

## Structural Comparison between Dimeric Copper(II) Formate and Acetate in Pyridine and Urea Adducts

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**Abstract.** Tetrakis( $\mu$ -acetato- $O,O'$ )-bis(pyridine)dimeric copper,  $[\text{Cu}(\text{CH}_3\text{COO})_2\text{C}_5\text{H}_5\text{N}]_2$ ,  $M_r = 521.46$ ,  $\lambda(\text{Mo } K\alpha) = 0.71073 \text{ \AA}$ ,  $F(000) = 1064$ ,  $T = 299 \text{ (2) K}$ ; (I) orthorhombic,  $Pbca$ ,  $a = 13.079 \text{ (2)}$ ,  $b = 8.594 \text{ (1)}$ ,  $c = 19.572 \text{ (5) \AA}$ ,  $V = 2199.9 \text{ (7) \AA}^3$ ,  $Z = 4$ ,  $D_x = 1.57 \text{ Mg m}^{-3}$ ,  $\mu = 1.98 \text{ mm}^{-1}$ , final  $R = 0.034$  for 1607 observed unique reflections; (II) monoclinic,  $A2/a$ ,  $a = 12.520 \text{ (2)}$ ,  $b = 17.310 \text{ (4)}$ ,  $c = 9.930 \text{ (2) \AA}$ ,  $\beta = 96.73 \text{ (2)^\circ}$ ,  $V = 2137.2 \text{ (7) \AA}^3$ ,  $Z = 4$ ,  $D_x = 1.62 \text{ Mg m}^{-3}$ ,  $\mu = 2.04 \text{ mm}^{-1}$ , final  $R = 0.030$  for 1443 reflections. Tetrakis( $\mu$ -acetato- $O,O'$ )-bis(urea)dimeric copper dihydrate,  $[\text{Cu}(\text{CH}_3\text{COO})_2(\text{NH}_2)_2\text{CO}]_2 \cdot 2\text{H}_2\text{O}$ , (III),  $M_r = 519.43$ , monoclinic,  $P2_1/c$ ,  $a = 8.758 \text{ (1)}$ ,  $b = 14.152 \text{ (2)}$ ,  $c = 8.502 \text{ (1) \AA}$ ,  $\beta = 109.01 \text{ (1)^\circ}$ ,  $V = 996.3 \text{ (2) \AA}^3$ ,  $Z = 2$ ,  $D_x = 1.73 \text{ Mg m}^{-3}$ ,  $\mu = 2.20 \text{ mm}^{-1}$ ,  $F(000) = 492$ ,  $T = 300 \text{ (2) K}$ , final  $R = 0.022$  for 1941 reflections. Tetrakis( $\mu$ -formato- $O,O'$ )-bis(urea)dimeric copper,  $[\text{Cu}(\text{HCOO})_2(\text{NH}_2)_2\text{CO}]_2$ , (IV),  $M_r = 427.29$ , triclinic,  $P\bar{1}$ ,  $a = 6.797 \text{ (2)}$ ,  $b = 6.687 \text{ (1)}$ ,  $c = 9.088 \text{ (1) \AA}$ ,  $\alpha = 116.46 \text{ (1)}$ ,  $\beta = 76.64 \text{ (2)}$ ,  $\gamma = 113.01 \text{ (1)^\circ}$ ,  $V = 339.6 \text{ (1) \AA}^3$ ,  $Z = 1$ ,  $D_x = 2.09 \text{ Mg m}^{-3}$ ,  $\mu = 3.20 \text{ mm}^{-1}$ ,  $F(000) = 214$ ,  $T = 298 \text{ (2) K}$ , final  $R = 0.030$  for 1812 reflections. Structures of the copper acetates (I), (II) and (III), and formate (IV) have been redetermined accurately to confirm that there exist no structural correlations with the magnitudes of the spin superexchange interactions. In formates, the mean Cu–O distance in the  $\text{Cu}_2(\text{RCOO})_4$  cage is longer by 0.008 (3) and 0.007 (2)  $\text{\AA}$ , and the Cu–L length (L stands for the coordinating atom of an axial ligand) shorter by 0.032 (4) and 0.015 (2)  $\text{\AA}$  than those in acetates, for pyridine and urea adducts respectively. However, these small differences do not seem to affect the magnetic properties since there is the same order of variation between the orthorhombic (I) and monoclinic (II) structures of  $[\text{Cu}(\text{CH}_3\text{COO})_2\text{py}]_2$ , the difference in

Cu–O and Cu–N bond lengths being 0.002 (3) and 0.028 (4)  $\text{\AA}$ , respectively.

