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Magneto-Structural Correlations of Dimeric Copper(II) Trichloroacetates

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Abstract

Sixteen crystal structures of dimeric copper(II) trichloroacetates, (I)–(XVI), have been determined by single-crystal X-ray diffraction. In crystals of the compounds which have small $-2J$ values, less than 200 cm^{-1}, the coordination geometry around the Cu atom is deformed from square pyramidal (SP) to trigonal bipyramidal (TBP), and the Cu···Cu interatomic distance is elongated. The longer the Cu···Cu distance, the smaller the $-2J$ value, indicating that the spin super exchange interaction is weaker in the TBP than in the SP structure. The magnetic orbitals in the TBP structure may consist mainly of copper d_{z^2} orbitals (z along the axial direction of the TBP), which are perpendicular to each other at the two Cu atoms, and overlap only slightly with each other on the bridging carboxylate ligands. (I): Tetrakis(μ-trichloroacetato-O,O')-bis(2-ethylpyridine)dicopper(II), $[Cu(C_2Cl_3O_2)_2C_7H_9N]_2$, $-2J = 79$ cm^{-1}. (II): Tetrakis(μ-trichloroacetato-O,O')-bis(2,3-dimethylpyridine)dicopper(II) monotoluene solvate, $[Cu(C_2Cl_3O_2)_2C_7H_9N]_2.C_7H_8$, $-2J = 95$ cm^{-1}. (III): Tetrakis(μ-trichloroacetato-O,O')-bis(2,5-dimethylpyridine)dicopper(II) monotoluene solvate, $[Cu(C_2Cl_3O_2)_2C_7H_9N]_2.C_7H_8$, $-2J = 102$ cm^{-1}. (IV): Tetrakis(μ-trichloroacetato-O,O')-bis(3,4-dimethylpyridine)dicopper(II), $[Cu(C_2Cl_3O_2)_2C_7H_9N]_2$, $-2J = 107$ cm^{-1}. (V): Tetrakis(μ-trichloroacetato-O,O')-bis(2-chloro-5-nitropyridine)dicopper(II), $[Cu(C_2Cl_3O_2)_2C_5H_3ClN_2O_2]_2$, $-2J = 131$ cm^{-1}. (VI): Tetrakis(μ-trichloroacetato-O,O')-bis(caffeine)dicopper(II), $[Cu(C_2Cl_3O_2)_2C_8H_{10}N_4O_2]_2$, $-2J = 136$ cm^{-1}. (VII): Tetrakis(μ-trichloroacetato-O,O')-bis(3-cyanopyridine)dicopper(II), $[Cu(C_2Cl_3O_2)_2C_6H_4N_2]_2$, $-2J =$

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138 cm^{-1}. (VIII): Tetrakis(μ-trichloroacetato-*O*,*O*')-bis(2,5-dichloropyridine)dicopper(II) monobenzene solvate, $[Cu(C_2Cl_3O_2)_2C_5H_3Cl_2N]_2.C_6H_6$, $-2J = 141$ cm^{-1}. (IX): Tetrakis(μ-trichloroacetato-*O*,*O*')-bis(2,5-dichloropyridine)dicopper(II), $[Cu(C_2Cl_3O_2)_2C_5H_3Cl_2N]_2$ $-2J = 191$ cm^{-1}. (X): Tetrakis-(μ-trichloroacetato-*O*,*O*')-bis(3-chloropyridine)dicopper(II), $[Cu(C_2Cl_3O_2)_2C_5H_4ClN]_2$, $-2J = 193$ cm^{-1}. (XI): Tetrakis(μ-trichloroacetato-*O*,*O*')-(caffeine)dicopper(II) ditoluene solvate, $Cu_2(C_2Cl_3O_2)_4C_8H_{10}N_4O_2].2C_7H_8$, $-2J = 220$ cm^{-1}. (XII): Tetrakis(μ-trichloroacetato-*O*,*O*')bis(4-cyanopyridine)dicopper(II), $[Cu(C_2Cl_3O_2)_2C_6H_4N_2]_2$, $-2J = 229$ cm^{-1}. (XIII): Tetrakis(μ-trichloroacetato-*O*,*O*')-bis(4,7-dichloroquinoline)dicopper(II), $[Cu(C_2Cl_3O_2)_2C_9H_5Cl_2N]_2$, $-2J = 237$ cm^{-1}. (XIV): Tetrakis-(μ-trichloroacetato-*O*,*O*')-bis(2-fluorobenzothiazole)-dicopper(II), $[Cu(C_2Cl_3O_2)_2C_7H_4FNS]_2$, $-2J = 240$ cm^{-1}. (XV): Tetrakis(μ-trichloroacetato-*O*,*O*')-bis(3,5-dichloropyridine)dicopper(II) monotoluene solvate, $[Cu(C_2Cl_3O_2)_2C_5H_3Cl_2N]_2.C_7H_8$. (XVI): Tetrakis($\mu$-trichloroacetato-*O*,*O*')-bis(3,5-dimethylpyridine)dicopper(II) dibenzene solvate, $[Cu(C_2Cl_3O_2)_2C_7H_9N]_2.2C_6H_6$. The $-2J$ values of (XV) and (XVI) after removal of solvent molecules from the crystals are 92 and 74 cm^{-1}, respectively.

