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Correlation of Electron Density and Spin-Exchange Interaction in Dimeric Copper(II) Formates, Acetates and Silanecarboxylates

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Abstract

The structures of six dimeric copper(II) formates and acetates with picoline as an axial ligand, (I)–(VI), have been determined at room temperature and electron density distributions in lithium acetate dihydrate, (VII), and copper(II) formate diurea dihydrate, (VIII), have been studied at 120 K. Mo $K\alpha$ radiation was used throughout (λ = 0·71073 Å): tetrakis(μ-formato-*O*,*O*′)-bis(α-picoline)dicopper(II), $[Cu(HCOO)_2\alpha\text{-pic}]_2$, (I), M_r = 493·42, triclinic, $P\bar{1}$, a = 7·310 (1), b = 10·493 (2), c = 7·291 (1) Å, α = 91·35 (2), β = 113·93 (1), γ = 109·24 (2)°, V = 474·5 (1) Å^3, Z = 1, D_x = 1·73 Mg m^{-3}, μ = 2·29 mm^{-1}, $F(000)$ = 250, R = 0·029 for 1675 reflections; $[Cu(HCOO)_2\beta\text{-pic}]_2$, (II), triclinic, $P\bar{1}$, a = 10·922 (3), b = 13·123 (2), c = 7·208 (2) Å, α = 98·64 (2), β = 109·11 (2), γ = 83·39 (2)°, V = 962·6 (3) Å^3, Z = 2, D_x = 1·70 Mg m^{-3}, μ = 2·26 mm^{-1}, $F(000)$ = 500, R = 0·032 for 2629 reflections; $[Cu(HCOO)_2\gamma\text{-pic}]_2$, (III), monoclinic, $P2_1/c$, a = 10·695 (2), b = 11·373 (2), c = 7·755 (1) Å, β = 90·13 (2)°, V = 942·7 (3) Å^3, Z = 2, D_x = 1·74 Mg m^{-3}, μ = 2·31 mm^{-1}, $F(000)$ = 500, R = 0·027 for 1474 reflections; tetrakis(μ-acetato-*O*,*O*′)-bis(α-picoline)dicopper(II), $[Cu(CH_3COO)_2\alpha\text{-pic}]_2$, (IV), M_r = 549·53, monoclinic, $P2_1/c$, a = 7·697 (1), b = 20·021 (3), c = 8·226 (1) Å, β = 116·0 (1)°, V = 1139·4 (3) Å^3, Z = 2, D_x = 1·60 Mg m^{-3}, μ = 1·92 mm^{-1}, $F(000)$ = 564, R = 0·051 for 1691 reflections; $[Cu(CH_3COO)_2\beta\text{-pic}]_2$, (V), triclinic, $P\bar{1}$, a = 8·315 (1), b = 20·242 (2), c = 7·789 (1) Å, α = 93·21 (1), β = 117·36 (1), γ = 92·74 (1)°, V = 1158·5 (2) Å^3, Z = 2, D_x = 1·58 Mg m^{-3}, μ = 1·89 mm^{-1}, $F(000)$ = 564, R = 0·063 for 3041 reflections; $[Cu(CH_3COO)_2\gamma\text{-pic}]_2$, (VI), monoclinic, $P2_1/c$, a = 10·499 (1), b = 13·031 (2), c = 8·880 (1) Å, β = 102·16 (1)°, V = 1187·6 (2) Å^3, Z = 2, D_x = 1·55 Mg m^{-3}, μ =

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1·84 mm^{-1}, $F(000) = 564$, $R = 0{\cdot}034$ for 1832 reflections; lithium acetate dihydrate, $LiCH_3COO.2H_2O$, (VII), $M_r = 102{\cdot}01$, orthorhombic, *Cmmm*, $a = 6{\cdot}7291$ (7), $b = 10{\cdot}8764$ (7), $c = 6{\cdot}5734$ (5) Å, $V = 481{\cdot}09$ (7) Å^3, $Z = 4$, $D_x = 1{\cdot}41$ Mg m^{-3}, $\mu = 0{\cdot}125$ mm^{-1}, $F(000) = 216$, $R = 0{\cdot}035$ for 1357 reflections; copper(II) formate diurea dihydrate, $Cu(HCOO)_2.2CO(NH_2)_2.2H_2O$, (VIII), $M_r = 309{\cdot}71$, monoclinic, $P2_1/c$, $a = 8{\cdot}1584$ (9), $b = 8{\cdot}3683$ (4), $c = 8{\cdot}0088$ (5) Å, $\beta = 95{\cdot}813$ (7)°, $V = 543{\cdot}96$ (7) Å^3, $Z = 2$, $D_x = 1{\cdot}89$ Mg m^{-3}, $\mu = 2{\cdot}05$ mm^{-1}, $F(000) = 318$, $R = 0{\cdot}024$ for 5427 reflections. The structures of the picoline adducts (I)–(VI) show no important geometrical differences in the $Cu_2(COO)_4$ cage between the copper acetates and formates. The observed deformation-density distributions in the CH_3COO^- (VII) and $HCOO^-$ (VIII) ions are in accord with theoretical expectations. Mulliken population analysis of eight carboxylate ions using STO-6G basis sets indicates that the electron population of the carboxylate group of the bridging ligand correlates with the $-2J$ values of the binuclear copper(II) carboxylates. The key point that determines the strength of the spin-exchange interaction is the $2p_x$ orbital population of the carboxylate C atom (x is parallel to the C—R bond axis in the RCOO$^-$ ion). The electron population on a carboxylate O atom is shown to exhibit a roughly linear correlation with the pK_a value of the parent carboxylic acid. The conundrum of why formate and fluoroacetate are exceptions to the correlation of $-2J$ with pK_a value has been solved in this paper.

Introduction

Dimeric copper(II) carboxylates which contain four bridging carboxylato ligands have antiferromagnetic properties with a singlet ground state. The spin superexchange pathway is expected to predominate, *i.e.*, their magnetic properties result from the coupling of the unpaired electrons in the $d_{x^2-y^2}$ orbitals of Cu^{2+} ions through the bridging ligands (Goodgame, Hill, Marshall, Skapski, Smart & Troughton, 1969; Hay, Thibeault & Hoffmann, 1975). The spin-exchange interaction, as measured by $-2J$, is much larger in binuclear copper(II) formates than in the corresponding acetates. For example, the $-2J$ values are 501 cm^{-1} for $[Cu(HCOO)_2py]_2$ and 333 cm^{-1} for $[Cu(CH_3COO)_2py]_2$ (py = pyridine), although their molecular dimensions are similar (Uekusa, Ohba, Saito, Kato, Tokii & Muto, 1989). In the present study, the structures and magnetic properties of the picoline adducts of copper(II) formate and acetate have been determined in order to confirm that no magneto-structural correlation exists for the dimeric copper(II) complexes having square-pyramidal coordination around each Cu atom. The charge distribution in the bridging ligands, $HCOO^-$ and CH_3COO^- ions, has also been investigated both experimentally and theoretically in order to obtain data which may lead to a solution of the spin-exchange conundrum.

The structures of (IV), (VII) and (VIII) have been redetermined in the present study. The original papers reporting the crystal structures are: (IV) Pavelcik & Hanic (1978); (VII) Galigne, Mouvet & Falgueiretters (1970); and (VIII) Kiriyama & Kitahara (1976).

Experimental

Intensities were measured on a Rigaku AFC-5 four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. Cell parameters were refined by least-squares fit of 20–50 2θ values ($20 < 2\theta < 30°$). Five standard reflections showed no significant variation except for (IV). The structures were solved by the Patterson–Fourier method. The coordinates and anisotropic thermal parameters of the non-H atoms were refined by block-diagonal least squares so as to minimize the function $\sum w(|F_o| - |F_c|)^2$ with $w^{-1} = \sigma^2(|F_o|) + (0{\cdot}015|F_o|)^2$. H atoms were either located in a difference synthesis map or calculated theoretically and included in the refinement. The complex neutral-atom scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The calculations were carried out using the *UNICS*III computation program system (Sakurai & Kobayashi, 1979) on a FACOM M-380R computer at Keio University. Atomic coordinates are listed in Table 1, with bond lengths and bond angles given in Table 2.* Experimental details are given below. (I): Green plate-like crystal, 0·25 × 0·20 × 0·10 mm, 2299 reflections measured ($2\theta \leq 55°$, h 0→9, k − 13→12, l − 9→8), 1775 observed with $|F_o| > 3\sigma(|F_o|)$, 1675 unique [$R_{\rm int}(F) = 0{\cdot}009$] after absorption correction ($0{\cdot}79 < A < 0{\cdot}89$). Six of the nine H atoms were found from a difference synthesis and the others calculated, final $R(F) = 0{\cdot}029$, $wR = 0{\cdot}036$, $S = 1{\cdot}56$ for 1675 unique reflections. Reflection/parameter (r/p) ratio 10·2, $\Delta/\sigma < 0{\cdot}13$, $-0{\cdot}34 < \Delta\rho < 0{\cdot}65$ e Å^{-3}. (II): Green plate-like crystal, 0·55 × 0·40 × 0·20 mm, 4660 reflections measured ($2\theta \leq 55°$, h 0→14, k − 16→17, l − 9→8), 2778 observed, 2629 unique ($R_{\rm int} = 0{\cdot}011$, $0{\cdot}44 < A < 0{\cdot}66$). Twelve of the 18 H atoms were found, $R = 0{\cdot}032$, $wR = 0{\cdot}035$, $S = 1{\cdot}42$ for 2629 unique reflections. $r/p = 8{\cdot}1$, $\Delta/\sigma <$