**Introduction.** The magnitude of the magnetic exchange interaction in dimers with  $S_1 = S_2 = \frac{1}{2}$  can be estimated by the singlet–triplet separation,  $-2J$ . The most attractive puzzle in magneto-structural correlations in dimeric copper(II) carboxylates is the question ‘Why do dimeric copper(II) formates, with stronger parent acid ( $\text{p}K_a = 3.75$ ), show much larger  $-2J$  values ( $\text{ca } 500 \text{ cm}^{-1}$ ) than the corresponding copper(II) acetate dimers with weaker parent acid ( $\text{p}K_a = 4.75$ ), whose  $-2J$  values are  $\text{ca } 300 \text{ cm}^{-1}$ ?’ (Hay, Thibault & Hoffmann, 1975). In order to compare the structures of copper formates and acetates precisely, the present study focused on the pyridine (py) and urea (ur) adducts and their crystal structures were redetermined except for  $[\text{Cu}(\text{HCOO})_2\text{py}]_2$  (Bernard, Borel, Busnot & Leclaire, 1979). The original papers reporting the structure determinations are: (I) Hanic, Štampelová & Hanicová (1964); (II) Barclay & Kennard (1961); (III) Ablov, Yablokov, Simonov, Landa, Malinovskii & Milkova (1971); and (IV) Yawney & Doedens (1970). The crystals of  $[\text{Cu}(\text{CH}_3\text{COO})_2\text{py}]_2$  exhibit polymorphism. Both orthorhombic (I) and monoclinic (II) modifications have been examined to see the variation of the molecular structure in the different packing modes.

**Experimental.** The complexes were prepared as described previously [(I) and (II) Kokot & Martin (1964); (III) and (IV) Kishita, Inoue & Kubo (1964)]. Crystals of (I) and (II) grow simultaneously from an acetonitrile solution. They can be easily distinguished by their crystal habit. Orthorhombic crystals are hexagonal plates surrounded with  $\{100\}$ ,  $\{110\}$  and  $\{001\}$  planes. Monoclinic ones are relatively small

needle-like crystals with forms {011}, {111} and  $\bar{1}11$ . (I): A green tabular crystal was ground into a sphere 0.45 (2) mm in diameter. Rigaku AFC-5 four-circle diffractometer, Mo K $\alpha$ , graphite monochromator. Cell parameters refined by least squares for 20  $2\theta$  values ( $20 < 2\theta < 30^\circ$ ), intensity measurement performed up to  $2\theta = 55^\circ$  ( $h: 0 \rightarrow 12, k: -8 \rightarrow 8, l: -18 \rightarrow 18$  for  $4 < 2\theta \leq 40^\circ$ ;  $h: 0 \rightarrow 16, k: 0 \rightarrow 11, l: 0 \rightarrow 25$  for  $40 < 2\theta \leq 55^\circ$ ). Variation of  $|F_o|$  of five standard reflections,  $0.983 \leq \sum(|F_o|/|F_o|_{\text{initial}})/5 \leq 1.009$ . 5329 reflections measured, 3920 reflections observed with  $|F_o| > 3\sigma(|F_o|)$ , 1607 unique ( $R_{\text{int}} = 0.011$ ). Correction for absorption ( $\mu r = 0.45, 0.521 \leq A \leq 0.527$ ). All H atoms found from difference synthesis, coordinates and anisotropic thermal parameters refined,  $\sum w|F_o| - |F_o|^2$  minimized,  $w^{-1} = \sigma^2(|F_o|) + (0.015|F_o|)^2$ , final  $R = 0.034, wR = 0.045, S = 2.2$  for 1607 unique reflections.\* Complex neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974). Reflection/parameter ratio 9.0,  $\Delta/\sigma < 0.21$ , heights in final difference synthesis  $-0.87 < \Delta\rho < 0.29 \text{ e } \text{\AA}^{-3}$ . UNICSIII program system (Sakurai & Kobayashi, 1979), FACOM M-380R computer of this university. Atomic coordinates are listed in Table 1 and bond lengths and bond angles in Table 2. (II): A green acicular crystal,  $0.2 \times 0.2 \times 0.3 \text{ mm}$ .  $2\theta_{\text{max}} = 55^\circ$  ( $h: 0 \rightarrow 9, k: -16 \rightarrow 16, l: -9 \rightarrow 9$  for  $4 < 2\theta \leq 40^\circ$ ;  $h: 0 \rightarrow 16, k: 0 \rightarrow 22, l: -12 \rightarrow 12$  for  $40 < 2\theta \leq 55^\circ$ ),  $0.985 \leq \sum(|F_o|/|F_o|_{\text{initial}})/5 \leq 1.001$ . 4162 reflections measured, 2536 reflections observed, 1443 unique ( $R_{\text{int}} = 0.016$ ),  $0.565 \leq A \leq 0.703$ . Final  $R = 0.030, wR = 0.033, S = 1.1$  for 1443 unique reflections. Reflection/parameter ratio 6.8,  $\Delta/\sigma < 0.26, -0.48 < \Delta\rho < 0.28 \text{ e } \text{\AA}^{-3}$ . (III): A dark-green tabular crystal was obtained from an ethanol solution and ground into a sphere 0.37 (2) mm in diameter. It was dehydrated although we intended to prepare the anhydrate (Ablov, Yablokov, Simonov, Landa, Malinovski & Milkova, 1971).  $2\theta_{\text{max}} = 55^\circ$  ( $h: -11 \rightarrow 11, k: -18 \rightarrow 0, l: -11 \rightarrow 11$ ),  $0.995 \leq \sum(|F_o|/|F_o|_{\text{initial}})/5 \leq 1.006$ . 4576 reflections measured, 3778 observed, 1941 unique ( $R_{\text{int}} = 0.011$ ),  $\mu r = 0.41, 0.861 \leq A \leq 0.864$ . Final  $R = 0.022, wR = 0.029, S = 1.4$  for 1941 unique reflections. Reflection/parameter ratio 11.1,  $\Delta/\sigma < 0.27, -0.30 < \Delta\rho < 0.26 \text{ e } \text{\AA}^{-3}$ . (IV): A green tabular crystal,  $0.5 \times 0.5 \times 0.3 \text{ mm}$ , obtained from methanol solution. The triclinic unit cell reported by Yawney & Doedens (1970) seems to be left-handed. Observed cell constants can be trans-

