

Structural Comparisons Between Copper(II) Triorganosilanecarboxylate, -germanecarboxylate and -acetate Dimers

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Abstract. Tetrakis(μ -methylphenylsilanecarboxylato-*O,O'*)-bis(quinoline)dycopper(II), $[\text{Cu}(\text{C}_{14}\text{H}_{13}\text{O}_2\text{Si})_2(\text{C}_9\text{H}_7\text{N})_2]_2$, (I), $M_r = 1350.7$, triclinic, $P\bar{1}$, $a = 12.415$ (3), $b = 14.601$ (2), $c = 11.515$ (2) Å, $\alpha = 98.46$ (2), $\beta = 113.71$ (2), $\gamma = 109.06$ (2)°, $V = 1710.1$ (7) Å³, $Z = 1$, $D_m = 1.29$ (2), $D_x = 1.31$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.75$ mm⁻¹, $F(000) = 702$, $T = 299$ (2) K, final $R = 0.045$ for 3857 observed unique reflections. Tetrakis(μ -methylphenylacetato-*O,O'*)-bis(quinoline)dycopper(II) diquinoline, $[\text{Cu}(\text{C}_{15}\text{H}_{13}\text{O}_2)_2(\text{C}_9\text{H}_7\text{N})_2]_2 \cdot 2\text{C}_9\text{H}_7\text{N}$, (II), $M_r = 1544.7$, triclinic, $P\bar{1}$, $a = 12.277$ (2), $b = 12.996$ (1), $c = 13.777$ (1) Å, $\alpha = 93.24$ (1), $\beta = 109.19$ (1), $\gamma = 105.83$ (1)°, $V = 1971.2$ (4) Å³, $Z = 1$, $D_m = 1.32$ (2), $D_x = 1.30$ Mg m⁻³, $\mu = 0.60$ mm⁻¹, $F(000) = 806$, $T = 297$ (2) K, final $R = 0.038$ for 6071 reflections. Tetrakis(μ -dimethylphenylacetato-*O,O'*)-bis(quinoline)dycopper(II), $[\text{Cu}(\text{C}_{10}\text{H}_{11}\text{O}_2)_2(\text{C}_9\text{H}_7\text{N})_2]_2$, (III), $M_r = 1038.1$, monoclinic, $P2_1/c$, $a = 11.717$ (3), $b = 20.151$ (5), $c = 11.129$ (2) Å, $\beta = 106.86$ (2)°, $V = 2514.7$ (9) Å³, $Z = 2$, $D_m = 1.36$ (2), $D_x = 1.38$ Mg m⁻³, $\mu = 0.91$ mm⁻¹, $F(000) = 1084$, $T = 301$ (2) K, final $R = 0.034$ for 3636 reflections. Tetrakis(μ -triphenylgermanecarboxylato-*O,O'*)-bis(quinoline)dycopper(II) tribenzene, $[\text{Cu}(\text{C}_{19}\text{H}_{15}\text{GeO}_2)_2(\text{C}_9\text{H}_7\text{N})_2]_2 \cdot 3\text{C}_6\text{H}_6$, (IV), $M_r = 2011.2$, monoclinic, $P2_1/n$, $a = 18.211$ (2), $b = 27.634$ (4), $c = 19.143$ (4) Å, $\beta = 102.45$ (2)°, $V = 9407$ (3) Å³, $Z = 4$, $D_m = 1.38$ (2), $D_x = 1.38$ Mg m⁻³, $\mu = 1.75$ mm⁻¹, $F(000) = 4112$, $T = 120$ (2) K, final $R = 0.059$ for 4070 reflections. Tetrakis(μ -triphenylsilanecarboxylato-*O,O'*)-bis(2-picoline)dycopper(II)

tribenzene, $[\text{Cu}(\text{C}_{19}\text{H}_{15}\text{O}_2\text{Si})_2(\text{C}_6\text{H}_7\text{N})_2]_2 \cdot 3\text{C}_6\text{H}_6$, (V), $M_r = 1761.3$, triclinic, $P\bar{1}$, $a = 16.993$ (2), $b = 19.457$ (2), $c = 16.136$ (3) Å, $\alpha = 97.21$ (1), $\beta = 114.66$ (1), $\gamma = 100.89$ (1)°, $V = 4635$ (1) Å³, $Z = 2$, $D_m = 1.29$ (2), $D_x = 1.26$ Mg m⁻³, $\mu = 0.57$ mm⁻¹, $F(000) = 1840$, $T = 300$ (2) K, final $R = 0.090$ for 6757 reflections. The structures of the five complexes listed above have been determined to be of the copper(II) acetate monohydrate type having a square-pyramidal coordination geometry around the Cu atom. In the triorganosilanecarboxylates, (I) and (V), and triorganogermanecarboxylate, (IV), the Cu...Cu distances are 2.676 (1), 2.701 (2) and 2.686 (2) Å, and the average Cu—O distances are 1.975 (3), 1.984 (17) and 1.984 (9) Å, respectively; the Cu...Cu distances in the triorganoacetates, (II) and (III), are 2.696 (1) and 2.683 (1) Å, and the mean Cu—O distances are 1.971 (1) and 1.978 (2) Å, respectively. There exist no special features in the dimensions of the $[\text{Cu}_2(\text{RCOO})_2]$ cage of the silane- or germanecarboxylates which can account for the much stronger spin superexchange interactions (the singlet-triplet energy separation, $-2J \sim 1000$ cm⁻¹).