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* Lists of structure factors, anisotropic thermal parameters, and atomic parameters for H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53649 (176 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters* [× 10^4; × 10^5 *for* Cu *and compounds* (VII) *and* (VIII)] *and equivalent isotropic temperature factors* (*Hamilton*, 1959)

$$B_{\rm eq} = (4/3)\textstyle\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$ (Å^2 × 10)
Compound (I)				
Cu	14769 (5)	13142 (3)	7521 (5)	31
O(1)	−840 (3)	1719 (2)	−1459 (3)	48
O(2)	3232 (3)	429 (2)	2709 (3)	46
O(3)	2416 (4)	828 (2)	−1263 (3)	48
O(4)	−10 (4)	1312 (2)	2501 (3)	49
N	3531 (4)	3484 (2)	1821 (3)	38
C(1)	−2596 (5)	825 (3)	−2657 (5)	43
C(2)	1544 (5)	−305 (3)	−2394 (5)	46
C(3)	5623 (5)	4093 (4)	2395 (4)	48
C(4)	6616 (6)	5542 (4)	2942 (5)	61
C(5)	5479 (7)	6299 (4)	2926 (6)	64
C(6)	3284 (7)	5687 (4)	2335 (5)	59
C(7)	2368 (6)	4303 (3)	1793 (5)	48
C(8)	6807 (6)	3209 (4)	2463 (6)	60
Compound (II)				
Cu(1)	25698 (4)	23969 (3)	26433 (6)	33
Cu(2)	51871 (4)	22604 (3)	39142 (6)	34
O(1)	2817 (2)	1009 (2)	1223 (4)	48
O(2)	2770 (2)	3761 (2)	4259 (4)	51
O(3)	2797 (2)	1722 (2)	5017 (4)	47
O(4)	2795 (2)	3032 (2)	486 (4)	52
O(5)	4982 (2)	911 (2)	2241 (4)	48
O(6)	4966 (3)	2952 (2)	1561 (4)	58
O(7)	4962 (2)	1609 (2)	6077 (4)	47
O(8)	4941 (2)	3636 (2)	5337 (4)	52
N(1)	490 (2)	2376 (2)	1617 (4)	33
N(2)	7266 (2)	2106 (2)	4970 (4)	36
C(1)	3899 (3)	576 (3)	1321 (5)	43
C(2)	3877 (4)	1482 (3)	6176 (5)	43
C(3)	3873 (4)	3171 (3)	398 (5)	53
C(4)	3860 (4)	4076 (3)	5206 (6)	47
C(5)	−22 (3)	1479 (3)	1414 (6)	43
C(6)	−1331 (4)	1383 (3)	769 (6)	48
C(7)	−2157 (3)	2234 (3)	288 (5)	47
C(8)	−1666 (3)	3186 (3)	490 (5)	39
C(9)	−322 (3)	3213 (3)	1173 (5)	36
C(10)	−2529 (4)	4150 (3)	11 (7)	64
C(11)	7974 (3)	2919 (3)	5283 (5)	35
C(12)	9305 (3)	2881 (3)	6041 (5)	37
C(13)	9936 (3)	1937 (3)	6480 (5)	44
C(14)	9234 (4)	1098 (3)	6168 (6)	51
C(15)	7911 (3)	1203 (3)	5419 (6)	43
C(16)	10029 (4)	3836 (3)	6382 (6)	58
Compound (III)				
Cu	10913 (3)	2683 (3)	7323 (4)	25
O(1)	1675 (2)	520 (2)	−1655 (2)	39
O(2)	423 (2)	1886 (2)	745 (3)	39
O(3)	165 (2)	−72 (2)	2872 (2)	39
O(4)	1421 (2)	−1427 (2)	462 (3)	40
N	2831 (2)	720 (2)	2006 (3)	28
C(1)	949 (3)	387 (3)	−2908 (4)	37
C(2)	−638 (3)	2120 (3)	181 (4)	39
C(3)	3864 (3)	87 (3)	1748 (4)	32
C(4)	5003 (3)	357 (3)	2484 (4)	34
C(5)	5104 (3)	1307 (3)	3561 (3)	31
C(6)	4039 (3)	1953 (3)	3840 (3)	36
C(7)	2933 (3)	1641 (3)	3064 (3)	33
C(8)	6345 (3)	1638 (3)	4362 (4)	48
Compound (IV)				
Cu	8785 (7)	5636 (3)	49001 (7)	24
O(1)	3234 (4)	144 (2)	6774 (4)	34
O(2)	−1742 (4)	789 (1)	3061 (4)	36
O(3)	191 (4)	893 (2)	6811 (4)	36
O(4)	1311 (4)	47 (1)	3059 (4)	33
N	2489 (4)	1464 (2)	4658 (4)	26
C(1)	3204 (6)	−431 (2)	7371 (5)	28
C(2)	5102 (6)	−711 (2)	8755 (6)	41
C(3)	−711 (6)	536 (2)	7436 (5)	27
C(4)	−1095 (7)	829 (2)	8941 (6)	42
C(5)	4330 (6)	1339 (2)	5003 (7)	34
C(6)	5543 (6)	1800 (2)	4821 (7)	40
C(7)	4871 (7)	2434 (3)	4285 (7)	42
C(8)	3015 (7)	2570 (2)	3934 (7)	40
C(9)	1845 (6)	2085 (2)	4149 (6)	33
C(10)	−191 (7)	2245 (3)	3833 (9)	62
Compound (V)				
Cu(1)	3284 (12)	5160 (5)	−7689 (13)	25
Cu(2)	6025 (12)	55565 (5)	46114 (13)	25
O(1)	2096 (7)	−53 (3)	−1037 (8)	37
O(2)	−1536 (8)	930 (3)	−246 (8)	35
O(3)	2159 (8)	823 (3)	1869 (8)	41
O(4)	−1666 (7)	53 (3)	−3204 (7)	38
O(5)	−1283 (8)	5970 (3)	5080 (8)	37
O(6)	2273 (7)	4974 (3)	4263 (8)	35
O(7)	2251 (8)	5672 (3)	7456 (8)	41
O(8)	−1242 (8)	5271 (3)	1943 (7)	43
N(1)	888 (9)	1316 (3)	−2220 (10)	35
N(2)	1621 (8)	6454 (3)	3886 (9)	29
C(1)	2352 (10)	−621 (4)	−499 (10)	28
C(2)	3781 (12)	−964 (5)	−783 (14)	41
C(3)	2483 (10)	500 (4)	3244 (11)	31
C(4)	3973 (12)	760 (5)	5229 (14)	52
C(5)	1883 (11)	1869 (4)	−1169 (13)	37
C(6)	2246 (11)	2416 (5)	−2093 (13)	39
C(7)	1543 (13)	2323 (5)	−4075 (15)	53
C(8)	528 (15)	1762 (5)	−5176 (14)	50
C(9)	241 (14)	1256 (5)	−4149 (12)	44
C(10)	3398 (13)	3004 (5)	−893 (17)	55
C(11)	−2320 (10)	5643 (4)	5536 (11)	27
C(12)	−3687 (12)	5998 (5)	5907 (13)	41
C(13)	2202 (10)	5249 (4)	8559 (10)	30
C(14)	3490 (13)	5416 (5)	10703 (12)	47
C(15)	1135 (11)	6572 (4)	2099 (12)	32
C(16)	1629 (11)	7156 (4)	1483 (12)	35
C(17)	2781 (12)	7607 (5)	2951 (13)	40
C(18)	3312 (14)	7520 (5)	4837 (14)	52
C(19)	2747 (13)	6939 (4)	5296 (13)	44
C(20)	975 (15)	7244 (5)	−532 (15)	53
Compound (VI)				
Cu	−10419 (4)	2785 (3)	5109 (4)	27
O(1)	−1863 (2)	475 (2)	−1685 (2)	43
O(2)	91 (2)	−27 (2)	2524 (2)	40
O(3)	−235 (2)	1646 (2)	523 (3)	40
O(4)	−1539 (2)	−1184 (2)	300 (3)	39
N	−2660 (2)	845 (2)	1473 (3)	31
C(1)	−1236 (3)	330 (2)	−2722 (3)	34
C(2)	816 (3)	1833 (2)	146 (4)	33
C(3)	−1930 (4)	556 (3)	−4362 (4)	51
C(4)	1249 (4)	2933 (3)	225 (5)	51
C(5)	−2643 (3)	1792 (2)	2050 (4)	36
C(6)	−3636 (3)	2175 (3)	2674 (4)	41
C(7)	−4695 (3)	1584 (3)	2741 (4)	43
C(8)	−4706 (3)	607 (3)	2153 (4)	50
C(9)	−3686 (3)	269 (3)	1555 (4)	42
C(10)	−5791 (4)	1965 (5)	3464 (6)	81
Compound (VII)				
Li	0	50000	28428 (13)	10 (1)
C(1)	0	28657 (3)	0	7 (1)
C(2)	0	14756 (3)	0	11 (1)
O(1)	21691 (5)	50000	50000	9 (1)
O(2)	0	18589 (3)	50000	10 (1)
O(3)	0	34065 (2)	16947 (3)	11 (1)
Compound (VIII)				
Cu	0	0	0	5 (1)
C(*F*)	−1551 (6)	26880 (5)	23341 (5)	8 (1)
C(*U*)	62949 (6)	4464 (5)	36179 (6)	7 (1)
O(1*F*)	−6715 (5)	20506 (4)	9654 (4)	8 (1)
O(2*F*)	−5588 (5)	40702 (4)	27502 (4)	7 (1)
O(*U*)	53979 (6)	−1973 (5)	24261 (5)	10 (1)
O(*W*)	27973 (5)	9575 (5)	2338 (6)	9 (1)
N(1)	62868 (7)	20287 (5)	38729 (7)	11 (1)
N(2)	73149 (7)	−4398 (6)	46703 (7)	11 (1)

0·19, $-0{\cdot}43 < \Delta\rho < 0{\cdot}33$ e Å^{-3}. (III): Green plate-like crystal, 0·40 × 0·38 × 0·15 mm, 2265 reflections measured ($2\theta \leq 55°$, h − 13→13, k 0→14, l 0→9), 1551 observed, 1474 unique ($R_{\rm int} = 0{\cdot}012$, $0{\cdot}52 < A <$ 0·71). All nine H atoms found, $R = 0{\cdot}027$, $wR =$ 0·029, $S = 1{\cdot}15$ for 1474 unique reflections. $r/p = 9{\cdot}0$, $\Delta/\sigma < 0{\cdot}20$, $-0{\cdot}31 < \Delta\rho < 0{\cdot}27$ e Å^{-3}. (IV): A green prismatic crystal was ground into a sphere of

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

Compound (I)