Table 1. *Positional parameters* ( $\times 10^4$ ; for Cu  $\times 10^5$ ) and *equivalent isotropic temperature factors* (Hamilton, 1959)

|       | x          | y         | z         | $B_{\text{eq}}(\text{\AA}^2) \times 10$ |
|-------|------------|-----------|-----------|---|
| (I)   |            |           |           |   |
| Cu    | 3304 (3)   | 7426 (4)  | 5477 (2)  | 21                                      |
| O(1)  | 1115 (2)   | -653 (3)  | -846 (1)  | 34                                      |
| O(2)  | 1668 (2)   | 569 (3)   | 87 (1)    | 34                                      |
| O(3)  | -550 (2)   | 1354 (2)  | -932 (1)  | 32                                      |
| O(4)  | 0 (2)      | 2581 (3)  | -2 (1)    | 34                                      |
| N     | 911 (2)    | 2022 (3)  | 1435 (1)  | 27                                      |
| C(1)  | 331 (3)    | 2311 (5)  | 1979 (2)  | 42                                      |
| C(2)  | 679 (4)    | 3133 (5)  | 2533 (2)  | 58                                      |
| C(3)  | 1655 (4)   | 3676 (5)  | 2535 (2)  | 60                                      |
| C(4)  | 2261 (3)   | 3415 (5)  | 1976 (2)  | 52                                      |
| C(5)  | 1858 (3)   | 2593 (4)  | 1436 (2)  | 35                                      |
| C(6)  | 1805 (2)   | -73 (4)   | -478 (2)  | 28                                      |
| C(7)  | 2886 (3)   | -187 (6)  | -731 (2)  | 45                                      |
| C(8)  | -358 (2)   | 2559 (4)  | -597 (2)  | 25                                      |
| C(9)  | -592 (3)   | 4085 (4)  | -930 (2)  | 39                                      |
| (II)  |            |           |           |   |
| Cu(1) | 25000      | 5295 (3)  | 0         | 25                                      |
| Cu(2) | 25000      | 20474 (3) | 0         | 25                                      |
| O(1)  | 3644 (2)   | 1915 (1)  | 1538 (2)  | 39                                      |
| O(2)  | 1419 (2)   | 1930 (1)  | 1288 (3)  | 41                                      |
| O(3)  | 1500 (2)   | 651 (1)   | 1370 (3)  | 39                                      |
| O(4)  | 3713 (2)   | 635 (1)   | 1445 (2)  | 36                                      |
| N(1)  | 2500       | -724 (2)  | 0         | 33                                      |
| N(2)  | 2500       | 3293 (2)  | 0         | 24                                      |
| C(1)  | 4016 (3)   | 1276 (2)  | 1945 (3)  | 29                                      |
| C(2)  | 1163 (3)   | 1290 (2)  | 1735 (3)  | 31                                      |
| C(3)  | 2236 (3)   | 3696 (2)  | 1056 (3)  | 31                                      |
| C(4)  | 2223 (3)   | 4485 (2)  | 1101 (4)  | 41                                      |
| C(5)  | 394 (3)    | 1284 (2)  | 2778 (4)  | 48                                      |
| C(6)  | 4872 (3)   | 1268 (2)  | 3121 (4)  | 48                                      |
| C(7)  | 3379 (3)   | -1122 (2) | -191 (4)  | 42                                      |
| C(8)  | 3411 (4)   | -1912 (2) | -201 (5)  | 60                                      |
| C(9)  | 2500       | -2311 (3) | 0         | 69                                      |
| C(10) | 2500       | 4883 (3)  | 0         | 46                                      |
| (III) |            |           |           |   |
| Cu    | 13322 (2)  | 2104 (2)  | 12060 (2) | 17                                      |
| O(1)  | 502 (2)    | 1512 (1)  | 626 (2)   | 31                                      |
| O(2)  | 2340 (2)   | 292 (1)   | -546 (2)  | 32                                      |
| O(3)  | -66 (2)    | 40 (1)    | 2570 (2)  | 30                                      |
| O(4)  | 1780 (2)   | -1158 (1) | 1368 (2)  | 32                                      |
| O(5)  | 3493 (1)   | 533 (1)   | 3191 (2)  | 25                                      |
| N(1)  | 3376 (3)   | 2122 (1)  | 3221 (3)  | 55                                      |
| N(2)  | 5315 (2)   | 1338 (1)  | 5237 (2)  | 31                                      |
| C(1)  | 1520 (2)   | 171 (1)   | -2061 (2) | 21                                      |
| C(2)  | 2374 (3)   | 297 (2)   | -3314 (3) | 33                                      |
| C(3)  | -784 (2)   | 1736 (1)  | -482 (2)  | 22                                      |
| C(4)  | -1151 (3)  | 2770 (2)  | -763 (3)  | 38                                      |
| C(5)  | 4031 (2)   | 1303 (1)  | 3851 (2)  | 23                                      |
| OW    | 5389 (2)   | 1415 (1)  | 308 (2)   | 47                                      |
| (IV)  |            |           |           |   |
| Cu    | -10009 (3) | -2416 (4) | 13803 (3) | 18                                      |
| O(1)  | 1109 (3)   | 2884 (3)  | 2572 (2)  | 31                                      |
| O(2)  | -2754 (2)  | 1387 (3)  | 1208 (2)  | 27                                      |
| O(3)  | -2730 (3)  | -3253 (3) | -230 (2)  | 29                                      |
| O(4)  | 1088 (2)   | -1782 (3) | 1116 (2)  | 27                                      |
| O(5)  | -2878 (2)  | -832 (3)  | 3454 (2)  | 27                                      |
| N(1)  | -1331 (4)  | -2884 (4) | 3967 (3)  | 32                                      |
| N(2)  | -4188 (4)  | -1881 (4) | 5604 (3)  | 36                                      |
| C(1)  | 2472 (4)   | 3943 (4)  | 1749 (3)  | 27                                      |
| C(2)  | -2460 (3)  | 2057 (4)  | 75 (3)    | 23                                      |
| C(3)  | -2783 (3)  | -1818 (4) | 4320 (2)  | 21                                      |

formed into the reported values if  $a$  and  $b$  and  $\alpha$  and  $\beta$  are exchanged. Possible enantiomorphism of this crystal was excluded by examination of five more crystals.  $2\theta_{\text{max}} = 60^\circ$  ( $h: -9 \rightarrow 9, k: -9 \rightarrow 9, l: 0 \rightarrow 12$ ),  $0.993 \leq \sum(|F_o|/|F_o|_{\text{initial}})/5 \leq 1.005$ . 2098 reflections measured, 1912 observed, 1812 unique ( $R_{\text{int}} = 0.006$ ),  $0.691 \leq A \leq 0.817$ . Final  $R = 0.030, wR = 0.041, S = 2.1$  for 1812 unique reflections. Reflection/parameter ratio 14.6,  $\Delta/\sigma < 0.14, -1.19 < \Delta\rho < 0.98 \text{ e } \text{\AA}^{-3}$ .