Introduction

In the copper(II) carboxylate dimers, an antiferromagnetic spin-exchange interaction exists between the two copper(II) atoms through the four bridging carboxylate ions. The magnitude of the exchange interaction is given by $-2J$, the separation energy between the singlet ground state and the triplet state. The $-2J$ value differs greatly between copper(II) acetate (*ca* 340 cm^{-1}), formate (*ca* 500 cm^{-1}) and triorganosilanecarboxylate dimers (*ca* 1000 cm^{-1}; Steward, McAfee, Chang, Piskor, Schreiber, Jury, Taylor, Pletcher & Chen, 1986). A previous study revealed that these differences in the $-2J$ value are not the result of any geometrical features, but result from the different electronic structures of the bridging ligands. The key point which 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; Yamanaka, Uekusa, Ohba, Saito, Iwata, Kato, Tokii, Muto & Steward, 1991). When the bridging carboxylate ions are identical and the axial ligands are interchanged among the pyridine derivatives, the changes in the $-2J$ values usually lie in a narrow range (with 40 cm^{-1}). For example, $-2J = 482$–501 cm^{-1} for copper(II) formates, 300–340 cm^{-1} for copper(II) acetates, 330–360 cm^{-1} for copper(II) propionates and 366–403 cm^{-1} for copper(II) trimethylacetates (Kato & Muto, 1988). In contrast to this trend, copper(II) trichloroacetate dimers show a wide range of $-2J$ values (from 80 to 240 cm^{-1}) (Muto, Nakashima, Tokii, Kato & Suzuki, 1987), and the reflectance and ESR spectra suggest that the coordination geometry around the copper atom is trigonal bipyramidal (TBP) in crystals for which small $-2J$ values are observed.

Although a large number of structures have been reported for copper(II) carboxylate dimers, only three have TBP geometry: $[Cu(Ph_3CCOO)_2(py)]_2$.benzene ($-2J = 187$ cm^{-1}; Steward, Kato, Chang, Sax, Chang, Jury, Muto, Tokii, Taura, Pletcher & Yoo, 1991), $[Cu(Cl_3CCOO)_2(tempo)]_2$ (tempo = 2,2,5,5-tetramethylpyrrolin-1-one) and $[Cu(Cl_3CCOO)_2(proxyl)]_2$ (proxyl = 2,2,5,5-tetramethylpyrrolinyl-1-oxy) (Porter, Dickman & Doedens, 1986). The monodentate ligands of the latter two dimers are radicals, and the compounds are diamagnetic. The effect of the TBP geometry on the spin super-exchange interactions between the Cu^{II} atoms has not been extensively investigated yet. In the present study, the structures of 16 copper(II) trichloroacetate dimers have been determined in order to establish correlations between $-2J$ values and the deformation of the cage structure from the SP towards the TBP arrangement. Correlations between the molecular structure and the ESR, IR and reflectance spectra have also been investigated (Horie, Tokii, Muto, Steward, Chang, Suzuki, Uekusa, Ohba, Husebye & Kato, 1992). Crystal data are summarized in Table 1.