Cu···Cu'	2·736 (1)	N—C(7)	1·389 (5)
Cu—O(1)	1·985 (2)	C(3)—C(4)	1·417 (5)
Cu—O(2)	1·977 (2)	C(3)—C(8)	1·452 (7)
Cu—O(3)	1·976 (3)	C(4)—C(5)	1·323 (7)
Cu—O(4)	1·982 (3)	C(5)—C(6)	1·386 (6)
Cu—N	2·182 (2)	C(6)—C(7)	1·353 (5)
O(1)—C(1)	1·245 (3)	C(1)—O(2')	1·237 (4)
O(3)—C(2)	1·236 (4)	C(2)—O(4')	1·235 (4)
N—C(3)	1·321 (4)		

O(1)—Cu—O(2)	165·4 (1)	Cu—N—C(7)	112·2 (2)
O(1)—Cu—O(3)	89·4 (1)	C(3)—N—C(7)	118·1 (3)
O(1)—Cu—O(4)	88·7 (1)	N—C(3)—C(4)	120·1 (4)
O(1)—Cu—N	92·3 (1)	N—C(3)—C(8)	116·9 (4)
O(2)—Cu—O(3)	89·5 (1)	C(4)—C(3)—C(8)	123·0 (3)
O(2)—Cu—O(4)	88·7 (1)	C(3)—C(4)—C(5)	120·7 (4)
O(2)—Cu—N	102·2 (1)	C(4)—C(5)—C(6)	120·4 (4)
O(3)—Cu—O(4)	165·3 (1)	C(5)—C(6)—C(7)	117·7 (5)
O(3)—Cu—N	100·3 (1)	N—C7)—C(6)	122·9 (4)
O(4)—Cu—N	94·4 (1)	O(1)—C(1)—O(2')	128·2 (3)
Cu—O(1)—C(1)	123·8 (2)	O(3)—C(2)—O(4')	128·8 (4)
Cu—O(3)—C(2)	123·3 (2)	Cu—O(2)—C(1')	122·6 (2)
Cu—N—C(3)	129·7 (2)	Cu—O(4)—C(2')	122·6 (2)

Compound (II)

Cu(1)···Cu(2)	2·694 (1)	O(7)—C(2)	1·242 (5)
Cu(1)—O(1)	1·986 (3)	O(8)—C(4)	1·234 (5)
Cu(1)—O(2)	1·976 (3)	N(1)—C(5)	1·329 (5)
Cu(1)—O(3)	1·975 (3)	N(1)—C(9)	1·338 (4)
Cu(1)—O(4)	1·965 (3)	N(2)—C(11)	1·338 (5)
Cu(1)—N(1)	2·148 (2)	N(2)—C(15)	1·334 (4)
Cu(2)—O(5)	1·978 (3)	C(5)—C(6)	1·366 (5)
Cu(2)—O(6)	1·976 (3)	C(6)—C(7)	1·364 (5)
Cu(2)—O(7)	1·980 (3)	C(7)—C(8)	1·385 (6)
Cu(2)—O(8)	1·974 (3)	C(8)—C(9)	1·390 (4)
Cu(2)—N(2)	2·141 (2)	C(8)—C(10)	1·501 (5)
O(1)—C(1)	1·236 (4)	C(11)—C(12)	1·373 (4)
O(2)—C(4)	1·245 (4)	C(12)—C(13)	1·374 (5)
O(3)—C(2)	1·240 (4)	C(12)—C(16)	1·505 (6)
O(4)—C(3)	1·235 (5)	C(13)—C(14)	1·363 (6)
O(5)—C(1)	1·245 (4)	C(14)—C(15)	1·365 (5)
O(6)—C(3)	1·244 (4)		

O(1)—Cu(1)—O(2)	166·6 (1)	Cu(2)—O(7)—C(2)	122·6 (3)
O(1)—Cu(1)—O(3)	88·4 (1)	Cu(2)—O(8)—C(4)	122·9 (2)
O(1)—Cu(1)—O(4)	89·5 (1)	Cu(1)—N(1)—C(5)	118·1 (2)
O(1)—Cu(1)—N(1)	93·1 (1)	Cu(1)—N(1)—C(9)	123·9 (2)
O(2)—Cu(1)—O(3)	90·5 (1)	C(5)—N(1)—C(9)	118·0 (3)
O(2)—Cu(1)—O(4)	88·6 (1)	Cu(2)—N(2)—C(11)	121·5 (2)
O(2)—Cu(1)—N(1)	100·2 (1)	Cu(2)—N(2)—C(15)	121·4 (2)
O(3)—Cu(1)—O(4)	166·4 (1)	C(11)—N(2)— C(15)	117·0 (3)
O(3)—Cu(1)—N(1)	94·5 (1)	O(1)—C(1)—O(5)	127·9 (3)
O(4)—Cu(1)—N(1)	99·0 (1)	O(3)—C(2)—O(7)	127·9 (4)
O(5)—Cu(2)—O(6)	89·8 (1)	O(4)—C(3)—O(6)	128·8 (4)
O(5)—Cu(2)—O(7)	89·4 (1)	O(2)—C(4)—O(8)	128·7 (3)
O(5)—Cu(2)—O(8)	166·5 (1)	N(1)—C(5)—C(6)	122·7 (3)
O(5)—Cu(2)—N(2)	95·5 (1)	C(5)—C(6)—C(7)	119·3 (4)
O(6)—Cu(2)—O(7)	166·6 (1)	C(6)—C(7)—C(8)	120·0 (3)
O(6)—Cu(2)—O(8)	88·0 (1)	C(7)—C(8)—C(9)	116·8 (3)
O(6)—Cu(2)—N(2)	98·4 (1)	C(7)—C(8)—C(10)	122·3 (3)
O(7)—Cu(2)—O(8)	89·6 (1)	C(9)—C(8)—C(10)	121·0 (3)
O(7)—Cu(2)—N(2)	95·0 (1)	N(1)—C(9)—C(8)	123·3 (3)
O(8)—Cu(2)—N(2)	98·0 (1)	N(2)—C(11)—C(12)	124·3 (3)
Cu(1)—O(1)—C(1)	123·0 (2)	C(11)—C(12)—C(13)	117·0 (3)
Cu(1)—O(2)—C(4)	121·7 (2)	C(11)—C(12)—C(16)	121·1 (3)
Cu(1)—O(3)—C(2)	123·1 (3)	C(13)—C(12)—C(16)	122·0 (3)
Cu(1)—O(4)—C(3)	122·8 (3)	C(12)—C(13)—C(14)	119·7 (3)
Cu(2)—O(5)—C(1)	122·5 (2)	C(13)—C(14)—C(15)	119·7 (3)
Cu(2)—O(6)—C(3)	121·8 (3)	N(2)—C(15)—C(14)	122·3 (4)

Compound (III)

Cu···Cu'	2·665 (1)	N—C(7)	1·335 (4)
Cu—O(1)	1·976 (2)	C(3)—C(4)	1·379 (5)
Cu—O(2)	1·974 (2)	C(4)—C(5)	1·370 (5)
Cu—O(3)	1·973 (2)	C(5)—C(6)	1·373 (5)
Cu—O(4)	1·971 (2)	C(5)—C(8)	1·512 (4)
Cu—N	2·166 (2)	C(6)—C(7)	1·373 (4)
O(1)—C(1)	1·252 (4)	C(1)—O(3')	1·245 (4)
O(2)—C(2)	1·244 (4)	C(2)—O(4')	1·253 (4)
N—C(3)	1·334 (4)		

O(1)—Cu—O(2)	89·1 (1)	Cu—N—C(7)	122·4 (2)
O(1)—Cu—O(3)	167·6 (1)	C(3)—N—C(7)	116·7 (2)
O(1)—Cu—O(4)	89·1 (1)	N—C(3)—C(4)	123·3 (3)
O(1)—Cu—N	96·9 (1)	C(3)—C(4)—C(5)	119·8 (3)
O(2)—Cu—O(3)	89·8 (1)	C(4)—C(5)—C(6)	117·0 (3)
O(2)—Cu—O(4)	167·7 (1)	C(4)—C(5)—C(8)	121·0 (3)
O(2)—Cu—N	95·0 (1)	C(6)—C(5)—C(8)	122·0 (3)
O(3)—Cu—O(4)	89·3 (1)	C(5)—C(6)—C(7)	120·5 (3)
O(3)—Cu—N	95·5 (1)	N—C(7)—C(6)	122·8 (3)
O(4)—Cu—N	97·3 (1)	O(1)—C(1)—O(3')	127·6 (3)
Cu—O(1)—C(1)	120·9 (2)	O(2)—C(2)—O(4')	127·9 (3)
Cu—O(2)—C(2)	121·8 (2)	Cu—O(3)—C(1')	123·9 (2)
Cu—N—C(3)	121·0 (2)	Cu—O(4)—C(2')	122·6 (2)

Compound (IV)

Cu—Cu'	2·673 (1)	C(1)—C(2)	1·512 (5)
Cu—O(1)	1·980 (3)	C(3)—C(4)	1·512 (7)
Cu—O(2)	1·971 (2)	C(5)—C(6)	1·367 (7)
Cu—O(3)	1·979 (4)	C(6)—C(7)	1·369 (7)
Cu—O(4)	1·979 (3)	C(7)—C(8)	1·355 (8)
Cu—N	2·246 (4)	C(8)—C(9)	1·387 (7)
O(1)—C(1)	1·256 (6)	C(9)—C(10)	1·506 (7)
O(3)—C(34)	1·253 (6)	C(1)—O(2")	1·242 (4)
N—C(5)	1·341 (6)	C(3)—O(4")	1·255 (4)
N—C(9)	1·336 (6)		