Introduction. Recently, new copper(II) carboxylates, $[\text{Cu}(\text{R}_3\text{XCOO})_2\text{L}]_2$ where $X = \text{Si}$ or Ge in the bridging ligand, have been synthesized (R and L stand for the organic group and axial ligand, respectively). The magnitude of the spin superexchange coupling ($-2J \sim 1000$ cm⁻¹) for these complexes is much larger than observed for the copper(II) acetates ($X = \text{C}$, $-2J \sim 300$ cm⁻¹) and copper(II) formates ($X = \text{H}$, $-2J \sim 500$ cm⁻¹) (Steward, McAfee, Chang,

Piskor, Schreiber, Jury, Taylor, Pletcher & Chen, 1986; Kato & Muto, 1988). For $X = \text{Si}$, the dimeric structure having the $[\text{Cu}_2(\text{COO})_4]$ cage was confirmed by the crystal-structure analysis of $[\text{Cu}(\text{PhMe}_2\text{SiCOO})_2(\text{H}_2\text{O})_2]$ (Steward *et al.*, 1986). In the present study the structural comparison between $X = \text{Si}$ and C for $[\text{Cu}(\text{Ph}_2\text{MeXCOO})_2(\text{quinoline})_2]$, (I) and (II), has been performed to investigate the magneto-structural correlation in these systems. In the course of this study, other related complexes (III)–(V) have also been examined. It is important to confirm the square-pyramidal environment around Cu in these complexes since trigonal bipyramidal coordination has been observed in $[\text{Cu}(\text{Ph}_3\text{C-COO})_2\text{py}]_2$, benzene (Steward, Kato, Chang, Sax, Chang, Taura, Jury, Muto, Tokii, Pletcher & Yoo, 1984).

Experimental. The single crystals were obtained from benzene solutions containing a small amount of the apical ligand. D_m was measured by flotation in a mixture of cyclohexane and carbon tetrachloride. X-ray intensity data were collected on a Rigaku AFC-5 four-circle diffractometer with Mo $K\alpha$ radiation monochromatized by a graphite plate. Structures were solved by Patterson and Fourier methods. Cell parameters refined by least squares for 2θ values ($20 < 2\theta < 30^\circ$).

All H atoms in (I)–(III) found from difference synthesis. Positional parameters of all atoms, anisotropic thermal parameters of non-H atoms and isotropic thermal parameters of H atoms refined by block-diagonal least squares, $\sum w||F_o| - |F_c||^2$ minimized, $w^{-1} = \sigma^2(|F_o|) + (0.015|F_o|)^2$. Complex neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974). Calculations were carried out on a FACOM M-380R computer at Keio University using UNICSIII computation program system (Sakurai & Kobayashi, 1979). Atomic coordinates are listed in Table 1 and selected bond lengths and bond angles in Table 2. Experimental details are given below.

(I). A green prismatic crystal, $0.4 \times 0.3 \times 0.2$ mm, cut from a polycrystalline block. Intensity measurement performed up to $2\theta = 50^\circ$ ($h: -14 \rightarrow 14$, $k: -17 \rightarrow 17$, $l: -13 \rightarrow 0$). Variation of $|F_o|$ of five standard reflections, $0.977 < \sum(|F_o|/|F_o|_{\text{initial}})/5 < 1.002$. Correction for absorption ($0.75 < A < 0.87$). 6362 reflections measured, 4065 reflections observed with $|F_o| > 3\sigma(|F_o|)$, 3857 unique ($R_{\text{int}} = 0.016$). Final $R = 0.045$, $wR = 0.041$, $S = 1.3$ for 3857 unique reflections. Reflection/parameter ratio 7.2, $\Delta/\sigma < 0.13$, maximum and minimum peaks of final $\Delta\rho$ map 0.37 and -0.33 e \AA^{-3} respectively.

(II). A green prismatic crystal, $0.5 \times 0.5 \times 0.3$ mm. $2\theta_{\text{max}} = 55^\circ$ ($h: -15 \rightarrow 15$, $k: -16 \rightarrow 0$, $l: -17 \rightarrow 17$). $0.976 < \sum(|F_o|/|F_o|_{\text{initial}})/5 < 1.003$. 9266 reflections

Table 1. Positional parameters [$\times 10^4$; for Cu $\times 10^5$ in (I), (II), (III)] and equivalent isotropic temperature factors (Hamilton, 1959)