Experimental

Experimental details are listed in Table 2. The compounds were synthesized by Muto *et al.* (1987). The magnetic data for crystalline samples sometimes depend on the solvent of crystallization, because of differences between the crystal and molecular structures. For example, the $-2J$ values of the 2,5-Cl_2-py adducts are (VIII) 141 and (IX) 191 cm^{-1} when the crystals are grown from benzene and cyclohexane solutions, respectively. Except for (V) the X-ray intensities were measured at Keio University on a Rigaku AFC-5 four-circle diffractometer using the θ–2θ or ω-scan technique with Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) monochromatized by a graphite plate at $T = 297$–300 K. Cell parameters were refined by least squares for 16–50 2θ values ($20 < 2\theta < 30°$). An absorption correction was applied using the Gaussian numerical integration method (Busing & Levy, 1957). The structures were solved by Patterson and Fourier methods. The positional parameters, anisotropic thermal parameters of non-H atoms, and isotropic thermal parameters of H atoms were refined by block-diagonal least squares. The function

Table 1. *Crystal data*

	(I)	(II)	(III)	(IV)	(V)	(VI)	(VII)	(VIII)
M_r	990.88	1083.58	1083.60	990.88	1093.71	1165.56	984.83	1151.44
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/a$	$P2_1/c$	$P\bar{1}$	$C2/c$	$P\bar{1}$	$P2_1/a$
a (Å)	11.144 (1)	21.544 (4)	21.010 (1)	20.567 (2)	13.603 (2)	20.048 (2)	10.952 (1)	20.370 (2)
b (Å)	18.291 (2)	18.099 (4)	18.725 (2)	10.414 (2)	14.122 (2)	17.575 (2)	16.338 (2)	18.296 (3)
c (Å)	9.206 (1)	11.423 (2)	11.574 (1)	18.231 (2)	9.796 (2)	12.350 (1)	10.833 (1)	11.505 (2)
α (°)	97.56 (1)				98.269 (1)		106.80 (1)	
β (°)	100.53 (1)	99.49 (2)	104.90 (1)	106.13 (1)	93.762 (1)	106.01 (2)	97.02 (1)	100.35 (1)
γ (°)	84.05 (1)				80.286 (1)		71.90 (1)	
V (Å^3)	1822.8 (3)	4393 (2)	4400.3 (2)	3751 (2)	1834.0 (5)	4182.7 (7)	1762.8 (3)	4218 (1)
Z	2	4	4	4	2	4	2	4
D_x (Mg m^{-3})	1.81	1.64	1.64	1.76	1.98	1.85	1.86	1.81
μ(Mo $K\alpha$) (mm^{-1})	2.103	1.752	1.749	2.043	*	1.857	2.175	2.079
F(000)	980	2160	2160	1960	1068	2312	964	2256

	(IX)	(X)	(XI)	(XII)	(XIII)	(XIV)	(XV)	(XVI)
M_r	1072.59	1003.66	1155.08	984.83	1172.66	1082.92	1164.73	1147.1
Crystal system	Triclinic	Triclinic	Tetragonal	Monoclinic	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P4_2/ncm$	$P2_1/a$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$C2/c$
a (Å)	11.359 (1)	10.246 (1)	15.731 (2)	20.788 (5)	10.201 (1)	10.336 (2)	10.859 (2)	19.547 (3)
b (Å)	17.928 (2)	10.739 (1)		17.951 (4)	11.688 (2)	11.381 (3)	19.225 (2)	14.990 (1)
c (Å)	9.324 (1)	9.598 (1)	19.115 (3)	9.693 (2)	9.301 (1)	9.272 (1)	10.692 (2)	17.181 (3)
α (°)	97.35 (1)	103.27 (1)			107.37 (1)	107.30 (1)	91.01 (1)	
β (°)	103.04 (1)	111.23 (1)		99.45 (2)	100.45 (1)	94.63 (2)	97.89 (2)	106.93 (2)
γ (°)	92.66 (1)	62.36 (1)			73.99 (1)	66.53 (2)	81.11 (1)	
V (Å^3)	1829.0 (9)	869.6 (8)	4730 (1)	3568 (1)	1011.4 (2)	954.3 (4)	2184.4 (6)	4816.0 (9)
Z	2	1	4	4	1	1	2	4
D_x (Mg m^{-3})	1.95	1.92	1.62	1.83	1.93	1.88	1.77	1.58
μ(Mo $K\alpha$) (mm^{-1})	2.390	2.356	1.642	2.149	2.169	2.125	2.008	1.603
F(000)	1044	490	2304	1928	574	530	1144	2296

* μ(Cu $K\alpha$) = 11.584 mm^{-1}.