O(1)—Cu—O(2)	167·0 (1)	O(1)—C(1)—C(2)	117·2 (4)
O(1)—Cu—O(3)	89·7 (1)	O(3)—C(3)—C(4)	117·2 (4)
O(1)—Cu—O(4)	88·3 (1)	N—C(5)—C(6)	124·0 (4)
O(1)—Cu—N	93·3 (1)	C(5)—C(6)—C(7)	118·8 (5)
O(2)—Cu—O(3)	89·6 (1)	C(6)—C(7)—C(8)	118·0 (5)
O(2)—Cu—C(4)	89·5 (1)	C(7)—C(8)—C(9)	121·0 (4)
O(2)—Cu—N	99·6 (1)	N—C(9)—C(8)	121·3 (4)
O(3)—Cu—O(4)	167·3 (2)	N—C(9)—C(10)	117·8 (4)
O(3)—Cu—N	98·8 (1)	C(8)—C(9)—C(10)	120·9 (4)
O(4)—Cu—N	93·8 (1)	O(1)—C(1)—O(2")	125·9 (2)
Cu—O(1)—C(1)	121·7 (3)	O(3)—C(2)—O(4")	125·7 (3)
Cu—O(3)—C(3)	121·7 (3)	O(2")—C(1)—C(3)	117·0 (3)
Cu—N—C(5)	113·9 (3)	O(4")—C(2)—C(4)	117·4 (3)
Cu—N—C(9)	129·2 (3)	Cu—O(2)—C(1")	125·1 (2)
C(5)—N—C(9)	116·9 (4)	Cu—O(4)—C(2")	121·0 (2)

Compound (V)

Cu(1)···Cu(1')	2·621 (2)	Cu(2)···Cu(2")	2·635 (2)
Cu(1)—O(1)	1·987 (7)	Cu(2)—O(5)	1·977 (7)
Cu(1)—O(2)	1·984 (7)	Cu(2)—O(6)	1·965 (7)
Cu(1)—O(3)	1·954 (5)	Cu(2)—O(7)	1·991 (5)
Cu(1)—O(4)	1·997 (4)	Cu(2)—O(8)	1·964 (4)
Cu(1)—N(1)	2·175 (8)	Cu(2)—N(2)	2·178 (7)
O(1)—C(1)	1·240 (10)	O(5)—C(11)	1·249 (12)
O(3)—C(3)	1·215 (11)	O(7)—C(13)	1·259 (11)
O(2')—C(1)	1·245 (12)	O(6''')—C(11)	1·268 (10)
O(4')—C(3)	1·273 (10)	O8''')—C(13)	1·219 (10)
N(1)—C(5)	1·339 (9)	N(2)—C(15)	1·299 (11)
N(1)—C(9)	1·339 (11)	N(2)—C(19)	1·376 (9)
C(1)—C(2)	1·499 (15)	C(11)—C(12)	1·500 (15)
C(3)—C(4)	1·513 (10)	C(13)—C(14)	1·519 (10)
C(5)—C(6)	1·446 (15)	C(15)—C(16)	1·412 (13)
C(6)—C(7)	1·374 (14)	C(16)—C(17)	1·361 (11)
C(6)—C(10)	1·467 (13)	C(16)—C(20)	1·431 (14)
C(7)—C(8)	1·368 (13)	C(17)—C(18)	1·351 (15)
C(8)—C(9)	1·411 (16)	C(18)—C(19)	1·371 (15)

O(1)—Cu(1)—O(2)	168·3 (3)	O(5)—Cu(2)—O(6)	168·0 (3)
O(1)—Cu(1)—O(3)	89·5 (2)	O(5)—Cu(2)—O(7)	88·9 (3)
O(1)—Cu(1)—O(4)	90·0 (2)	O(5)—Cu(2)—O(8)	89·3 (3)
O(1)—Cu(1)—N(1)	93·7 (3)	O(5)—Cu(2)—N(2)	96·3 (3)
O(2)—Cu(1)—O(3)	89·2 (3)	O(6)—Cu(2)—O(7)	90·1 (2)
O(2)—Cu(1)—O(4)	88·9 (2)	O(6)—Cu(2)—O(8)	89·2 (2)
O(2)—Cu(1)—N(1)	98·0 (3)	O(6)—Cu(2)—N(2)	95·7 (3)
O(3)—Cu(1)—O(4)	168·3 (2)	O(7)—Cu(2)—O(8)	167·6 (2)
O(3)—Cu(1)—N(1)	97·2 (2)	O(7)—Cu(2)—N(2)	96·9 (2)
O(4)—Cu(1)—N(1)	94·5 (2)	O(8)—Cu(2)—N(2)	95·6 (2)
Cu(1)—O(1)—C(1)	124·4 (6)	Cu(2)—O(5)—C(11)	122·0 (6)
Cu(1)—O(3)—C(3)	122·6 (5)	Cu(2)—O(7)—C(13)	121·2 (5)
Cu(1)—N(1)—C(5)	119·5 (6)	Cu(2)—N(2)—C(15)	121·8 (5)
Cu(1)—N(1)—C(9)	120·2 (5)	Cu(2)—N(2)—C(19)	121·6 (5)
C(5)—N(1)—C(9)	120·3 (7)	C(15)—N(2)—C(19)	116·6 (7)
O(1)—C(1)—C(2)	116·4 (9)	O(5)—C(11)—C(12)	118·6 (8)
O(3)—C(3)—C(4)	119·4 (7)	O(7)—C(13)—C(14)	115·3 (7)
N(1)—C(5)—C(6)	120·9 (8)	N(2)—C(15)—C(16)	125·9 (7)
C(5)—C(6)—C(7)	115·9 (9)	C(15)—C(16)—C(17)	114·5 (8)
C(5)—C(6)—C(10)	119·5 (8)	C(15)—C(16)—C(20)	121·4 (8)
C(7)—C(6)—C(10)	124·5 (10)	C(17)—C(16)—C(20)	124·1 (9)
C(6)—C(7)—C(8)	124·2 (10)	C(16)—C(17)—C(18)	122·5 (10)
C(7)—C(8)—C(9)	115·9 (9)	C(17)—C(18)—C(19)	118·7 (9)
N(1)—C(9)—C(8)	122·9 (9)	N(2)—C(19)—C(18)	121·7 (9)
O(1)—C(1)—C(2')	126·2 (9)	O(5)—C(11)—O(6''')	124·0 (9)
O(3)—C(3)—O(4')	126·2 (7)	O(7)—C(13)—O(8''')	126·1 (7)
O(2')—C(1)—C(2)	117·4 (8)	O(6''')—C(11)—C(12)	117·4 (9)

Table 2 (*cont.*)

O(4^{i})—C(3)—C(4)	114·5 (7)	O(8^{iii})—C(13)—C(14)	118·6 (7)
Cu(1)—O(2)—C(1^{i})	121·0 (6)	Cu(2)—O(6)—C(11^{iii})	126·1 (6)
Cu(1)—O(4)—C(3^{i})	122·9 (5)	Cu(2)—O(8)—C(13^{iii})	125·0 (5)

Compound (VI)

Cu···Cu^{i}	2·641 (1)	C(1)—C(3)	1·514 (4)
Cu—O(1)	1·976 (2)	C(2)—C(4)	1·501 (5)
Cu—O(2)	1·968 (2)	C(5)—C(6)	1·373 (5)
Cu—O(3)	1·972 (3)	C(6)—C(7)	1·364 (5)
Cu—O(4)	1·974 (3)	C(7)—C(8)	1·375 (5)
Cu—N	2·185 (3)	C(7)—C(10)	1·515 (6)
O(1)—C(1)	1·254 (4)	C(8)—C(9)	1·365 (5)
O(3)—C(2)	1·243 (4)	C(1)—O(2^{i})	1·247 (5)
N—C(5)	1·335 (4)	C(2)—O(4^{i})	1·256 (4)
N—C(9)	1·327 (4)		

O(1)—Cu—O(2)	167·8 (1)	O(1)—C(1)—C(3)	117·2 (3)
O(1)—Cu—O(3)	89·2 (1)	O(3)—C(2)—C(4)	116·9 (3)
O(1)—Cu—O(4)	88·8 (1)	N—C(5)—C(6)	122·7 (3)
O(1)—Cu—N	97·4 (1)	C(5)—C(6)—C(7)	120·5 (3)
O(2)—Cu—O(3)	90·1 (1)	C(6)—C(7)—C(8)	116·6 (3)
O(2)—Cu—O(4)	89·3 (1)	C(6)—C(7)—C(10)	122·2 (4)
O(2)—Cu—N	94·8 (1)	C(8)—C(7)—C(10)	121·2 (4)
O(3)—Cu—O(4)	167·8 (1)	C(7)—C(8)—C(9)	120·1 (3)
O(3)—Cu—N	93·5 (1)	N—C(9)—C(8)	123·5 (3)
O(4)—Cu—N	98·7 (1)	O(1)—C(1)—O(2^{i})	125·8 (4)
Cu—O(1)—C(1)	121·2 (2)	O(3)—C(3)—O(4^{i})	126·0 (4)
Cu—O(3)—C(2)	125·5 (2)	Cu—O(2)—C(1^{i})	125·4 (2)
Cu—N—C(5)	120·9 (2)	Cu—O(4)—C(3^{i})	124·9 (3)
Cu—N—C(9)	122·5 (2)	O(2^{i})—C(1)—C(2)	117·0 (3)
C(5)—N—C(9)	116·6 (3)	O(4^{i})—C(3)—C(4)	116·8 (3)

Compound (VII)

C(1)—C(2)	1·5119 (5)	Li—O(1)	2·0350 (7) (2 ×)
C(1)—O(3)	1·2597 (3)	Li—O(3)	1·8903 (4) (2 ×)

C(2)—C(1)—O(3)	117·83 (2)	O(1)—Li—O(1^{v})	91·66 (4)
O(3)—C(1)—O(3^{iv})	124·33 (3)	O(3)—Li—O(3^{vi})	132·94 (5)
O(1)—Li—O(3)	106·15 (2) (4 ×)		

Compound (VIII)

Cu—O(1*F*)	1·9820 (4) (2 ×)	C(*U*)—N(1)	1·3399 (6)
C(*F*)—O(1*F*)	1·2530 (5)	C(*U*)—N(2)	1·3456 (7)
C(*F*)—O(2*F*)	1·2568 (6)	Cu—O(2*F*^{vii})	1·9732 (3) (2 ×)
C(*U*)—O(*U*)	1·2630 (6)	Cu—O(*W*)	2·4081 (5) (2 ×)

O(1*F*)—C(*F*)—O(2*F*)	123·35 (4)	Cu—O(1*F*)—C(*F*)	128·91 (3)
O(*U*)—C(*U*)—N(1)	121·68 (4)	O(1*F*)—Cu—O(2*F*^{vii})	91·87 (1) (2 ×)
O(*U*)—C(*U*)—N(2)	120·83 (4)	O(1*F*)—Cu—O(*W*)	88·79 (1) (2 ×)
N(1)—C(*U*)—N(2)	117·48 (4)	O(*W*)—Cu—O(2*F*^{vii})	86·03 (1) (2 ×)

Symmetry codes: (i) $-x, -y, -z$; (ii) $-x, -y, 1-z$; (iii) $-x, 1-y, 1-z$; (iv) $x, y, -z$; (v) $-x, y, z$; (vi) $x, 1-y, z$; (vii) $-x, -\frac{1}{2}+y, \frac{1}{2}-z$.