	x	y	z	B_{eq} ($\text{\AA}^2 \times 10$)
(I)				
Cu	-4260 (4)	-2234 (3)	8670 (5)	25
Si(1)	2981 (1)	-1178 (1)	1724 (1)	35
Si(2)	-2830 (1)	-3090 (1)	-2966 (1)	35
O(1)	1004 (2)	-662 (2)	1464 (3)	37
O(2)	-1535 (3)	-1526 (2)	-640 (2)	43
O(3)	-1673 (2)	334 (2)	22 (3)	39
O(4)	832 (2)	1180 (2)	2091 (2)	38
N(1)	-1167 (3)	-877 (2)	2138 (3)	33
C(1)	1711 (3)	-668 (3)	927 (3)	29
C(2)	-1544 (3)	-1762 (3)	-1742 (4)	31
C(10)	2189 (4)	-2266 (3)	2207 (4)	42
C(11)	2822 (5)	-2396 (4)	3429 (5)	60
C(12)	2209 (7)	-3221 (5)	3740 (7)	93
C(13)	972 (7)	-3924 (5)	2849 (8)	101
C(14)	269 (6)	-3828 (5)	1628 (8)	95
C(15)	945 (5)	-2982 (4)	1342 (6)	65
C(20)	-3129 (4)	-3963 (3)	-1992 (4)	38
C(21)	-3432 (5)	-3727 (3)	-980 (5)	54
C(22)	-3659 (5)	-4376 (4)	-267 (6)	68
C(23)	-3605 (6)	-5292 (4)	-547 (6)	74
C(24)	-3318 (6)	-5557 (4)	-1522 (6)	72
C(25)	-3066 (5)	-4904 (3)	-2228 (5)	54
C(30)	3522 (4)	-1593 (3)	529 (4)	42
C(31)	2689 (5)	-2355 (5)	-646 (6)	95
C(32)	3096 (7)	-2659 (6)	-1562 (6)	110
C(33)	4336 (7)	-2213 (6)	-1244 (6)	97
C(34)	5165 (6)	-1512 (7)	-108 (8)	141
C(35)	4747 (6)	-1212 (6)	761 (7)	118
C(40)	-2296 (4)	-3628 (3)	-4094 (4)	38
C(41)	-1005 (4)	-3407 (3)	-3700 (5)	52
C(42)	-640 (5)	-3858 (4)	-4555 (6)	66
C(43)	-1574 (5)	-4522 (4)	-5785 (6)	70
C(44)	-2830 (6)	-4755 (4)	-6203 (5)	69
C(45)	-3198 (4)	-4305 (3)	-5376 (5)	55
C(50)	4360 (5)	-78 (4)	3209 (5)	60
C(60)	-4287 (4)	-2885 (3)	-3945 (5)	59
C(71)	-1143 (4)	-1761 (3)	2159 (5)	49
C(72)	-1393 (6)	-2261 (4)	3039 (6)	70
C(73)	-1618 (5)	-1808 (4)	3950 (6)	71
C(74)	-1685 (4)	-857 (4)	3968 (4)	49
C(75)	-1925 (5)	-334 (4)	4894 (4)	65
C(76)	-1960 (5)	562 (4)	4864 (5)	72
C(77)	-1791 (5)	986 (4)	3919 (5)	69
C(78)	-1534 (4)	524 (3)	3008 (5)	50
C(79)	-1455 (3)	-408 (3)	3026 (4)	35
(II)				
Cu	11188 (2)	-1085 (2)	3449 (2)	24
O(1)	246 (1)	-1590 (1)	461 (1)	36
O(2)	752 (1)	-606 (1)	-1125 (1)	34
O(3)	1586 (1)	1379 (1)	41 (1)	33
O(4)	1118 (1)	477 (1)	1706 (1)	36
N(1)	3021 (2)	-146 (2)	1076 (1)	35
C(1)	-871 (2)	-1923 (2)	250 (2)	27
C(2)	-245 (2)	-700 (2)	-1834 (2)	28
C(10)	-1418 (2)	-3103 (2)	404 (2)	30
C(30)	-1526 (2)	-2977 (2)	1481 (2)	30
C(31)	-655 (3)	-3084 (2)	2368 (2)	50
C(32)	-783 (3)	-2943 (3)	3330 (2)	61
C(33)	-1751 (3)	-2691 (2)	3425 (2)	53
C(34)	-2615 (2)	-2567 (2)	2555 (2)	47
C(35)	-2501 (2)	-2703 (2)	1594 (2)	38
C(50)	-2665 (2)	-3689 (2)	-439 (2)	35
C(51)	-3351 (3)	-4663 (2)	-281 (2)	52
C(52)	-4468 (3)	-5237 (3)	-1010 (2)	71
C(53)	-4931 (3)	-4863 (3)	-1919 (2)	73
C(54)	-4255 (3)	-3917 (3)	-2099 (2)	62
C(55)	-3126 (2)	-3341 (2)	-1374 (2)	43
C(70)	-568 (2)	-3763 (2)	354 (2)	41
C(20)	-330 (2)	-1083 (2)	-2946 (2)	30
C(40)	-87 (2)	-2183 (2)	-2991 (2)	35
C(41)	-243 (3)	-2881 (2)	-2303 (2)	47
C(42)	-71 (3)	-3882 (2)	-2397 (2)	65
C(43)	261 (4)	-4200 (3)	-3172 (3)	85
C(44)	418 (5)	-3532 (4)	-3871 (3)	101
C(45)	250 (3)	-2529 (3)	-3783 (2)	68
C(60)	-1583 (2)	-1192 (2)	-3746 (2)	32
C(61)	-2561 (2)	-2083 (2)	-3877 (2)	52
C(62)	-3698 (3)	-2202 (3)	-4596 (3)	70
C(63)	-3878 (3)	-1436 (3)	-5205 (3)	75

Table 1 (cont.)