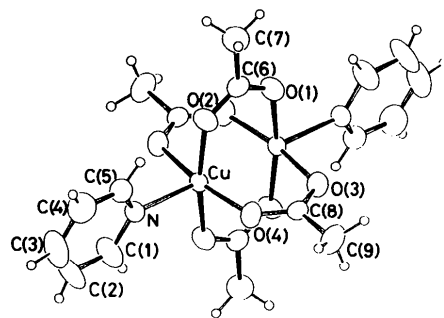
\* Lists of structure factors, anisotropic thermal parameters, atomic parameters for H atoms and bond lengths and bond angles involving H atoms, and those in the axial ligands, and a comparison of polymorphic crystal structures of [Cu(CH<sub>3</sub>COO)<sub>2</sub>py]<sub>2</sub> have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51466 (77 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

**Discussion.** The original large *R* values, (I) 0.098, (II) 0.13, (III) 0.167 and (IV) 0.089, are probably due to the limited precision of photographic data. The present

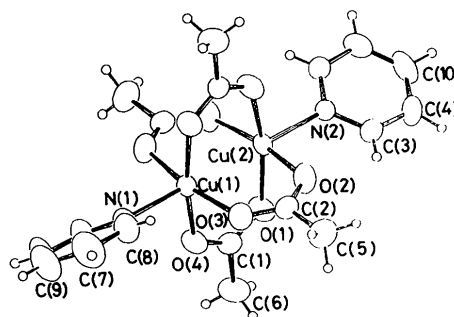
study achieved much lower *R* values, from 0.022 to 0.034, and reduced the e.s.d.'s in the atomic parameters to a quarter by collecting symmetry-related

Table 2. Bond lengths (Å) and bond angles (°)