$\sum w(|F_o| - |F_c|)^2$ was minimized with $w^{-1} = \sigma^2(|F_o|) + (0.015|F_o|)^2$. H atoms were either located in difference syntheses or calculated theoretically and included in the refinement except for (II), (III), (V), (VIII), (XI), (XII), (XV) and (XVI), for which the Cl atoms of the bridging ligands are extensively disordered. 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 (Sakurai & Kobayashi, 1979) and the *XTAL*3.0 (Hall & Stewart, 1990) computation program systems on a FACOM M-780/10 computer and MIPS RS3230 workstation at Keio University. The intensity data for (V) were collected at the University of Pittsburg using a Picker FACS-1 four-circle diffractometer with graphite-monochromated Cu $K\alpha$ radiation (λ = 1.5418 Å) by θ–2θ scan at room temperature. The structure was solved by direct methods and refined by full-matrix least squares using the program *QWKREF* (Furey, Wang & Sax, 1982). Atomic coordinates are listed in Table 3, and selected bond lengths and bond angles in Table 4.* The space groups were unambiguously determined from systematic absences for (II) $P2_1/n$ ($h + l = 2n + 1$ for $h0l$ and $k = 2n + 1$ for $0k0$); for (III), (VIII) and (XII) $P2_1/a$ ($h = 2n + 1$ for $h0l$ and $k = 2n + 1$ for $0k0$); (IV) $P2_1/c$ ($l = 2n + 1$ for $h0l$ and $k = 2n + 1$ for $0k0$); and (XI) $P4_2/ncm$ ($h + k = 2n + 1$ for $hk0$, $l = 2n + 1$ for $h0l$). For (I), (V), (VII), (IX), (X), (XIII), (XIV) and (XV), the space group $P\bar{1}$ was determined by successful refinement of a centrosymmetric model. Systematic absences for (VI) and (XVI) ($h + k = 2n + 1$ for hkl and h or $l = 2n + 1$ for $h0l$) indicated either Cc or $C2/c$. The refinement was successful using the centrosymmetric space group $C2/c$.

Rotational disorder of the trichloromethyl group of Cl_3CCOO^- around the C—C bond was observed in most of the compounds. The positions of the chlorine atoms were split into two or three sets with the estimated occupancy factors listed in Table 3. The chlorine atoms with the largest occupancy factor were refined anisotropically and the other sites isotropically. R factors for (II), (VIII) and (XI) are larger than 0.07 as a result of disorder of the solvent molecules of crystallization or of the monodentate ligands. In (II), the toluene of crystallization adopts two possible orientations in the same plane with an occupancy factor of 0.5 (see scheme below). In (VIII), one of the 2,5-Cl_2-pyridines, which contains the N(2) atom, showed large thermal parameters ($0.07 < U_{eq} < 0.23$ Å^2) suggesting static disorder. In (XI), the Cu···Cu dimeric unit lies on a site with $2/m$ symmetry and the caffeine molecule is at a $2mm$ site with the O(12), C(2), C(5) and N(7) atoms on a 4_2 screw axis (see scheme below). Therefore, the caffeine molecule shows orientational disorder around

* Lists of structure factors, anisotropic thermal parameters, bond lengths and bond angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55099 (156 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS0591]

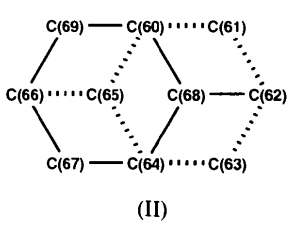
Table 2. *Experimental data and structure-refinement parameters*

	(I)	(II)	(III)	(IV)	(V)	(VI)	(VII)	(VIII)
Color	Pale green	Pale green	Pale blue	Pale green	Pale green	Pale green	Pale green	Pale green
Solvent for recrystallization	Benzene	Toluene	Toluene	Benzene	Benzene	Chloroform	Chloroform	Benzene
Crystal dimensions (mm)	0.50 × 0.25 × 0.20	0.50 × 0.50 × 0.25	0.55 × 0.20 × 0.20	0.45 × 0.25 × 0.15	0.40 × 0.30 × 0.20	0.40 × 0.20 × 0.15	0.30 × 0.25 × 0.20	0.60 × 0.20 × 0.20
$2\theta_{max}$ (°)	55	50	50	50	120*	55	55	50
h	−14 to 14	−25 to 25	0 to 24	−24 to 24	0 to 15	0 to 26	−14 to 14	0 to 24
k	0 to 23	0 to 21	0 to 22	0 to 12	−16 to 16	0 to 22	−21 to 21	0 to 21
l	−11 to 11	0 to 13	−13 to 13	0 to 21	−11 to 11	−16 to 16	−14 to 0	−13 to 13
Variation of F_o for standard reflections†	0.995–1.005	0.975–1.000	0.984–1.002	0.985–1.006	0.927–1.000	0.992–1.004	0.976–1.000	0.981–1.004
No. of reflections measured	8610	8496	8165	7291	5460	4940	8521	7831
No. of reflections observed‡	5392	3539	3684	3138	3142	3248	4499	3129
No. of unique reflections	5205	3367	3576	3023	2874	3152	4248	3030
R_{int}	0.011	0.016	0.014	0.022	0.025	0.016	0.014	0.014
Relative transmission factors	0.58–0.69	0.45–0.66	0.62–0.75	0.59–0.76	0.62–1.00	0.61–0.81	0.57–0.71	0.61–0.73
H atoms	18/18 found	Not included	Not included	13/18 found	Not included	12/12 found	7/8 found	Not included
$R(F)$	0.055	0.077	0.066	0.050	0.081	0.035	0.064	0.087
$wR(F)$	0.065	0.074	0.065	0.039	0.086	0.038	0.051	0.084
S	2.42	2.39	2.28	2.36	4.56	1.45	3.13	2.68
Reflection/parameter ratio	9.71	6.09	6.22	6.05	6.13	10.4	9.02	6.54
$(\Delta/\sigma)_{max}$	0.03	0.46	0.22	0.12	0.82	0.15	0.06	0.47
$\Delta\rho$(min., max.) (e Å^{-3})	−1.31, 1.21	−0.52, 0.72	−0.51, 0.51	−0.55, 0.59	−1.23, 0.78	−0.47, 0.47	−1.05, 0.81	−0.70, 1.07

