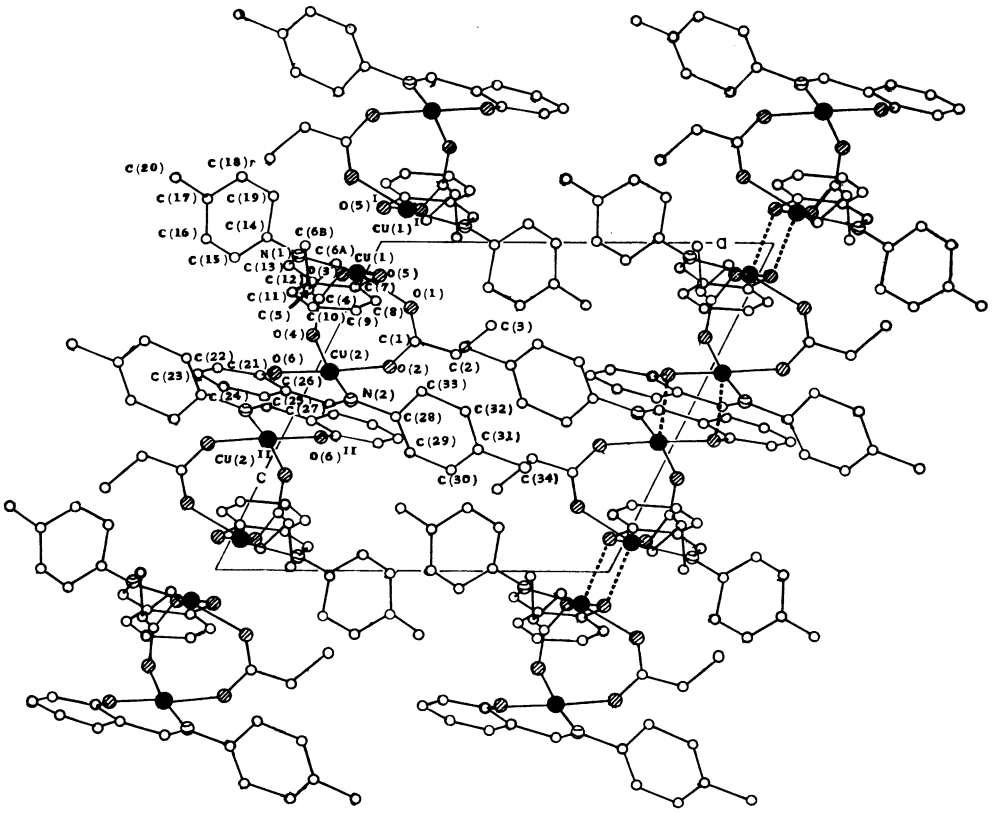

Fig. 2. A view of the packing along the b axis.

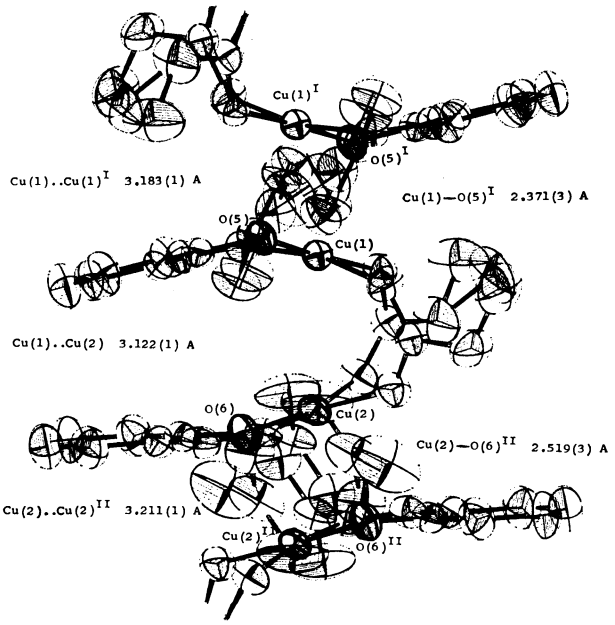

Fig. 3. A portion of the chain structure.

(A view of the packing along the b axis is shown in Fig. 2.) The apical O–Cu–basal atom angles for Cu(1) vary from 84.7(1) to 102.5(1)° and those for Cu(2) vary from 86.1(1) to 100.6(1)°, implying that the coordination sphere about each copper atom is a distorted square pyramid. The C–O distances O–C–O and O–C–C angles of the propionate groups are normal,[7–11] with average values of 1.246 Å, 126.2 and 116.9°, respectively. The $\begin{matrix}O\\O\end{matrix}\!\!>$C–C planes retain their planarity (Table 5). Such planarity was also observed for dimeric copper(II) carboxylates.[12–16] The Cu(1)–Cu(2) distance is 3.122(1) A, being longer than the Cu–Cu distances of dimeric copper(II) carboxylates (*ca.* 2.5—2.8 Å). When the number of bridging carboxylate groups is reduced from 4 to 2, the metal-metal distance becomes longer. Such a tendency was also found in the rhodium(II)[17] and molybdenum(II)[18] complexes with structures similar to the present one. The two basal planes of the distorted square pyramids around copper atoms incline toward each other making a dihedral angle of 35.9°, whereas those of copper(II) carboxylates are parallel. The Cu–O–C angles of the carboxylate groups have a mean value of 129.0°, larger than the angles observed in copper(II) acetate (a mean value of 123.1°). The above facts imply that a reduction of the number of bridging carboxylate groups weakens the binding force between the two copper atoms and opens the carboxylate group bridges.

The binuclear units are linked in a mode of out-of-plane coordination by the phenolic oxygens of upper and lower binuclear units, forming a one-dimensional polymeric chain along the c axis. The chains are separated from each other with the shortest interchain contact (excluding hydrogen atoms) of 3.594(19) Å. Consequently, any interchain magnetic interactions should be very small. There are two types of magnetic interaction between copper ions in the one-dimensional chain (Fig. 3). One is the magnetic interaction *via* two triatomic bridges of the propionate groups (Cu(1)–

Cu(2) 3.122(1) Å), and the other is the interaction *via* monatomic out-of-plane bridges of the phenolic oxygen atoms (Cu(1)–Cu(1)^{I} 3.183(1) Å, Cu(2)–Cu(2)^{II} 3.211(1) Å). Because the Cu–Cu separations of both types are longer than 3 Å, a direct interaction can not be maintained. Therefore, a "superexchange" mechanism should be operative in this system. Considered from the fact that the magnetic behavior of the present complex can be explained by a binuclear model, it is reasonable that the observed magnetic interactions are within each binuclear unit and inter-dimer interactions are negligible. It has been known that the out-of-plane interaction in copper(II) complexes is very weak compared to the interaction *via* triatomic carboxylate bridges.[19,20] Accordingly, it is natural that the antiferromagnetic behavior of the present complex can be explained mainly by a pairwise interaction between Cu(1) and Cu(2) *via* two triatomic carboxylate bridges. This view seems to be compatible with the fact that the $2J$ value of the present complex is about one third of that of copper(II) carboxylate (for example, $2J=-284$ cm^{-1} for copper(II) acetate monohydrate,[21] $2J=-300$ cm^{-1} for anhydrous copper(II) propionate[22]).

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