	x	y	z	B_{eq} ($\text{\AA}^2 \times 10$)		x	y	z	B_{eq} ($\text{\AA}^2 \times 10$)
C(029)	-1803 (8)	1904 (6)	5471 (8)	8	C(233)	127 (9)	1191 (7)	6377 (10)	64
C(910)	8318 (10)	615 (7)	5362 (10)	32	C(234)	-61 (9)	901 (7)	5483 (11)	68
C(911)	7577 (11)	565 (7)	4897 (10)	37	C(235)	663 (8)	1005 (7)	5196 (9)	52
C(912)	8000 (9)	-23 (6)	6154 (9)	17	C(310)	-1308 (7)	2922 (6)	1744 (8)	37
C(913)	8494 (10)	324 (7)	5976 (10)	30	C(311)	-1645 (8)	2171 (6)	1422 (9)	47
C(914)	7089 (10)	219 (7)	5062 (10)	30	C(312)	-2461 (9)	1829 (7)	596 (10)	59
C(915)	7307 (10)	-79 (7)	5678 (10)	26	C(313)	-2913 (9)	2314 (7)	110 (11)	68
C(920)	4723 (10)	443 (7)	4654 (10)	29	C(314)	-2622 (9)	3025 (7)	392 (10)	64
C(921)	4913 (10)	409 (7)	5431 (10)	30	C(315)	-1787 (8)	3367 (7)	1224 (9)	52
C(922)	5169 (11)	-36 (7)	5747 (10)	35	C(320)	133 (7)	4310 (6)	3041 (8)	40
C(930)	175 (12)	4578 (8)	4677 (11)	51	C(321)	221 (9)	4778 (7)	3820 (10)	60
C(931)	121 (13)	4545 (9)	5350 (12)	62	C(322)	512 (11)	5522 (9)	3875 (12)	89
C(932)	-10 (13)	5004 (9)	5693 (13)	65	C(323)	712 (10)	5758 (8)	3193 (11)	79
C(940)	6428 (12)	4502 (8)	4149 (12)	52	C(324)	648 (9)	5273 (7)	2437 (10)	66
C(941)	6627 (14)	4807 (10)	3711 (13)	72	C(325)	349 (8)	4532 (6)	2369 (9)	49
C(942)	7282 (17)	5114 (11)	4033 (16)	105	C(330)	-673 (7)	3078 (6)	3791 (8)	37
C(943)	7742 (17)	4920 (12)	4733 (17)	116	C(331)	-1553 (8)	3034 (7)	3633 (10)	57
C(944)	7464 (16)	4570 (10)	5100 (15)	95	C(332)	-1834 (10)	2779 (8)	4318 (11)	75
C(945)	6757 (14)	4385 (10)	4834 (13)	73	C(333)	-1252 (10)	2593 (8)	5071 (11)	71
(V)					C(334)	-385 (10)	2660 (8)	5266 (11)	72
Cu(1)	1427 (1)	1798 (1)	2533 (1)	27	C(335)	-61 (8)	2895 (7)	4604 (10)	56
Cu(2)	2529 (1)	3080 (1)	3626 (1)	28	C(410)	394 (7)	2831 (6)	-401 (8)	41
Si(1)	4440 (2)	1809 (2)	3291 (3)	36	C(411)	191 (9)	2693 (7)	-1376 (10)	61
Si(2)	2475 (2)	1467 (2)	5555 (2)	31	C(412)	-760 (10)	2378 (8)	-2086 (11)	78
Si(3)	-311 (2)	3307 (2)	2898 (3)	33	C(413)	-1428 (10)	2241 (8)	-1807 (11)	77
Si(4)	1578 (2)	3239 (2)	491 (3)	37	C(414)	-1252 (9)	2382 (8)	-855 (11)	72
O(11)	2601 (4)	1597 (4)	2712 (5)	38	C(415)	-298 (9)	2705 (7)	-140 (10)	64
O(12)	1626 (4)	1535 (4)	3729 (5)	33	C(420)	1782 (8)	4214 (6)	698 (9)	44
O(13)	484 (4)	2260 (4)	2555 (5)	34	C(421)	2549 (10)	4670 (8)	1426 (11)	72
O(14)	1410 (5)	2260 (4)	1504 (5)	40	C(422)	2805 (11)	5468 (9)	1624 (13)	94
O(21)	3478 (4)	2700 (4)	3498 (6)	41	C(423)	2152 (10)	5743 (8)	1020 (12)	84
O(22)	2653 (4)	2555 (4)	4638 (5)	34	C(424)	1346 (11)	5329 (9)	296 (12)	88
O(23)	1427 (4)	3280 (4)	3581 (5)	37	C(425)	1188 (9)	4551 (7)	116 (10)	67
O(24)	2209 (5)	3350 (4)	2391 (5)	39	C(430)	2325 (7)	2887 (6)	89 (9)	41
N(1)	494 (6)	703 (7)	1632 (7)	64	C(431)	2746 (9)	3301 (7)	-349 (10)	65
N(2)	3548 (7)	4079 (5)	4678 (8)	58	C(432)	3295 (10)	3008 (8)	-683 (11)	76