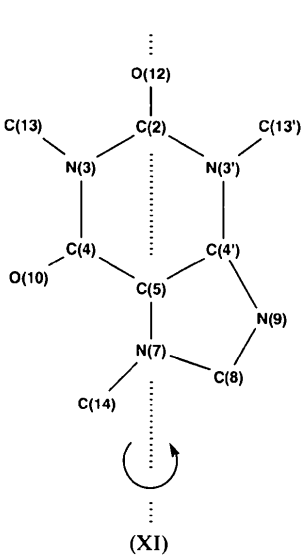
	(IX)	(X)	(XI)	(XII)	(XIII)	(XIV)	(XV)	(XVI)
Color	Pale green	Pale green	Pale green	Pale green	Green	Green	Pale blue	Pale green
Solvent for recrystallization	Cyclohexane	Benzene	Toluene	Tetrachloro-methane	Benzene	Benzene	Toluene	Benzene
Crystal dimensions (mm)	0.40 × 0.20 × 0.15	0.45 × 0.45 × 0.30	0.40 × 0.35 × 0.20	0.60 × 0.20 × 0.13	0.35 × 0.30 × 0.20	0.35 × 0.25 × 0.20	0.45 × 0.30 × 0.20	0.60 × 0.40 × 0.20
$2\theta_{max}$ (°)	55	55	50	50	55	55	50	55
h	−14 to 14	−13 to 13	0 to 18	−24 to 24	−13 to 13	−13 to 13	−12 to 12	0 to 25
k	0 to 23	−13 to 13	0 to 18	0 to 21	0 to 15	−14 to 14	−22 to 22	0 to 19
l	−12 to 12	−12 to 0	0 to 22	0 to 11	−12 to 12	0 to 12	0 to 12	−22 to 22
Variation of F_o for standard reflections†	0.989–1.003	0.990–1.000	0.991–1.002	0.978–1.000	0.993–1.000	0.991–1.016	0.956–1.000	0.957–1.001
No. of reflections measured	8670	4242	5362	7327	4879	4662	8260	5695
No. of reflections observed‡	4787	3368	2957	3314	3637	2935	4822	2822
No. of unique reflections	4627	3159	1189	3088	3513	2751	4466	2729
R_{int}	0.011	0.008	0.022	0.017	0.010	0.012	0.017	0.015
Relative transmission factors	0.62–0.73	0.54–0.59	0.68–0.77	0.66–0.77	0.51–0.67	0.56–0.69	0.56–0.70	0.53–0.75
H atoms	6/6 found	4/4 found	Not included	Not included	5/5 found	4/4 found	Not included	Not included
$R(F)$	0.045	0.041	0.093	0.061	0.045	0.052	0.068	0.064
$wR(F)$	0.037	0.037	0.095	0.042	0.054	0.060	0.063	0.069
S	2.67	3.90	3.35	2.61	2.10	2.22	2.15	2.39
Reflection/parameter ratio	10.5	13.9	7.3	6.50	9.90	9.90	7.95	9.06
$(\Delta/\sigma)_{max}$	0.08	0.05	0.33	0.35	0.11	0.08	0.22	0.19
$\Delta\rho$(min., max.) (e Å^{-3})	−0.84, 0.93	−0.70, 0.61	−0.85, 0.93	−0.68, 0.65	−1.06, 1.38	−0.88, 1.18	−0.61, 0.58	−0.52, 0.57

* Cu $K\alpha$.
† $\langle |F_o|/|F_o|_{initial} \rangle$.
‡ $|F_o| > 3\sigma(|F_o|)$.

the pseudo-intramolecular twofold axis, but the positions of the N(9), O(10), C(8) and C(14) atoms could be separated.