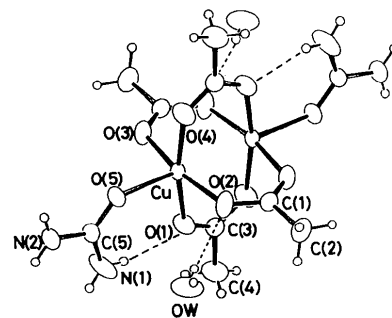
|                 |           |                    |           |
|-----------------|-----------|--------------------|-----------|
| (I)             |           |                    |           |
| Cu—O(2)         | 1.974 (3) | O(1)—C(6)          | 1.258 (4) |
| Cu—O(4)         | 1.960 (2) | O(2)—C(6)          | 1.248 (4) |
| Cu—N            | 2.191 (2) | O(3)—C(8)          | 1.251 (4) |
| Cu—O(1)'        | 1.980 (3) | O(4)—C(8)          | 1.255 (4) |
| Cu—O(3)'        | 1.974 (2) | C(6)—C(7)          | 1.501 (5) |
| Cu—Cu'          | 2.641 (1) | C(8)—C(9)          | 1.497 (5) |
| O(2)—Cu—O(4)    | 90.3 (1)  | O(3)—C(8)—C(9)     | 117.1 (3) |
| O(2)—Cu—N       | 95.3 (1)  | O(4)—C(8)—C(9)     | 117.9 (3) |
| O(4)—Cu—N       | 96.1 (1)  | O(3)'—Cu—N         | 96.1 (1)  |
| Cu—O(2)—C(6)    | 124.4 (2) | O(1)'—Cu—N         | 96.7 (1)  |
| Cu—O(4)—C(8)    | 125.4 (2) | O(4)—Cu—O(1)'      | 89.0 (1)  |
| Cu—N—C(1)       | 122.1 (2) | O(1)—Cu—O(3)'      | 89.5 (1)  |
| Cu—N—C(5)       | 120.5 (2) | O(3)'—Cu—O(2)      | 88.6 (1)  |
| O(1)—C(6)—O(2)  | 125.4 (3) | O(2)—Cu—O(1)'      | 168.0 (1) |
| O(1)—C(6)—C(7)  | 117.4 (3) | O(4)—Cu—O(3)'      | 167.8 (1) |
| O(2)—C(6)—C(7)  | 117.2 (3) | Cu—O(1)'—C(6)      | 122.1 (2) |
| O(3)—C(8)—O(4)  | 125.0 (3) | Cu—O(3)'—C(8)      | 121.8 (2) |
| (II)            |           |                    |           |
| Cu(1)—O(3)      | 1.965 (6) | O(1)—C(1)          | 1.249 (4) |
| Cu(1)—O(4)      | 1.972 (5) | O(2)—C(2)          | 1.249 (5) |
| Cu(1)—N(1)      | 2.170 (4) | O(3)—C(2)          | 1.252 (5) |
| Cu(2)—O(1)      | 1.981 (5) | O(4)—C(1)          | 1.256 (5) |
| Cu(2)—O(2)      | 1.979 (5) | C(1)—C(6)          | 1.490 (7) |
| Cu(2)—N(2)      | 2.156 (4) | C(2)—C(5)          | 1.494 (7) |
| Cu—Cu'          | 2.628 (1) |                    |           |
| O(3)—Cu(1)—O(4) | 89.2 (3)  | Cu(1)—N(1)—C(8)    | 121.2 (2) |
| O(3)—Cu(1)—N(1) | 96.1 (2)  | Cu(2)—N(2)—C(3)    | 121.6 (3) |
| O(4)—Cu(1)—N(1) | 95.3 (2)  | O(1)—C(1)—O(4)     | 124.8 (4) |
| O(1)—Cu(2)—O(2) | 88.7 (3)  | O(1)—C(1)—C(6)     | 117.9 (4) |
| O(1)—Cu(2)—N(2) | 96.6 (2)  | O(4)—C(1)—C(6)     | 117.3 (4) |
| O(2)—Cu(2)—N(2) | 95.9 (2)  | O(2)—C(2)—O(3)     | 124.8 (4) |
| Cu(2)—O(1)—C(1) | 124.1 (3) | O(2)—C(2)—C(5)     | 117.7 (4) |
| Cu(2)—O(2)—C(2) | 123.0 (3) | O(3)—C(2)—C(5)     | 117.4 (4) |
| Cu(1)—O(3)—C(2) | 123.9 (3) | O(3)—Cu(1)—O(4)'   | 89.7 (2)  |