0·35 mm diameter. Intensity of standard reflections continuously decreased by 17% in $|F_o|$ suggesting radiation damage. Intensities were corrected based on the standard reflections. 2782 reflections measured ($2\theta \le 55°$, h − 9→8, k 0→26, l 0→10), 1808 observed, 1691 unique ($R_{\rm int} = 0·019$, $0·610 < A < 0·614$). Four of the 13 H atoms were found, $R = 0·051$, $wR = 0·040$, $S = 1·99$ for 1691 unique reflections. $r/p = 8·5$, $\Delta/\sigma < 0·98$, $-0·52 < \Delta\rho < 0·59$ e Å^{-3}. (V): Crystal 0·35 × 0·20 × 0·20 mm, 5451 reflections measured ($2\theta \le 55°$, h 0→10, k − 26→26, l − 10→8), 3131 observed, 3041 unqiue ($R_{\rm int} = 0·015$, $0·61 < A < 0·73$). The structure determination was not straightforward (because of the pseudo-A-centered symmetry except for the picoline methyl groups) [see Fig. 1(V*c*)]. Positions of all H atoms were calculated, $R = 0·063$, $wR = 0·077$, $S = 2·66$ for 3041 unique reflections. $r/p = 7·7$, $\Delta/\sigma < 0·14$, $-0·84 < \Delta\rho < 1·04$ e Å^{-3}. (VI): Green tabular crystal, 0·35 × 0·30 × 0·20 mm, 2870 reflections measured ($2\theta \le 55°$, h − 13→13, k 0→16, l 0→11), 1928 observed, 1832 unique ($R_{\rm int} = 0·014$, $0·61 < A < 0·73$). Eight of the 13 H atoms were found, $R = 0·034$, $wR = 0·035$, $S = 1·32$ for 1832 unique reflections. $r/p = 9·3$, $\Delta/\sigma < 0·12$, $-0·32 < \Delta\rho < 0·31$ e Å^{-3}.

Intensity measurements of (VII) and (VIII) were performed at 120 K using cold N_2 gas to reduce thermal smearing of the electron density distribution. (VII): Colorless prismatic crystal, 0·40 × 0·45 × 0·45 mm, coated with an adhesive to protect against deliquescence, 7663 reflections measured ($2\theta \le 120°$, h 0→16, k − 26→26, l − 16→16), 4585 observed reflections. After absorption correction ($0·93 < A < 0·97$), conventionally refined by the program *RADIEL* (Coppens, Guru Row, Leung, Stevens, Becker & Yang, 1979). Positional and thermal parameters of non-H atoms were refined based on high-order reflections with $\sin\theta/\lambda \ge 0·6$ Å^{-1} in order to avoid bias from the aspherical distribution of the valence electrons. An isotropic secondary-extinction correction parameter did not reduce R significantly. The acetate ion lies in a special position with site symmetry *mm*2. Therefore, the methyl H atoms are disordered: a torus-shaped electron density around the extension of the C—C bond axis which lies on a twofold axis suggested random azimuthal orientation of the methyl group. The methyl H atoms were tentatively located in fourfold equivalent positions with an occupation factor of $\frac{3}{4}$. After averaging equivalent reflections ($R_{\rm int} = 0·023$), $R = 0·035$, $wR = 0·040$, $S = 1·56$ for 1357 unique reflections. $r/p = 39·9$, $\Delta/\sigma < 0·03$. (VIII): A blue plate-like crystal was ground into a sphere 0·45 mm in diameter, 12 005 reflections measured ($2\theta \le 60°$, h − 11→11, k − 11→11, l 0→11; $60 < 2\theta \le 120°$, h − 19→19, k 0→20, l 0→19), 8300 observed, 5427 unique ($R_{\rm int} = 0·010$, $0·51 < A < 0·54$). High-order refinement was based on the reflections with $\sin\theta/\lambda \ge 0·6$ Å^{-1}. An isotropic secondary-extinction correction, $g = 0·32\,(2) \times 10^{-4}$, reduced R from 0·026 to 0·024. Final $R = 0·024$, $wR = 0·031$, $S = 1·26$ for 5427 unique reflections. $r/p = 49·0$, $\Delta/\sigma < 0·15$.

Theoretical calculations

A theoretical deformation density for the formate ion has been described previously (Kikkawa, Ohba, Saito, Kamata & Iwata, 1987). For the acetate ion, a similar calculation was carried out by an *ab initio* SCF method, using a MIDI4* basis set with the

Table 3. *Comparison of the average dimensions in* $[Cu(RCOO)_2pic]_2$ *and their* $-2J$ *values for compounds* (I)–(VI)

	(I)	(II)	(III)	(IV)	(V)	(VI)
Cu···Cu (Å)	2·736 (1)	2·694 (1)	2·665 (1)	2·673 (1)	2·628 (2)	2·641 (1)
Cu—N (Å)	2·182 (2)	2·145 (2)	2·166 (2)	2·246 (4)	2·177 (8)	2·185 (3)
Cu—O (Å)	1·980 (3)	1·976 (3)	1·974 (2)	1·977 (7)	1·977 (7)	1·973 (3)
C—O (Å)	1·238 (4)	1·240 (5)	1·249 (4)	1·253 (6)	1·246 (12)	1·249 (4)
Shift of Cu (Å)[a]	0·253 (1)	0·231 (2)	0·226 (1)	0·221 (2)	0·207 (3)	0·210 (1)
O—C—O (°)	128·5 (4)	128·3 (4)	127·8 (3)	125·9 (4)	125·6 (9)	125·8 (3)
Δ(Cu—N—C) (°)[b]	17·5 (2)	3·1 (2)	1·4 (2)	15·3 (3)	0·5 (5)	1·6 (2)
O—Cu—N—C (°)[c]	44·5 (3)	35·3 (3)	27·1 (2)	28·3 (4)	15·1 (7), 9·8 (7)	11·2 (2)
$-2J$ (cm^{-1})[d]	482	489	507	332	326	333

Notes: (*a*) The deviations of the Cu atoms from the O_4 plane. (*b*) The difference between the two Cu—N—C bond angles. (*c*) The smallest absolute value of the O—Cu—N—C torsional angle. (*d*) The $-2J$ values were determined by two of the authors (MK and TT) by the Faraday method in the temperature range 80–300 K. The cryomagnetic data fittings to the Bleaney–Bowers equation were made using the *SALS* program with a fixed value of 60×10^{-6} cgs emu (1 cgs emu = $4\pi \times 10^{-6}$ m^3) for temperature-independent paramagnetism, $N\alpha$.

program system *MOLYX* (Nanbu, Nakata & Iwata, 1989) and on VAX 11/750 and NEWS-830 computers. The C—O, C—C, C—H bond lengths and O—C—O, C—C—H bond angles were assumed to be 1·257, 1·509 and 1·09 Å, and 124·0 and 109·9°, respectively, based on the X-ray structural data of $CH_3COONa.3H_2O$ (Wei & Ward, 1977) and $LiCH_3COO.2H_2O$ in the present study. Mulliken population analyses (Mulliken, 1955) for $RCOO^-$ ions ($R = CH_3$, H, $SiMe_3$, CCl_3, $CHCl_2$, CH_2Cl, CF_3, CHF_2, CH_2F, CMe_3 and CH_2CH_3) were also carried out using an STO-6G basis set. The idealized bond lengths and bond angles were derived from the X-ray structural data of the dimeric copper carboxylate complexes. For the Me_3SiCOO^- ion, the C—O, C—Si, Si—Me bond lengths and O—C—O, C—Si—Me bond angles were assumed to be 1·268, 1·917 and 1·863 Å, and 125 and 104·8°, respectively, from the X-ray data of $[Cu(Ph_2MeSiCOO)_2quinoline]_2$ (Uekusa, Ohba, Saito, Kato, Steward, Tokii & Muto, 1990). The electron population for the acetate ion showed no significant dependence on the O—C—C—H torsion angles. However, the halocarboxylate ions have unbalanced effective charges for oxygen depending on the O—C—C—*X* torsion angles. The sum of the gross electron populations for the two O atoms in these ions is almost constant with fluctuations of less than 0·003 e. The average number of electrons for an O atom is cited in the *Discussion*.