(II)



(XI)

Crystal structure analyses of $[Cu(Cl_3CCOO)_2$-(3-Me-py)$]_2$ ($-2J = 83$ cm^{-1}) and $[Cu(Cl_3CCOO)_2$(2,4-Me_2-py)$]_2.C_6H_6$ ($-2J = 99$ cm^{-1}) were not carried out because two independent dimers exist in these crystals and a sufficient number of reflections could not be collected. Crystals of the 3-Me-py adduct are monoclinic, $C2/c$, $a = 37.288$ (6), $b = 20.997$ (8), $c = 18.201$ (3) Å, $\beta = 96.56$ (1)°, $V = 14157$ (6) Å^3, $Z = 16$; crystals of the 2,4-Me_2-py adduct are triclinic, $P\bar{1}$, $a = 11.316$ (4), $b = 20.669$ (6), $c = 19.121$ (6) Å, $\alpha = 90.66$ (2), $\beta = 106.83$ (2), $\gamma = 89.04$ (2)°, $V = 4280$ (2) Å^3, $Z = 4$. Magnetic susceptibilities over the temperature range 80–300 K were determined by one of the present authors (TT) using the Faraday method. The procedure for determining the $-2J$ value from cryomagnetic data based on the Bleaney–Bowers equation is described elsewhere (Uekusa, Ohba, Satio, Kato, Steward, Tokii & Muto, 1990). A small discontinuity of the magnetic susceptibility of (XI) at *ca* 240 K suggests a phase transition. On lowering the temperature by using a nitrogen-gas-

Table 3. *Fractional atomic coordinates and thermal parameters* ($Å^2$) *with e.s.d.'s in parentheses, and occupancy parameters for non-*H *atoms*