C(10)	3345 (7)	2059 (5)	3117 (8)	34	C(433)	3436 (10)	2356 (8)	-578 (11)	72
C(20)	2236 (7)	1925 (5)	4512 (7)	28	C(434)	3085 (9)	1972 (7)	-100 (10)	64
C(30)	664 (7)	2890 (5)	3028 (7)	28	C(435)	2495 (8)	2233 (7)	243 (9)	51
C(40)	1769 (7)	2917 (5)	1617 (8)	33	C(021)	4334 (9)	3853 (7)	5338 (11)	66
C(110)	5262 (7)	2160 (6)	4547 (8)	36	C(022)	4939 (11)	4378 (9)	6064 (13)	101
C(111)	5031 (10)	1993 (8)	5253 (11)	76	C(023)	4847 (11)	5100 (9)	6094 (12)	87
C(112)	5648 (11)	2283 (8)	6249 (12)	87	C(024)	4181 (11)	5338 (8)	5504 (12)	83
C(113)	6504 (9)	2734 (7)	6468 (10)	62	C(025)	3478 (10)	4717 (8)	4733 (11)	80
C(114)	6717 (10)	2899 (8)	5795 (11)	74	C(026)	2725 (10)	4889 (8)	4048 (11)	72
C(115)	6123 (9)	2629 (7)	4815 (10)	63	C(910)	-2154 (11)	1035 (9)	2752 (12)	91
C(120)	4230 (7)	810 (6)	2967 (8)	39	C(911)	-1298 (11)	972 (9)	2998 (13)	97
C(121)	3463 (8)	393 (6)	2155 (9)	49	C(912)	-1105 (11)	351 (9)	2655 (12)	94
C(122)	3337 (9)	-376 (7)	1912 (10)	61	C(913)	-1866 (11)	-199 (9)	2063 (13)	99
C(123)	3998 (9)	-669 (7)	2464 (10)	61	C(914)	-2750 (12)	-149 (10)	1780 (14)	108
C(124)	4747 (10)	-269 (8)	3235 (11)	73	C(915)	-2918 (12)	510 (10)	2160 (14)	106
C(125)	4877 (8)	489 (7)	3507 (10)	54	C(920)	1822 (12)	3930 (10)	7366 (13)	103
C(130)	4901 (7)	2277 (6)	2579 (9)	44	C(921)	2108 (12)	3726 (10)	6722 (14)	111
C(131)	4679 (8)	2901 (7)	2333 (10)	57	C(922)	2282 (13)	4183 (11)	6199 (15)	125
C(132)	5086 (10)	3306 (8)	1837 (11)	79	C(923)	2334 (14)	4910 (11)	6442 (16)	140
C(133)	5711 (10)	3020 (8)	1644 (11)	75	C(924)	2220 (13)	5189 (10)	7212 (15)	123
C(134)	5935 (10)	2406 (8)	1883 (11)	79	C(925)	1823 (13)	4642 (10)	7576 (14)	119
C(135)	5521 (9)	1998 (7)	2332 (10)	59	C(930)	5361 (12)	371 (10)	-492 (13)	105
C(210)	3528 (7)	2011 (6)	6594 (8)	38	C(931)	5314 (11)	-370 (9)	-570 (13)	98
C(211)	3798 (8)	2753 (7)	6814 (10)	54	C(932)	4967 (12)	-756 (9)	-51 (13)	104
C(212)	4563 (9)	3166 (7)	7672 (10)	66	C(940)	4182 (13)	5152 (11)	9827 (15)	123
C(213)	5023 (9)	2790 (7)	8303 (10)	61	C(941)	4464 (13)	5056 (10)	9110 (14)	120
C(214)	4763 (9)	2036 (7)	8109 (10)	62	C(942)	5246 (14)	4926 (11)	9250 (15)	132
C(215)	4026 (8)	1629 (6)	7254 (9)	48	C(011)	989	220	2095	91
C(220)	2612 (7)	568 (5)	5158 (8)	31	C(012)A*	591	-494	1815	109
C(221)	2901 (7)	451 (6)	4473 (8)	41	C(013)A*	-255	-747	1115	97
C(222)	3015 (8)	-234 (6)	4198 (9)	48	C(014)A*	-704	-287	695	90
C(223)	2826 (8)	-785 (6)	4619 (9)	48	C(015)A*	-306	427	975	110
C(224)	2536 (8)	-689 (7)	5303 (9)	51	C(016)A*	-788	922	525	97
C(225)	2417 (8)	-10 (6)	5581 (9)	46	C(012)B*	546	-492	1706	112
C(230)	1546 (7)	1379 (5)	5889 (8)	34	C(013)B*	-345	-742	898	95
C(231)	1692 (9)	1699 (7)	6792 (10)	59	C(014)B*	-793	-281	478	91
C(232)	969 (10)	1599 (8)	7031 (11)	74	C(015)B*	-351	430	867	113
					C(016)B*	-832	925	416	102