| Cu(1)—O(4)—C(1) | 122.7 (3) | O(1)—Cu(2)—O(2)'   | 89.9 (2)  |
| (III)           |           |                    |           |
| Cu—O(1)         | 1.983 (1) | C(1)—C(2)          | 1.498 (4) |
| Cu—O(2)         | 1.967 (2) | C(3)—C(4)          | 1.501 (3) |
| Cu—O(3)         | 1.956 (2) | O(3)'—C(1)         | 1.241 (2) |
| Cu—O(4)         | 1.972 (1) | O(4)'—C(3)         | 1.253 (2) |
| Cu—O(5)         | 2.135 (1) | Cu—Cu'             | 2.624 (1) |
| O(1)—C(3)       | 1.251 (2) | N(1)···O(1)        | 2.886 (3) |
| O(2)—C(1)       | 1.266 (2) | OW···O(2)          | 2.987 (1) |
| O(1)—Cu—O(2)    | 88.6 (1)  | Cu—O(5)—C(5)       | 130.6 (1) |
| O(1)—Cu—O(3)    | 90.7 (1)  | O(2)—C(1)—C(2)     | 117.3 (2) |
| O(1)—Cu—O(4)    | 168.0 (1) | O(1)—C(3)—C(4)     | 117.4 (2) |
| O(1)—Cu—O(5)    | 99.0 (1)  | O(1)—C(3)—O(4)'    | 124.5 (1) |
| O(2)—Cu—O(3)    | 168.0 (1) | O(2)—C(1)—O(3)'    | 124.4 (2) |
| O(2)—Cu—O(4)    | 89.0 (1)  | Cu—O(3)'—C(1)      | 126.3 (1) |
| O(2)—Cu—O(5)    | 94.9 (1)  | Cu—O(4)'—C(3)      | 121.0 (1) |
| O(3)—Cu—O(4)    | 89.2 (1)  | O(3)'—C(1)—C(2)    | 118.3 (2) |
| O(3)—Cu—O(5)    | 97.0 (1)  | O(4)'—C(3)—C(4)    | 118.0 (2) |
| O(4)—Cu—O(5)    | 92.9 (1)  | N(1)—H(N1)2···O(1) | 157 (2)   |
| Cu—O(1)—C(3)    | 126.2 (1) | OW—H(OW)1···O(2)   | 176 (3)   |
| Cu—O(2)—C(1)    | 121.1 (1) |                    |           |
| (IV)            |           |                    |           |
| Cu—O(1)         | 1.989 (1) | O(1)—C(1)          | 1.248 (2) |
| Cu—O(2)         | 1.971 (2) | O(2)—C(2)          | 1.244 (3) |
| Cu—O(3)         | 1.974 (1) | O(3)'—C(1)         | 1.238 (1) |
| Cu—O(4)         | 1.975 (2) | O(4)'—C(2)         | 1.251 (2) |
| Cu—O(5)         | 2.120 (1) | N(1)···O(4)        | 2.957 (1) |
| Cu—Cu'          | 2.655 (1) |                    |           |
| O(1)—Cu—O(2)    | 89.5 (1)  | O(4)—Cu—O(5)       | 98.8 (1)  |
| O(1)—Cu—O(3)    | 167.6 (1) | Cu—O(1)—C(1)       | 118.5 (1) |
| O(1)—Cu—O(4)    | 89.5 (1)  | Cu—O(2)—C(2)       | 123.2 (1) |
| O(1)—Cu—O(5)    | 98.3 (0)  | Cu—O(5)—C(3)       | 133.4 (1) |
| O(2)—Cu—O(3)    | 89.8 (1)  | O(1)—C(1)—O(3)'    | 127.6 (2) |
| O(2)—Cu—O(4)    | 167.6 (1) | O(2)—C(2)—O(4)'    | 126.7 (2) |
| O(2)—Cu—O(5)    | 93.6 (1)  | Cu—O(3)'—C(1)      | 126.3 (1) |
| O(3)—Cu—O(4)    | 88.5 (1)  | Cu—O(4)'—C(2)      | 122.5 (1) |
| O(3)—Cu—O(5)    | 94.1 (0)  | N(1)—H(N1)2···O(4) | 155 (2)   |