Anisotropically refined atoms are flagged with an asterisk. $U_{eq} = (1/3)\Sigma_i\Sigma_j a_i^* a_j^* U_{ij} \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U	Occupancy
(I)					
Cu(1)	0.17764 (6)	0.33485 (4)	0.51979 (7)	0.0361 (2)*	
Cu(2)	0.31323 (6)	0.17395 (4)	0.42189 (7)	0.0390 (2)*	
O(11)	0.3359 (3)	0.3516 (2)	0.6429 (4)	0.041 (1)*	
O(12)	0.2554 (3)	0.3367 (2)	0.3396 (4)	0.044 (1)*	
O(13)	0.0275 (3)	0.3080 (2)	0.3927 (4)	0.041 (1)*	
O(14)	0.1624 (3)	0.2361 (2)	0.6493 (4)	0.041 (1)*	
O(21)	0.4227 (3)	0.2401 (2)	0.5703 (4)	0.048 (1)*	
O(22)	0.3468 (3)	0.2259 (2)	0.2657 (4)	0.047 (1)*	
O(23)	0.1108 (3)	0.1945 (2)	0.3237 (4)	0.044 (1)*	
O(24)	0.2619 (3)	0.1286 (2)	0.5755 (4)	0.045 (1)*	
N(1)	0.0776 (4)	0.4044 (2)	0.6515 (5)	0.035 (1)*	
N(2)	0.3326 (4)	0.0742 (2)	0.2983 (5)	0.040 (2)*	
C(1)	0.4240 (5)	0.3044 (3)	0.6309 (5)	0.036 (2)*	
C(2)	0.3158 (5)	0.2931 (3)	0.2599 (6)	0.037 (2)*	
C(3)	0.0261 (5)	0.2424 (3)	0.3290 (6)	0.036 (2)*	
C(4)	0.1894 (5)	0.1694 (3)	0.6474 (6)	0.038 (2)*	
C(5)	0.5526 (5)	0.3319 (3)	0.6904 (6)	0.042 (2)*	
C(6)	0.3547 (6)	0.3250 (3)	0.1291 (7)	0.052 (2)*	
C(7)	−0.1033 (5)	0.2229 (3)	0.2499 (7)	0.050 (2)*	
C(8)	0.1268 (6)	0.1268 (3)	0.7437 (7)	0.060 (3)*	
C(11)	−0.0093 (5)	0.3748 (3)	0.7031 (6)	0.044 (2)*	
C(12)	−0.0887 (6)	0.4160 (4)	0.7855 (7)	0.060 (3)*	
C(13)	−0.0784 (6)	0.4904 (4)	0.8137 (8)	0.075 (3)*	
C(14)	0.0062 (6)	0.5218 (3)	0.7600 (7)	0.063 (3)*	
C(15)	0.0869 (5)	0.4779 (3)	0.6781 (6)	0.041 (2)*	
C(16)	0.1835 (6)	0.5114 (3)	0.6241 (8)	0.059 (3)*	
C(17)	0.2858 (7)	0.5321 (4)	0.749 (1)	0.088 (4)*	
C(21)	0.2322 (6)	0.0363 (3)	0.2570 (7)	0.051 (2)*	
C(22)	0.2348 (7)	−0.0318 (4)	0.1752 (8)	0.068 (3)*	
C(23)	0.3410 (8)	−0.0616 (4)	0.1308 (8)	0.076 (3)*	
C(24)	0.4438 (7)	−0.0236 (4)	0.1704 (8)	0.072 (3)*	
C(25)	0.4379 (6)	0.0462 (3)	0.2538 (7)	0.051 (2)*	
C(26)	0.5509 (6)	0.0886 (4)	0.2997 (8)	0.066 (3)*	
C(27)	0.6145 (8)	0.0763 (5)	0.4490 (9)	0.088 (4)*	
Cl(1)	0.5531 (2)	0.3993 (1)	0.8487 (2)	0.0490 (6)*	0.80
Cl(2)	0.6609 (2)	0.2574 (1)	0.7386 (3)	0.0675 (8)*	0.80
Cl(3)	0.5857 (2)	0.3815 (1)	0.5496 (2)	0.0644 (8)*	0.80
Cl(4)	0.3990 (2)	0.4147 (1)	0.1828 (3)	0.0669 (9)*	0.80
Cl(5)	0.2190 (3)	0.3304 (1)	−0.0106 (2)	0.082 (1)*	0.80
Cl(6)	0.4671 (3)	0.2679 (2)	0.0526 (4)	0.130 (2)*	0.80
Cl(7)	−0.1105 (2)	0.1274 (1)	0.1964 (3)	0.082 (1)*	0.80
Cl(8)	−0.1402 (2)	0.2727 (2)	0.0888 (2)	0.081 (1)*	0.80
Cl(9)	−0.2133 (2)	0.2540 (2)	0.3637 (3)	0.080 (1)*	0.80
Cl(10)	0.0134 (3)	0.1812 (2)	0.8257 (4)	0.085 (1)*	0.70
Cl(11)	0.0696 (4)	0.0473 (2)	0.6400 (5)	0.143 (2)*	0.70
Cl(12)	0.2388 (3)	0.1065 (3)	0.9005 (4)	0.143 (2)*	0.70
Cl(51)	0.6002 (7)	0.3489 (5)	0.5296 (9)	0.053 (2)*	0.20
Cl(52)	0.6769 (7)	0.2643 (4)	0.6901 (8)	0.050 (2)*	0.20
Cl(53)	0.5724 (7)	0.3757 (4)	0.8643 (8)	0.048 (2)*	0.20