*Population parameters of the disordered carbon atoms = 0.5.

measured, 6357 reflections observed, 6071 unique ($R_{int} = 0.011$; $0.72 < A < 0.82$). Final $R = 0.038$, $wR = 0.042$, $S = 1.6$ for 6071 unique reflections. Reflection/parameter ratio 9.7, $\Delta/\sigma < 0.38$; $-0.21 < \Delta\rho < 0.26 \text{ e \AA}^{-3}$.

(III). A green tabular crystal, $0.5 \times 0.5 \times 0.3 \text{ mm}$. $2\theta_{max} = 55^\circ$ ($h: -15 \rightarrow 15$, $k: 0 \rightarrow 26$, $l: 0 \rightarrow 14$). $0.996 < \sum(|F_o|/|F_o|_{initial})/5 < 1.007$. 6076 reflections measured, 3825 reflections observed, 3636 unique ($R_{int} = 0.013$; $0.65 < A < 0.77$). Final $R = 0.034$, $wR = 0.038$,

Table 2 (cont.)

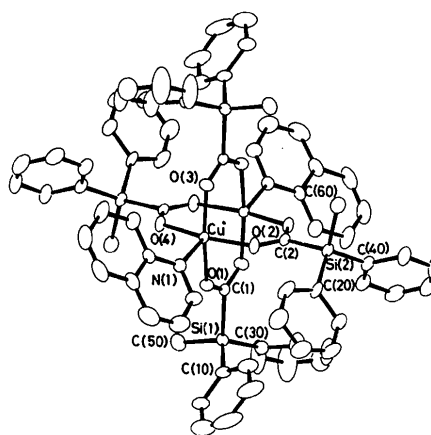
Cu(1)—Cu(2)—O(22)	82.2 (3)	C(310)—Si(3)—C(320)	110.0 (7)
Cu(1)—Cu(2)—O(23)	84.0 (2)	C(310)—Si(3)—C(330)	106.4 (7)
Cu(1)—Cu(2)—O(24)	82.7 (2)	C(320)—Si(3)—C(330)	114.0 (8)
Cu(1)—Cu(2)—N(2)	172.7 (2)	C(40)—Si(4)—C(410)	109.1 (6)
O(21)—Cu(2)—O(22)	87.9 (4)	C(40)—Si(4)—C(420)	111.0 (7)
O(21)—Cu(2)—O(23)	158.7 (3)	C(40)—Si(4)—C(430)	105.0 (8)
O(21)—Cu(2)—O(24)	89.5 (3)	C(410)—Si(4)—C(420)	108.0 (7)
O(21)—Cu(2)—N(2)	91.7 (3)	C(410)—Si(4)—C(430)	109.4 (8)
O(22)—Cu(2)—O(23)	91.4 (3)	C(420)—Si(4)—C(430)	114.2 (9)
O(22)—Cu(2)—O(24)	164.8 (3)	Cu(1)—O(11)—C(10)	124.2 (7)
O(22)—Cu(2)—N(2)	91.3 (3)	Cu(1)—O(12)—C(20)	122.3 (7)
O(23)—Cu(2)—O(24)	88.2 (3)	Cu(1)—O(13)—C(30)	122.9 (6)
O(23)—Cu(2)—N(2)	99.6 (3)	Cu(1)—O(14)—C(40)	124.2 (7)
O(24)—Cu(2)—N(2)	103.8 (3)	Cu(2)—O(21)—C(10)	122.8 (6)
C(10)—Si(1)—C(110)	107.5 (6)	Cu(2)—O(22)—C(20)	124.8 (6)
C(10)—Si(1)—C(120)	110.6 (7)	Cu(2)—O(23)—C(30)	123.0 (7)
C(10)—Si(1)—C(130)	108.3 (7)	Cu(2)—O(24)—C(40)	124.4 (7)
C(110)—Si(1)—C(120)	109.7 (7)	Si(1)—C(10)—O(11)	121.2 (8)
C(110)—Si(1)—C(130)	108.2 (7)	Si(1)—C(10)—O(21)	112.9 (7)
C(120)—Si(1)—C(130)	112.5 (9)	O(11)—C(10)—O(21)	125.7 (11)
C(20)—Si(2)—C(210)	110.2 (5)	Si(2)—C(20)—O(12)	114.7 (7)
C(20)—Si(2)—C(220)	105.9 (7)	Si(2)—C(20)—O(22)	120.2 (7)
C(20)—Si(2)—C(230)	111.0 (7)	O(12)—C(20)—O(22)	125.1 (10)
C(210)—Si(2)—C(220)	109.9 (7)	Si(3)—C(30)—O(13)	118.7 (8)
C(210)—Si(2)—C(230)	108.1 (7)	Si(3)—C(30)—O(23)	115.3 (8)
C(220)—Si(2)—C(230)	111.8 (9)	O(13)—C(30)—O(23)	126.0 (11)
C(30)—Si(3)—C(310)	112.1 (6)	Si(4)—C(40)—O(14)	115.5 (8)
C(30)—Si(3)—C(320)	106.5 (7)	Si(4)—C(40)—O(24)	120.0 (8)
C(30)—Si(3)—C(330)	107.8 (7)	O(14)—C(40)—O(24)	124.5 (11)

Prime means symmetry code $\bar{x}, \bar{y}, \bar{z}$.

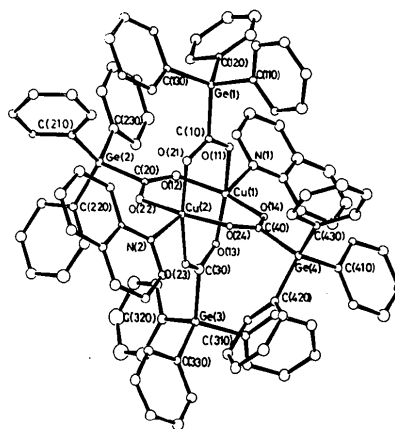
$S = 1.4$ for 3636 unique reflections. Reflection/parameter ratio 8.4, $\Delta/\sigma < 0.66$, $-0.31 < \Delta\rho < 0.30 \text{ e } \text{\AA}^{-3}$.

(IV). It was very difficult to obtain suitable crystals. A preliminary measurement at room temperature indicated decay of the crystal resulting from the release of the benzene of crystallization. In order to keep the crystal in good condition and to obtain a sufficient number of reflection data, the crystal specimen was maintained at 120 K with a stream of cold nitrogen gas. A dark green prismatic crystal, $0.3 \times 0.3 \times 0.5 \text{ mm}$. $2\theta_{\text{max}} = 40^\circ$ ($h: 0 \rightarrow 17$, $k: 0 \rightarrow 26$, $l: -18 \rightarrow 18$). $0.975 < \sum(|F_o|/|F_o|_{\text{initial}})/5 < 1.005$. 9845 reflections measured, 4721 reflections observed, 4070 unique ($R_{\text{int}} = 0.020$; $0.46 < A < 0.68$). Final $R = 0.059$, $wR = 0.069$, $S = 2.3$ for 4070 unique reflections. Reflection/parameter ratio 7.5, $\Delta/\sigma < 0.22$, $-0.66 < \Delta\rho < 0.76 \text{ e } \text{\AA}^{-3}$. The C atoms were refined isotropically to reduce the number of parameters. H atoms were not included in the refinement.