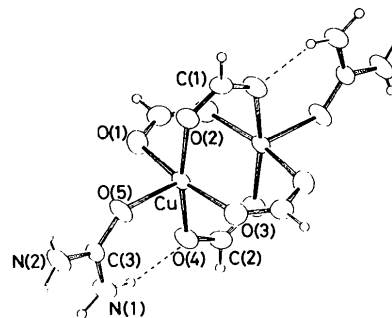
(I)



(II)



(III)



(IV)

Fig. 1. ORTEP drawings (Johnson, 1965) of the molecules with thermal ellipsoids scaled at the 50% probability level. H atoms are represented by circles of radius 0.08 Å.

reflections and preparing spherical specimens where possible. The molecular structures (I)–(IV) are shown in Fig. 1. The structures of (I) and (II) differ from each other with respect to the orientation of the py rings. (I) has a center of symmetry at the center of the molecule and (II) has a twofold axis passing through the Cu(1)···Cu(2) bond axis. The dihedral angles between the two py rings are 0 and 56.9 (3)° for (I) and (II), respectively. In the urea adducts, there are intramolecular hydrogen bonds. There is also an intermolecular hydrogen bond in (III) between water of crystallization and a bridging acetate. Hydrogen-bond distances and angles are given in Table 2. The Cu–O(1) bond distance in (III), 1.983 (1) Å, is longer than the other Cu–O distances, 1.956 (2), 1.967 (2) and 1.972 (1) Å. This may be due to the N(1)–H(N1)2···O(1) intramolecular hydrogen bond. The elongation of the Cu–O distance by the hydrogen bond is also observed in [Cu(CH<sub>3</sub>COO)<sub>2</sub>H<sub>2</sub>O]<sub>2</sub> (Brown & Chidambaram, 1973). On the other hand, this trend is not observed in (IV). The Cu–O(4) distance related to the intramolecular hydrogen bond, 1.975 (2) Å, is not longer than the others, 1.971 (2), 1.974 (2) and 1.989 (2) Å. The average dimensions of the Cu<sub>2</sub>–(RCO<sub>2</sub>)<sub>4</sub> cage are compared in Table 3. Those of [Cu(HCOO)<sub>2</sub>py]<sub>2</sub> were taken from Bernard, Borel, Busnot & Leclaire (1979). The Cu–O bond length of the copper formate is longer by 0.007 (2) ~ 0.008 (3) Å than the acetate having the same axial ligand *L*, and the Cu–*L* bond length is shorter by 0.015 (2) ~ 0.032 (4) Å.