Discussion

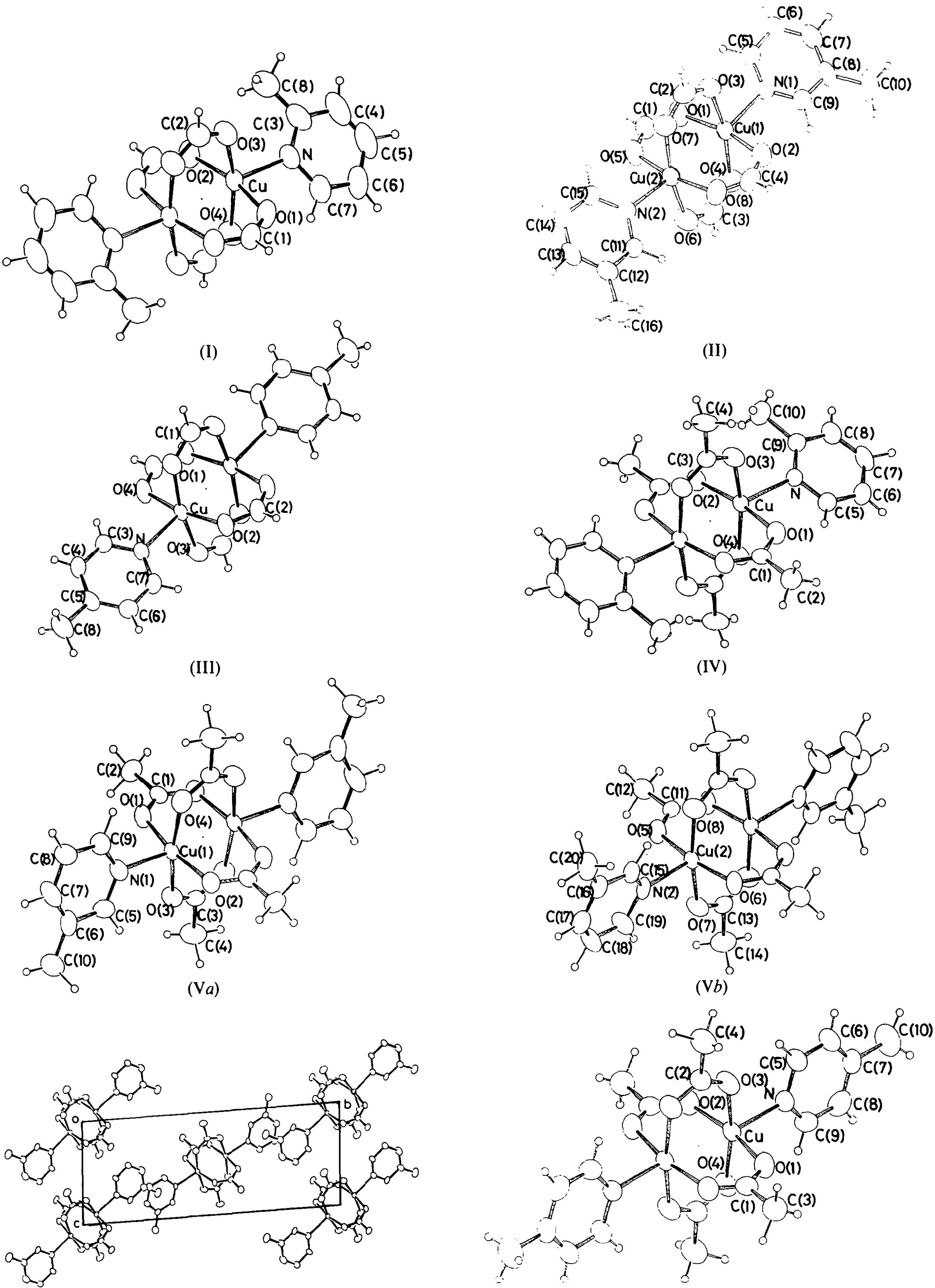
Molecular structure

Molecular structures for the copper(II) carboxylates, (I)–(VI), are shown in Fig. 1. Structure (IV) was analysed without difficulty ($R = 0{\cdot}051$) in spite of radiation damage to the crystal. The larger *R* value, 0·092, reported by Pavelcik & Hanic (1978) may be partly due to neglect of this effect on their photographic data. All complexes except (II) have a center of symmetry. The psuedo-*A*-centered crystal structure of (V), where there are two independent dimers, is shown in Fig. 1(V*c*).

The average dimensions of the central $Cu_2(COO)_4$ cage, in which spin exchange occurs, are listed along with the $-2J$ values in Table 3. The $-2J$ values are 482–507 cm^{-1} for the formates and 326–333 cm^{-1} for the acetates. On the other hand, the mean Cu—O bond lengths, 1·973 (3)–1·980 (7) Å, are almost the same, within experimental error, for formate and acetate. The mean O—C—O bond angles in the copper(II) formates, 127·8 (3)–128·5 (4)° are slightly larger than those for the acetates, 125·6 (9)–125·9 (4)°. The difference in the O—C—O bond angles is because of the ligands, and results in the Cu···Cu distances for the copper(II) formates being longer, by 0·024 (1)–0·066 (2) Å, than for the corresponding acetates. However the Cu···Cu distance is not directly related to the magnetic property as reported in a number of reviews (Melnik, 1982; Kato & Muto, 1988). Neither can we find any important differences in the cage structures for the formates and acetates which can be related to the spin-exchange interaction. Thus, we are encouraged to seek other properties of the system with which to correlate the $-2J$ values.

The molecular structures of the α-picoline adducts are strained compared to those of the β- and γ-picoline adducts, as a result of intramolecular repulsions between the carboxyl groups and the methyl moiety of the axial ligands. For example, the two Cu—N—C bond angles of the α-picoline adducts differ by 15·3 (3) and 17·5 (2)° for the acetate and the formate respectively, while the β- and γ-picoline adducts show a difference of less than 3°. Rotation of the α-picoline ligand about the Cu—N bond axis is expected to be constrained.

The Cu—N bond length for the acetate is 0·019 (3)–0·064 (4) Å longer than that observed for the corresponding formate. This trend was also observed for the pyridine adducts. However, orthorhombic and monoclinic modifications of $[Cu(CH_3COO)_2py]_2$ show a Cu—N difference of 0·028 (4) Å



(I) (II)

(III) (IV)

(V*a*) (V*b*)

(V*c*) (VI)

Fig. 1. *ORTEP* drawings (Johnson, 1965) of the molecules with the thermal ellipsoids scaled at the 50% probability level. The H atoms are represented by circles of radius 0·08 Å. (V*c*) shows the pseudo-*A*-centered structure of $[Cu(CH_3COO)_2\beta\text{-pic}]_2$.

(Uekusa *et al.*, 1989). The $-2J$ value appears to be insensitive to the structural factors related to the axial ligands.

Electron density distribution

The spin-exchange interactions in the copper(II) carboxylates appear to be related to the electron density in the carboxylato ligands. Experimental and theoretical deformation densities for the CH_3COO^- and the $HCOO^-$ ions are compared in Fig. 2. The reference densities subtracted are a superposition of densities for neutral spherical atoms. The features of the experimental deformation densities broadly agree with the theoretical densities, *i.e.*, the C—O bonding and the O-atom lone-pair peaks are consistent with sp^2 hybridization. The theoretical static deformation densities of the COO moiety in the acetate and formate ions are nearly identical as one would expect from the transferability of charge densities in small fragments (Eisenstein & Hirshfeld, 1983). The observed ratios of the peak heights for the C—O bonding and the oxygen lone-pair regions in the experimental deformation densities vary from 0·9 to 2·9 as listed in Table 4. The large variation suggests that the small differences in charge distribution on the carboxylate bridges would be difficult to detect by X-ray diffraction methods; therefore, the theoretical analysis was preferred for subsequent evaluation.

Table 4. *Observed ratios of the peak heights for* C—O *bonding and lone-pair regions in the experimental deformation density*

	(C—O bonding)/(lone pair)
$LiCH_3CO_2.2H_2O^a$	0·89
α-$Ca(HCO_2)_2{}^b$	0·93
$Cu(HCO_2)_2.2urea.2H_2O^a$	1·37
$Li(HCO_2).H_2O^c$	1·67
$NaHCO_2{}^d$	2·86

References: (*a*) Present study. (*b*) Fuess, Burger & Bats (1981). (*c*) Thomas, Tellgren & Almlof (1975). (*d*) Fuess, Bats, Dannohl, Meyer & Schweig (1982).

The gross electron populations of the carboxylate groups estimated with an STO-6G basis set are listed in Table 5 for (*a*) CH_3COO^-, (*b*) $HCOO^-$ and (*c*) Me_3SiCOO^- ions. The approximate $-2J$ values for the respective dimeric copper(II) carboxylates are (*a*) 300, (*b*) 500 and (*c*) 1000 cm^{-1} (Steward, McAfee, Chang, Piskor, Schreiber, Jury, Taylor, Pletcher & Chen, 1986). The effective charges on the C and O atoms of the COO^- moiety are (*a*) +0·233, −0·529,