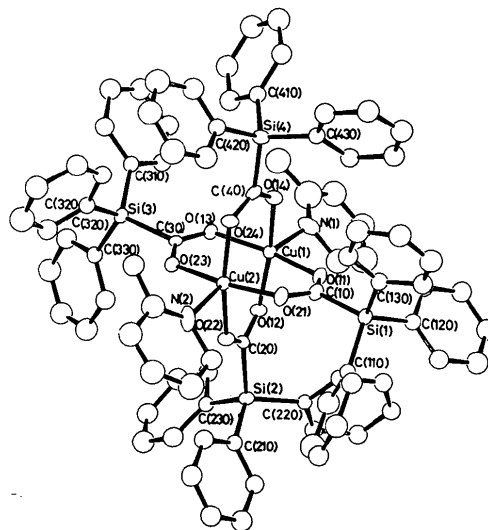
(V). A green prismatic crystal was ground into a sphere $0.60(2) \text{ mm}$ in diameter. $2\theta_{\text{max}} = 50^\circ$ ($h: -20 \rightarrow 20$, $k: -23 \rightarrow 23$, $l: 0 \rightarrow 19$). $0.933 < \sum(|F_o|/|F_o|_{\text{initial}})/5 < 1.000$. 17 608 reflections measured, 7072 reflections observed, 6757 unique ($R_{\text{int}} = 0.014$; $0.77 < A < 0.78$). The Fourier map indicated that one of the axial 2-picoline molecules is disordered. The disorder was treated assuming that the 2-picoline molecule takes two possible orientations related by a rotation of about 5° around the N(1)—C(011) bond axis with an occupancy of 0.5. The positional parameters of the disordered C atoms were estimated based on Fourier synthesis and not refined. The C atoms except for those in the carboxyl



(I)



(IV)



(V)

Fig. 1. ORTEP drawing (Johnson, 1971) of molecules (I), (IV) and (V) with thermal ellipsoids scaled at 30% probability level. The H atoms are omitted for clarity.

Table 3. A comparison of the average dimension of the $[\text{Cu}_2(\text{RCOO})_2]$ cage in $[\text{Cu}(\text{RCOO})_2L]_2$

	$R = \text{CH}_3$ $L = \text{py}$	$R = \text{H}$ $L = \text{py}$	$R = \text{Ph}_2\text{MeSi}$ $L = \text{quin}$ (I)	$R = \text{Ph}_2\text{MeC}$ $L = \text{quin}$ (II)	$R = \text{PhMe}_2\text{C}$ $L = \text{quin}$ (III)	$R = \text{Ph}_2\text{Ge}$ $L = \text{quin}$ (IV)	$R = \text{Ph}_2\text{Si}$ $L = 2\text{-pic}$ (V)
Cu...Cu (Å)	2.641 (1)	2.663 (1)	2.676 (1)	2.696 (1)	2.683 (1)	2.701 (2)	2.686 (2)
Cu—O average	1.974 (3)	1.976 (2)	1.975 (3)	1.971 (1)	1.978 (2)	1.984 (16)	1.984 (8)
minimum	1.960 (2)	1.965 (2)	1.962 (3)	1.953 (1)	1.963 (2)	1.948 (15)	1.958 (8)
maximum	1.980 (2)	1.981 (2)	1.981 (3)	1.984 (1)	1.994 (2)	2.031 (18)	2.015 (8)
Cu—L	2.191 (2)	2.162 (2)	2.195 (4)	2.234 (2)	2.220 (2)	2.184 (18)	2.269 (11)
Shift of Cu*	0.208 (1)	0.209 (1)	0.226 (2)	0.236 (6)	0.228 (3)	0.233 (6)	0.234 (5)
C—O	1.253 (4)	1.252 (3)	1.256 (6)	1.251 (3)	1.260 (3)	1.267 (26)	1.254 (13)
Cu—O—C (°)	123.4 (2)	122.3 (2)	124.1 (3)	124.0 (2)	124.0 (2)	123.2 (14)	123.6 (7)
O—C—O	125.2 (3)	127.5 (2)	125.0 (4)	125.6 (2)	124.7 (2)	125.6 (22)	125.3 (11)
$-2J$ (cm^{-1})†	330	501	1036	339	353	1100	1100
References	(a)	(b)	(c)	(c)	(c)	(c)	(c)

— $2J$ References: (a) Uekusa *et al.* (1989); (b) Bernard *et al.* (1979); (c) Present work.

*The shift of Cu atom from the O_4 plane.

†Magnetic susceptibilities in the temperature range of 80–300 K were determined by one of the authors (TT) by the Faraday method. The correction for diamagnetic contribution was made by use of Pascal's constants (Selwood, 1956).

The cryomagnetic data were fitted to the Bleaney–Bowers equation (1) allowing for the presence of paramagnetic impurity (Ginsberg, 1971),

$$\chi_A = \frac{Ng^2\beta^2}{3kT} \left[1 + \frac{1}{3} \exp(-2J/kT) \right]^{-1} (1-P) + \frac{Ng_i^2\beta^2 P}{4kT} + N\alpha \quad (1)$$

where P is the mole fraction of the noncoupled copper(II) impurity, g_i is the average g factor for the impurity which was fixed at 2.2 throughout the present study, and other symbols have their usual meanings. The best-fit parameters of $-2J$, g , and P were obtained by the non-linear least-squares fitting procedure. The quantity of fit was estimated by means of the discrepancy index

$$\sigma_{\text{dis}} = \left[\frac{\sum (\chi_{\text{obsd}} - \chi_{\text{calcd}})^2}{\sum \chi_{\text{obsd}}^2} \right]^{1/2}$$

The values of $-2J$ are summarized above.

bridges were refined isotropically. H atoms were not included.