However, these small differences may not be related to the difference in the magnetic properties since the Cu–O and Cu–N bond lengths of [Cu(CH<sub>3</sub>COO)<sub>2</sub>py]<sub>2</sub> alter by 0.002 (3) and 0.028 (4) Å in different packing modes. Hay, Thibeault & Hoffmann (1975) tentatively attributed the greater  $-2J$  value of copper formate to its Cu–O bond length which is shorter than that of the acetate, based on the structural data of [Me<sub>4</sub>N]<sub>2</sub>[Cu(RCOO)<sub>2</sub>(NCS)]<sub>2</sub> (*R* = H and Me; Goodgame, Hill, Marsham, Skapski, Smart & Troughton, 1969). However, the structure analysis of the acetate was incomplete (*R* = 0.10) owing to the disorder of the acetate groups.

The present study shows that the formates have longer Cu–O bond lengths than the acetates and that there is little magneto-structural correlation in these dimeric copper carboxylates. The formates have shorter C–O bond lengths and larger O–C–O bond angles than the acetates. This trend is also observed in the simple salts of LiHCOO.H<sub>2</sub>O (Thomas, Tellgren & Almlöf, 1975) and LiCH<sub>3</sub>COO.2H<sub>2</sub>O (Yamanaka *et al.*, 1989), the mean C–O and O–C–O values being 1.245 (2) Å and 125.5 (1)° for HCOO<sup>-</sup>, and 1.260 (1) Å and 124.3 (1)° for CH<sub>3</sub>COO<sup>-</sup>. Further investigations are needed to solve the puzzle stated in the Introduction.

Table 3. *A comparison of the average dimensions of the Cu(RCO<sub>2</sub>)<sub>4</sub> cage in [Cu(RCOO)<sub>2</sub>L]<sub>2</sub>*

|  | <i>R</i> = CH <sub>3</sub> , <i>L</i> = py |                 | <i>R</i> = CH <sub>3</sub> , <i>R</i> = H, |               |               |
|--|--|-----------------|--|---------------|---------------|
|  | (I) orthorhombic                           | (II) monoclinic | <i>L</i> = py <sup>(a)</sup>               | <i>L</i> = ur | <i>L</i> = ur |
| Cu···Cu (Å)                              | 2.641 (1)                                  | 2.628 (1)       | 2.641 (1)                                  | 2.624 (1)     | 2.655 (1)     |
| Cu– <i>L</i>                             | 2.191 (2)                                  | 2.163 (4)       | 2.145 (2)                                  | 2.135 (1)     | 2.120 (2)     |
| Cu–O                                     | 1.972 (3)                                  | 1.974 (3)       | 1.981 (2)                                  | 1.970 (2)     | 1.977 (2)     |
| C–O                                      | 1.253 (4)                                  | 1.252 (4)       | 1.245 (3)                                  | 1.253 (2)     | 1.245 (3)     |
| Shift of Cu <sup>(b)</sup>               | 0.208 (1)                                  | 0.207 (3)       | 0.207 (1)                                  | 0.200 (1)     | 0.213 (1)     |
| Cu–O–C(°)                                | 123.4 (2)                                  | 123.4 (3)       | 122.5 (2)                                  | 123.7 (1)     | 122.6 (2)     |
| O–C–O                                    | 125.2 (3)                                  | 124.8 (4)       | 127.0 (3)                                  | 124.5 (2)     | 127.2 (2)     |
| $-2J$ (cm <sup>-1</sup> ) <sup>(c)</sup> | 333  |                 | 501  | 323           | 506           |

(a) Bernard, Borel, Busnot & Leclaire (1979). (b) The deviations of the Cu atoms from the O<sub>4</sub> plane. (c) These values were determined by one of the authors (MK) by the Faraday method in the temperature range 80–300 K. The cryomagnetic data fittings to Bleaney–Bowers equation were made with SALS program using a fixed value of 60 × 10<sup>-6</sup> e.m.u. for temperature independent paramagnetism, *N*<sub>0</sub>. As a convenient statistical indicator of the quality of the least-squares fits, the discrepancy index,  $\sigma_{\text{dis}} = \{ \sum (X_{\text{obsd}} - X_{\text{calcd}})^2 / \sum X_{\text{obsd}}^2 \}^{1/2}$ , was employed. The value of  $\sigma_{\text{dis}}$  ranged from 2 × 10<sup>-3</sup> to 4 × 10<sup>-3</sup>, showing the high quality of the fits. The  $-2J$  value for (III) was obtained for the anhydrous form. The values of  $-2J$  for copper(II) acetate–pyridine were determined on a mixture of (I) and (II). However the discrepancy index, 2.2 × 10<sup>-3</sup>, indicates that the  $-2J$  values of these two forms are almost identical.

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