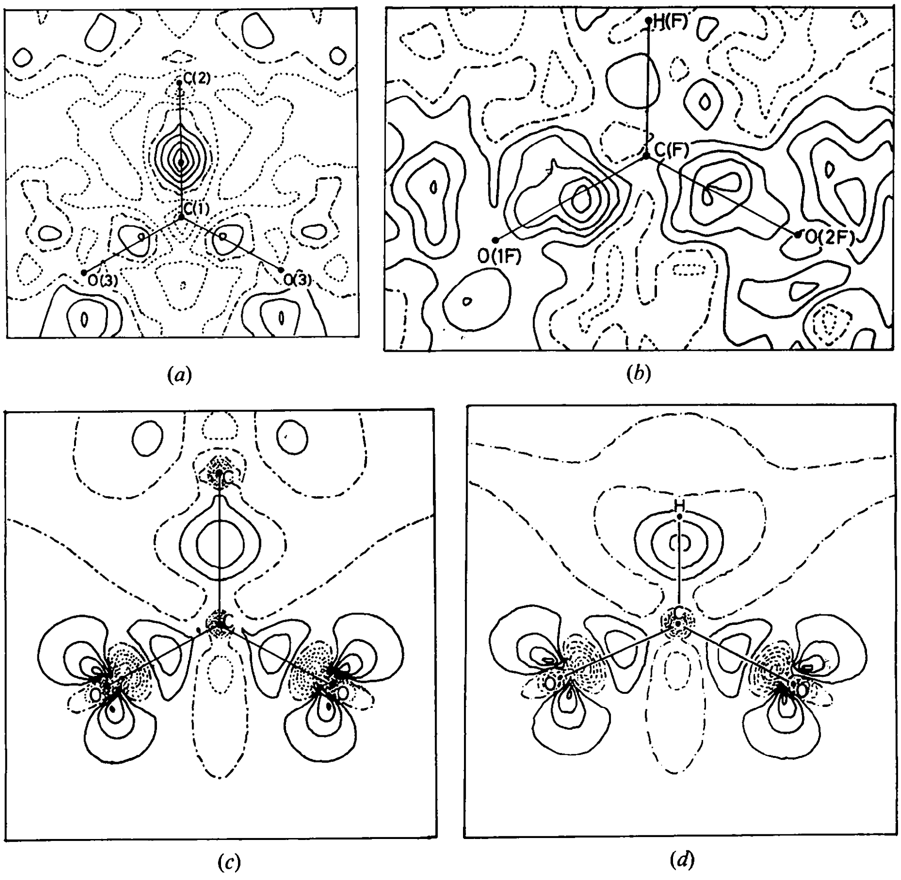
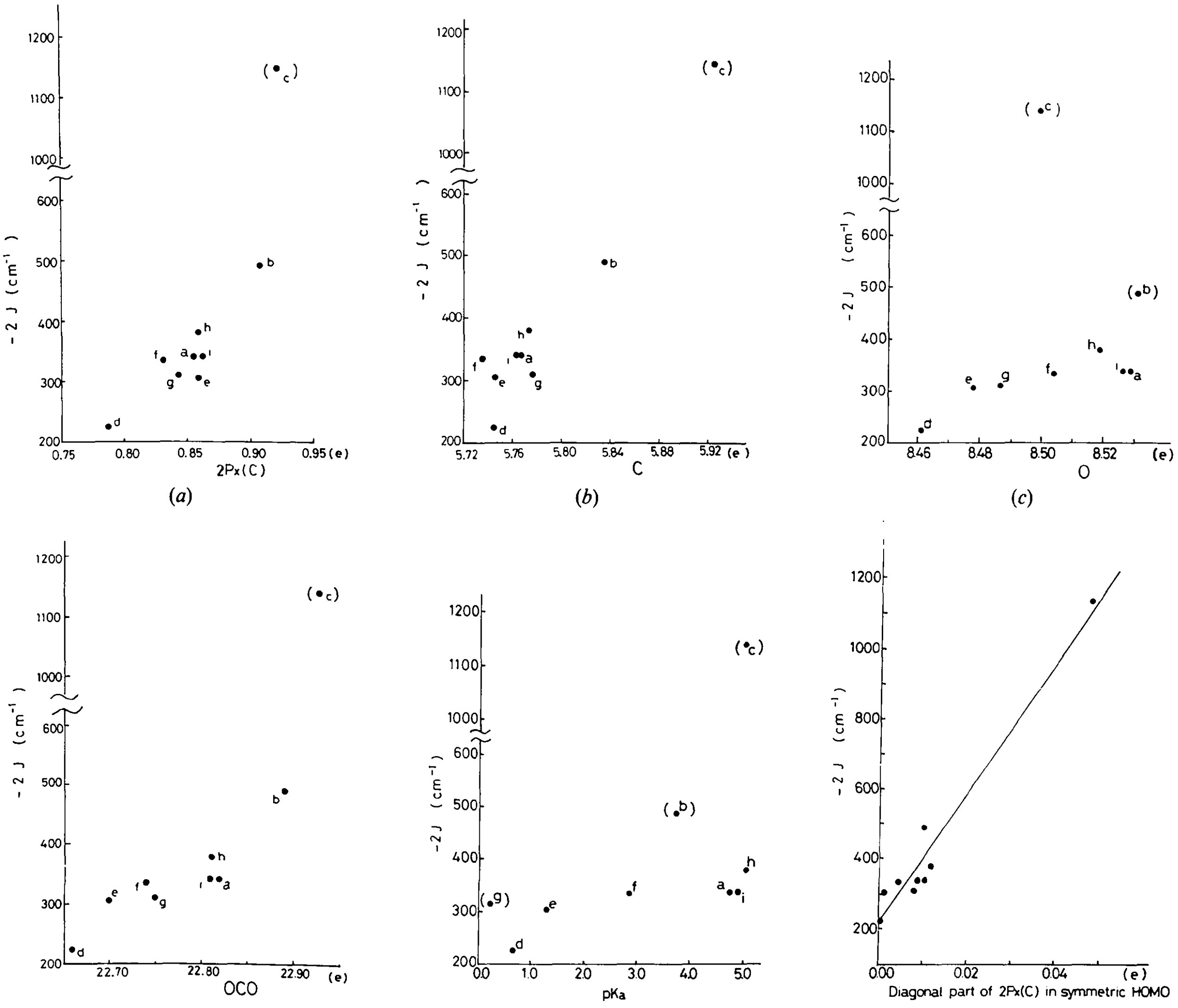


Fig. 2. Experimental deformation densities at 120 K in the plane of (*a*) $CH_3CO_2{}^-$ in (VII), (*b*) HCO_2^- in (VIII), and theoretical deformation densities using the MIDI4* basis set for (*c*) $CH_3CO_2^-$ (present work) and (*d*) HCO_2^- (Kikkawa *et al.*, 1987). The contour interval in (*a*) and (*b*) is 0·1 e Å^{-3}, and that in (*c*) and (*d*) is 0·2 e Å^{-3}. The negative contours are dotted, the zero contours chain-dotted.

(*b*) +0·164, −0·531, and (*c*) +0·072, −0·499 e, respectively. The net charges on the central C atoms differ slightly from each other. The key factor is the $2p_x$ orbital population (taking the x axis parallel to the C—Me, C—H or C—$SiMe_3$ bond); the values are (*a*) 0·855, (*b*) 0·908 and (*c*) 0·922, respectively. These results indicate that the greater the electron density on the carboxylate C atom, the stronger the antiferromagnetic interaction in the binuclear copper(II) carboxylate. This is in accord with the tendency of the spin-exchange interaction to increase as the carboxylate substituent becomes a stronger electron donor (Jotham, Kettle & Marks, 1972; Mrozinski & Heyduk, 1984). Although relating the magnetic properties of dimeric copper(II) carboxylates based on the charge distributions in the isolated carboxylato ligands involves some assumptions, a qualitative analysis seems appropriate. Population analyses for the carboxylate ions, (*d*) CCl_3COO^- (*e*) $CHCl_2COO^-$ (*f*) CH_2ClCOO^- (*g*) CF_3COO^- (*h*) CMe_3COO^- and (*i*) $CH_3CH_2COO^-$ were performed. The electron populations differ not only for the central carbon, but also for the terminal O atoms. Possible correlations between charge distribution in the carboxylate ions and the $-2J$ values of the copper(II) complexes are illustrated in Fig. 3.



(*a*) (*b*) (*c*)

(*d*) (*e*) (*f*)

Fig. 3. The average $-2J$ value of $[Cu(RCOO)_2L]_2$ listed in Table 6 *versus* (*a*) the partial $2p_x$ orbital population of the central C atom, (*b*) the gross electron population of the central C atom, (*c*) the gross electron population of the terminal O atom, (*d*) the total number of electrons in the O—C—O moiety of the isolated $RCOO^-$ ion, (*e*) the pK_a value of parent carboxylic acid in aqueous solution (Mehrotra & Bohra, 1983) and (*f*) the diagonal part of the $2p_x$ (C) electron population in the symmetric HOMO. The $-2J$ values are the averaged values for the observed data deposited. *a*–*i* stand for $R = CH_3$, H, $SiMe_3$ CCl_3, $CHCl_2$, CH_2Cl, CF_3, CH_2CH_3, CMe_3, respectively. The points in parentheses should be considered as exceptional.

Table 5. *Gross electron populations in the carboxylate groups of* (*a*) $CH_3CO_2^-$, (*b*) HCO_2^- *and* (*c*) $Me_3SiCO_2^-$ *ions*

The x axis is parallel to the C—C, C—H, or C—Si bond, and the z axis perpendicular to the CO_2 plane.

	(*a*)	(*b*)	(*c*)
Carbon			
s	3·069	3·079	3·161
p_x	0·855	0·908	0·922
p_y	0·884	0·878	0·883
p_z	0·958	0·970	0·962
Total	5·767	5·836	5·928
Oxygen			
s	3·864	3·862	3·869
p_x	1·746	1·760	1·742
p_y	1·395	1·394	1·392
p_z	1·523	1·515	1·514
Total	8·529	8·531	8·499

Table 6. *Selected* $-2J$ *values* (cm^{-1}) *for the dimeric copper*(II) *carboxylates*

Complex*	$-2J$ (cm^{-1})	Reference
$[Cu(Cl_3CCOO)_2PhCN]_2$	224	(*a*)
$[Cu(Cl_2CHCOO)_2py]_2$	288	(*a*)
$[Cu(Cl_2CHCOO)_2 3,5\text{-}Cl_2\text{-}py]_2$	312	(*a*)
$[Cu(Cl_2CHCOO)_2 4\text{-}CH_3C_6H_4CN]_2$	314	(*a*)
$[Cu(ClCH_2COO)_2py]_2$	333	(*a*)
$[Cu(ClCH_2COO)_2 3,5\text{-}Cl_2\text{-}py]_2$	340	(*a*)
$[Cu(F_3CCOO)_2quin]_2$	310	(*b*)
$[Cu(Me_3CCOO)_2py]_2$	366	(*a*)
$[Cu(Me_3CCOO)_2]_2$	403	(*a*)
$[Cu(Me_3CCOO)_2\alpha\text{-pic}]_2$	371	(*a*)
$[Cu(CH_3COO)_2py]_2$	333	(*a*)
$[Cu(CH_3COO)_2\alpha\text{-pic}]_2$	332	(*c*)
$[Cu(CH_3COO)_2\beta\text{-pic}]_2$	326	(*c*)
$[Cu(CH_3COO)_2\gamma\text{-pic}]_2$	333	(*c*)
$[Cu(CH_3COO)_2 3,5\text{-}Cl_2\text{-}py]_2$	349	(*a*)
$[Cu(HCOO)_2py]_2$	501	(*a*)
$[Cu(HCOO)_2\alpha\text{-pic}]_2$	482	(*c*)
$[Cu(HCOO)_2\beta\text{-pic}]_2$	489	(*c*)
$[Cu(HCOO)_2\gamma\text{-pic}]_2$	489	(*c*)
$[Cu(C_2H_5COO)_2py]_2$	340	(*c*)
$[Cu(PhMe_2SiCOO)_2H_2O]_2$	1000 ± 150	(*d*)
$[Cu(Ph_3SiCOO)_2py]_2$	1149	(*c*)
$[Cu(Ph_3SiCOO)_2DMSO]_2$	1182	(*c*)

References: (*a*) See the review of Kato & Muto (1988). (*b*) Melnik (1982). (*c*) Measured by one of the authors (TT or MK). (*d*) Steward *et al.* (1986).

* quin = quinoline, py = pyridine, pic = picoline.

Table 7. *Results of linear regression analyses carried out on the data shown in Fig.* 3

The equation used was $-2J = ax + b$, where x is the electron population or pK_a value and a and b are the coefficients to be determined. The exceptional points (shown in parentheses in Fig. 3) were excluded from the analysis. $R = \{\sum[(-2J)_{obs} - (-2J)_{calc}]^2/\sum[(-2J)_{obs}]^2\}^{1/2}$.