Final $R = 0.090$, $wR = 0.107$, $S = 3.7$ for 6757 unique reflections. Reflection/parameter ratio 10.8, $\Delta/\sigma < 0.22$, $-0.53 < \Delta\rho < 1.74 e \text{ \AA}^{-3}$. The relatively large R value may be due to the disorder of the axial ligand.

Discussion. The coordinates and bond lengths and angles of (I)–(V) are given in Tables 1 and 2.* The structures of (I), (IV) and (V) are shown in Fig. 1. The compounds (I)–(III) possess a crystallographic center of symmetry. All the molecules are composed of dimeric units and each Cu atom has a slightly distorted square-pyramidal environment with four O atoms of the bridging carboxylate groups in the basal plane and an N atom in the apical position. The average dimensions of the central $[\text{Cu}_2(\text{COO})_4]$ cage for the complexes are compared in Table 3. The Cu...Cu distances of (I)–(V) are in the range from 2.676 (1) to 2.701 (2) Å, and are slightly longer than the distances reported for copper(II) acetates which vary over the range 2.56 to 2.67 Å (Melnik, 1982). A longer Cu—Cu distance is accompanied by a larger shift of the Cu atom from the O_4 basal plane in accordance with the general trend reported by Melnik (1982). The Cu—N bond lengths, 2.184 (18)–

2.269 (11) Å, and average Cu—O bond lengths, 1.975 (1)–1.984 (8) Å, are normal. In comparing the average dimensions of the $[\text{Cu}_2(\text{COO})_4]$ cage in the triorganoacetates (II) and (III) with the triorgano-silanecarboxylates and -germanecarboxylates (I), (IV) and (V), no special features are evident which can account for the large difference in the magnetic properties ($-2J \sim 300 \text{ cm}^{-1}$ for the triorganoacetates and $ca 1000 \text{ cm}^{-1}$ for the triorganosilanecarboxylates and -germanecarboxylate). In a previous study (Uekusa, Ohba, Saito, Kato, Tokii & Muto, 1989), a structural comparison between copper(II) acetates and formates has shown that there are no significant structural differences in the $[\text{Cu}_2(\text{COO})_4]$ cage. The structural data for the pyridine adducts of these complexes are also included in Table 3. The present investigation confirms that there are no structural correlations with the magnitudes of the spin superexchange interactions in the dimeric copper(II) carboxylates having square-pyramidal coordination. This conclusion suggests that the unusually large spin exchange interaction in the copper(II) silanecarboxylates and germanecarboxylate is not the result of any special geometrical features but is related to the electronic structure in the bridging ligands (Yamanaka, Uekusa, Ohba, Saito, Iwata, Kato, Steward, Tokii & Muto, 1990). The environment around the Cu atom shows a smaller distortion from the square-pyramidal D_{4h} symmetry than observed for $[\text{Cu}(\text{PhMe}_2\text{-Si}(\text{COO})_2\text{H}_2\text{O})_2]$ (Steward *et al.*, 1986), which exhibits unusual long and short Cu—O(basal) bond lengths, 2.104 (1)–1.832 (7) Å. The dihedral angles between

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52946 (227 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the adjacent bridging O—C—O moieties deviate from the ideal angle, 90°, by 4–13° for the complexes listed in Table 3. This distortion may arise from intramolecular steric repulsions between the bulky R_3 groups. The average Si—C(carboxyl) bond length is longer by 0.05 (1)–0.07 (2) Å than the average Si—C(Ph) or Si—C(Me) bond length in (I) and (V), while the average C—C(carboxyl) bond length is almost the same as the average C—C(Ph) or C—C(Me) bond length in (II) and (III). The same trend is also observed for the Ge—C bond length in (IV). Long Si—C(carbonyl) and Ge—C(carbonyl) bonds of a similar length have been reported in the related acylsilanes and -germanes (Chieh & Trotter, 1969; Harrison & Trotter, 1968). The Si—C(Ph) and Ge—C(Ph) bond lengths are similar to those reported for Ph_4Si [1.872 (7) Å; Glidewell & Sheldrick, 1971] and Ph_4Ge [1.957 (4) Å; Karipides & Haller, 1972], respectively.

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Structure of *trans*-Dichlorobis(ethylenediamine)platinum(IV) Perchlorate, *trans*-[PtCl₂(NH₂CH₂CH₂NH₂)₂](ClO₄)₂

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Abstract. [PtCl₂(C₂H₈N₂)₂](ClO₄)₂, $M_r = 585.1$, orthorhombic, *Ccmb*, $a = 9.604$ (1), $b = 18.746$ (2), $c = 8.604$ (1) Å, $V = 1549.1$ (3) Å³, $Z = 4$, $D_x = 2.51$ Mg m⁻³, $\text{Mo } K\alpha$ ($\lambda = 0.71073$ Å), $\mu = 9.89$ mm⁻¹, $F(000) = 1112$, $T = 300$ K. $R = 0.018$ for 1360 unique observed reflections. The Pt atom is coordinated octahedrally by two Cl atoms in *trans* positions and four amino N atoms. The complex

cation has a center of symmetry; the five-membered chelate rings adopt the *meso* form with the ligands in symmetric *gauche* (synclinal) conformations. The geometry of the perchlorate ion is very close to a regular tetrahedron. Two-dimensional networks of the cations and anions are formed *via* N—H...O hydrogen bonds. There is no linear stacking chain such as ...Cl—Pt—Cl...Cl—Pt—Cl... in the crystal.