Source*	Variable	R	a	b	Exceptions
(*a*)	$2p_x$ of C	0·068	1890	−1254	Me_3SiCOO^-
(*b*)	C	0·112	1626	−9019	Me_3SiCOO^-
(*c*)	O	0·075	1518	−12585	Me_3SiCOO^- and $HCOO^-$
(*d*)	OCO	0·089	876	−19619	Me_3SiCOO^-
(*e*)	pK_a	0·075	23·4	245	Me_3SiCOO^-, $HCOO^-$ and CF_3COO^-
(*f*)	Diagonal part of $2p_x$ (C) in symmetric HOMO	0·115	20773	204	

* The source values (*a*)–(*f*) given in the table refer to Figs. 3(*a*)–3(*f*) respectively.

The $-2J$ values are the average of the selected data listed in Table 6 for the corresponding dimeric copper(II) carboxylates with a square-pyramidal coordination geometry around copper. From the graphs, one observes that the more the electrons are distributed in the $2p_x$ orbital of the central C atom, on the central C atom, and on the terminal O atoms or in the O—C—O moiety, the larger the $-2J$ value. Linear regression analyses were carried out on the data in the graphs excluding the exceptional points. The results are presented in Table 7.

The pK_a values for the carboxylic acids in aqueous solution are available except for silanecarboxylic acid (Mehrotra & Bohra, 1983). The pK_a for $Me_3SiCOOH$ is estimated at 5–6 from the observed pK_a in 45 and 76% alcohol–water media (Steward, Dziedzic, Johnson & Frohliger, 1971). In some series of binuclear copper(II) carboxylates the $-2J$ values tend to increase as the pK_a values of the parent acid of the bridging ligand increase; there are some exceptions such as formate and fluoroacetate (see Fig. 3*e*) (Hay *et al.*, 1975; Kato & Muto, 1988; Emori, Morishita & Muto, 1987; Emori, Tohyama & Muto, 1987; Emori, Nonaka & Muto, 1988; Emori, Kurihara & Muto, 1988). The anomaly of the formate ion may originate from the difference in the electronic structure of its carboxylate C atom, which influences the super spin-exchange interaction directly but not the acidity. The correlation between the electron population on a carboxylate O atom and the pK_a value of the parent acid in an aqueous solution is shown in Fig. 4, where (*j*) CHF_2COO^- and (*k*) CH_2FCOO^- ions are included. The fluoroacetate ions have larger effective negative charges on their O atoms than those of the corresponding chloroacetate ions, but the pK_a values are relatively

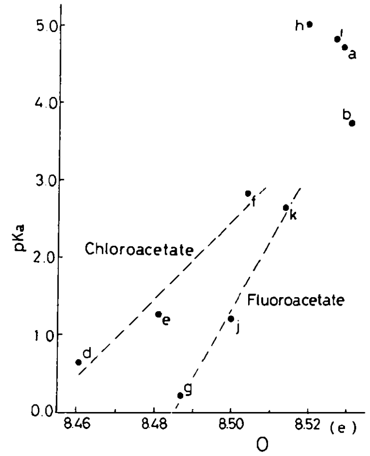


Fig. 4. The pK_a values of carboxylic acids in aqueous solution are plotted against the gross electron population of the carboxylate O atom. j and k stand for $R = CHF_2$ and CH_2F, respectively. Other symbols are the same as in Fig. 3.

small. This may explain why the fluoroacetate copper complexes show stronger spin-exchange interactions than expected from the pK_a values.

Magneto-structural correlation

The observed correlation between $-2J$ and the $2p_x$ orbital population of the carboxylate C atom is essentially in accordance with the spin-exchange mechanism proposed by Hay *et al.* (1975). In that mechanism, the symmetric metal MO overlaps with the symmetric highest occupied MO's (HOMO's) of the bridging carboxylate ions. The symmetric HOMO of the carboxylate ion is constructed from the $2p_x$ orbitals of the O atoms, predominantly with the $2s$ and $2p_x$ orbitals of the central C atom. The polar character of R in $R\text{COO}^-$ is transmitted primarily to the $2p_x$ orbital of the C atom. Even though the coefficient of the $2p_x$ (C) orbital is small in the symmetric HOMO, magnetic orbital overlaps can be constructed as $2p_x$ (O) $-$ $2p_x$ (C) $-$ $2p_x$ (O), which overlap with the symmetric metal MO (Pei, Nakatani, Kahn, Sletten & Renard, 1989). This appears to explain why only the electron population of the $2p_x$ (C) orbital correlates strongly with the spin-exchange interactions. The correlation of $-2J$ with the diagonal part of the $2p_x$ (C) electron population in the symmetric HOMO, *i.e.*, twice the square of the coefficient of the $2p_x$ (C) atomic orbital, is shown in Fig. 3(*f*). It became clear that the very large $-2J$ values observed for the copper(II) triorganosilanecarboxylates originate from the special electronic structure of the central C atom. [The coefficient of the $2s$ (C) atomic orbital in the symmetric HOMO decreases as that of the $2p_x$ (C) orbital increases]. On the other hand, the asymmetric HOMO of the carboxylate ion is predominantly constructed from the $2p_x$ and $2p_y$ orbitals of the O atoms and with the $2p_y$ orbital of the C atom (y lies along the O···O direction). The coefficient of the $2p_y$ (C) atomic orbital varies from 0·064 to 0·077, showing no modification by the polar effect of the substituent.

The electronic structure of the central C atom is the primary factor determining the strength of the spin superexchange interaction. A secondary factor may be the Cu—O bond strength, which can be estimated by the effective charge of the O atom, or assessed roughly from the pK_a of the carboxylic acid. However, it does not seem to be reflected in the Cu—O bond length explicitly. The atom X bonded to the COO^- ion is limited to C, H, and Si in the above. When X = Ge, the $-2J$ value is similar to that of the corresponding silanecarboxylate ion (Uekusa *et al.*, 1990). The $-2J$ value for a carbamato complex, $[\text{Cu(Et}_2\text{NCOO)}_2\text{NHEt}_2]_2$, was reported to be 80·2 (4) cm^{-1} after a correction for paramagnetic impurity fraction of 10% on the value of magnetic susceptibility. The central cage structure with a Cu···Cu distance of 2·658 (2) Å is normal (Agostinelli, Belli Dell'Amico, Calderazzo, Fiorani & Pelizzi, 1988). A molecular-orbital calculation for the NH_2COO^- ion using an STO-6G basis set gave a value of 0·0001 e for the diagonal part of the $2p_x$ (C) orbital in the symmetric HOMO. The number of electrons for the C and O atoms is 5·66 and 8·55. This result is in accordance with the conclusion that the main factor which determines the antiferromagnetic interaction in the dimeric copper(II) carboxylates is the electronic structure of the C atom in the bridge.

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Structure of the Organic Semiconducting Radical Cation Salt Tris(2,3,6,7-tetramethoxynaphthalene) Bis(hexafluoroarsenate)

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Abstract

$(C_{14}H_{16}O_4)_3^{2+}.2AsF_6^-$, $M_r = 1122{\cdot}67$, triclinic, $P\bar{1}$, $a = 10{\cdot}1564\,(15)$, $b = 11{\cdot}0323\,(13)$, $c = 11{\cdot}9157\,(12)$ Å, $\alpha = 77{\cdot}841\,(10)$, $\beta = 65{\cdot}935\,(9)$, $\gamma = 76{\cdot}633\,(11)^\circ$, $V = 1175{\cdot}9\,(2)$ Å^3, $Z = 1$, $D_x = 1{\cdot}585$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 15{\cdot}2$ cm^{-1}, $F(000) = 570$, $T = 298$ K, final $R(F) = 0{\cdot}049$ for 3950 unique reflexions. Triads of planar 2,3,6,7-tetramethoxynaphthalene (TMN) molecules form stacks along the *a* direction. The average interplanar distances are 3·27 Å in the triad (0·5° dihedral angle) and 3·362 (6) Å between the triads. The centrosymmetric TMN molecule in the middle of the triad is rotated by 35° around the stacking direction with respect to the two outer asymmetric TMN molecules, in order to achieve short C—H···O contacts in the triad and make room for the AsF_6^- ion. Between the stacks the TMN molecules are connected into infinite chains *via* short C—H···O contacts. A rigid-body *TLS* analysis of the anisotropic displacement parameters reveals the significant effect of these C—H···O contacts on the thermal motion of the molecules.

Introduction

Cation radical salts of naphthalene have attracted considerable interest in recent years and have resulted in the renaissance of cation radical salts of aromatic hydrocarbons (Keller, Nöthe, Pritzkow, Wehe, Werner, Koch & Schweitzer, 1980; Fritz, Gebauer, Friedrich, Ecker, Artes & Schubert, 1978; Kröhnke, Enkelmann & Wegner, 1980). These salts exhibit high conductivity and the narrowest ESR line (2·5 mG) found so far (Müller, von Schütz & Wolf, 1983). One great problem with these compounds is their instability; they decompose within minutes at room temperature. Connecting methoxy groups to the naphthalene molecule has been shown to stabilize the cation radical salts (Hellberg, 1987). The present investigation is part of a series of studies of the structures and physical properties of electrochemically prepared cation radical salts of substituted aromatic donors. One of the problems encountered has been to obtain crystals of sufficiently good quality for a structure determination. In most cases partly amorphous or polycrystalline samples are obtained. Solvent molecules from the electrocrystallization process can also be easily incorporated into the structure and disorder of the molecules often occurs. Here, an ordered and solvent-free structure is reported. The structure of the corresponding perchlorate will be published in a subsequent paper.

Experimental

Good quality solvent-free brittle single crystals of $(TMN)_3(AsF_6)_2$ with a reddish-black metallic lustre were kindly provided by Dr Jonas Hellberg of KTH, Stockholm. They were prepared by the electrolytic oxidation of TMN in CH_2Cl_2 solution in the presence of $^nBu_4N.AsF_6$ at a constant current of 4–6 μA and a temperature of 277–281 K. Details of the synthesis, conductivity and magnetic properties are given by Krzystek, von Schütz, Ahlgren, Hellberg, Söderholm & Olovsson (1986). A polyhedral crystal of size $0{\cdot}17 \times 0{\cdot}14 \times 0{\cdot}13$ mm was used. Intensity

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