Cl(61)	0.3627 (9)	0.4242 (6)	0.174 (1)	0.075 (3)*	0.20
Cl(62)	0.5144 (9)	0.2873 (5)	0.132 (1)	0.067 (2)*	0.20
Cl(63)	0.2705 (9)	0.3113 (5)	−0.026 (1)	0.072 (3)*	0.20
Cl(71)	−0.0942 (9)	0.1336 (6)	0.146 (1)	0.073 (3)*	0.20
Cl(72)	−0.1769 (9)	0.2688 (6)	0.122 (1)	0.079 (3)*	0.20
Cl(73)	−0.1880 (9)	0.2208 (6)	0.401 (1)	0.080 (3)*	0.20
Cl(81)	−0.0291 (8)	0.1673 (5)	0.736 (1)	0.112 (3)*	0.30
Cl(82)	0.1375 (8)	0.0336 (5)	0.7070 (9)	0.104 (3)*	0.30
Cl(83)	0.163 (1)	0.1465 (6)	0.922 (1)	0.141 (4)*	0.30
(II)					
Cu(1)	0.54578 (6)	0.25231 (9)	0.3683 (1)	0.0485 (5)*	
Cu(2)	0.69669 (6)	0.25242 (9)	0.3944 (1)	0.0496 (5)*	
O(11)	0.5886 (3)	0.1769 (4)	0.4866 (8)	0.052 (3)*	
O(12)	0.6948 (3)	0.1748 (5)	0.5122 (7)	0.055 (3)*	
O(21)	0.5516 (3)	0.3247 (5)	0.4920 (8)	0.059 (3)*	
O(22)	0.6570 (3)	0.3280 (5)	0.5169 (8)	0.060 (3)*	
O(31)	0.5847 (3)	0.3332 (5)	0.2565 (7)	0.053 (3)*	
O(32)	0.6896 (3)	0.3327 (5)	0.2803 (8)	0.059 (3)*	
O(41)	0.5497 (3)	0.1790 (5)	0.2456 (8)	0.058 (3)*	
O(42)	0.6553 (3)	0.1815 (5)	0.2694 (7)	0.058 (3)*	
N(1)	0.4541 (4)	0.2757 (5)	0.3118 (9)	0.046 (4)*	
N(2)	0.7884 (4)	0.2773 (6)	0.4469 (8)	0.047 (4)*	
C(10)	0.6418 (5)	0.1510 (6)	0.526 (1)	0.042 (4)*	
C(11)	0.6417 (6)	0.0828 (9)	0.604 (1)	0.081 (7)*	
C(20)	0.6052 (6)	0.3452 (7)	0.537 (1)	0.057 (5)*	
C(21)	0.6063 (7)	0.398 (1)	0.643 (2)	0.14 (1)*	
C(30)	0.6367 (5)	0.3571 (7)	0.242 (1)	0.053 (5)*	
C(31)	0.6364 (6)	0.4305 (9)	0.173 (1)	0.068 (6)*	
C(40)	0.6034 (6)	0.1591 (7)	0.228 (1)	0.054 (5)*	
C(41)	0.5991 (7)	0.094 (1)	0.139 (2)	0.099 (8)*	
C(101)	0.4068 (5)	0.2275 (8)	0.317 (1)	0.059 (5)*	
C(102)	0.3445 (5)	0.247 (1)	0.277 (1)	0.071 (6)*	
C(103)	0.3325 (6)	0.3172 (9)	0.229 (1)	0.076 (6)*	
C(104)	0.3803 (6)	0.3673 (9)	0.227 (1)	0.074 (6)*	
C(105)	0.4412 (6)	0.3461 (7)	0.271 (1)	0.055 (5)*	
C(106)	0.4260 (7)	0.1509 (8)	0.367 (1)	0.069 (6)*	
C(107)	0.2924 (6)	0.191 (1)	0.286 (1)	0.092 (7)*	
C(201)	0.8351 (5)	0.2284 (7)	0.439 (1)	0.047 (4)*	
C(202)	0.8991 (5)	0.2510 (8)	0.479 (1)	0.059 (5)*	
C(203)	0.9108 (6)	0.3204 (9)	0.520 (1)	0.074 (6)*	
C(204)	0.8622 (6)	0.3696 (8)	0.526 (1)	0.069 (6)*	
C(205)	0.8008 (6)	0.3484 (8)	0.489 (1)	0.061 (5)*	
C(206)	0.8182 (7)	0.1526 (8)	0.393 (1)	0.072 (6)*	
C(207)	0.9526 (6)	0.196 (1)	0.469 (2)	0.099 (8)*	
Cl(1)	0.5683 (3)	0.0432 (4)	0.5995 (9)	0.172 (5)*	0.75
Cl(2)	0.7002 (4)	0.0218 (4)	0.5811 (8)	0.147 (4)*	0.75
Cl(3)	0.6665 (5)	0.1123 (6)	0.7537 (6)	0.175 (5)*	0.75
Cl(4)	0.6722 (3)	0.4426 (4)	0.6944 (7)	0.123 (3)*	0.75
Cl(5)	0.5380 (3)	0.4451 (5)	0.6516 (9)	0.175 (5)*	0.75
Cl(6)	0.6101 (5)	0.3279 (7)	0.7736 (7)	0.191 (6)*	0.75
Cl(7)	0.5681 (3)	0.4510 (5)	0.0833 (8)	0.147 (4)*	0.70
Cl(8)	0.6982 (4)	0.4417 (5)	0.0966 (8)	0.145 (4)*	0.70
Cl(9)	0.6489 (7)	0.4985 (4)	0.2851 (8)	0.191 (6)*	0.70
Cl(10)	0.5367 (2)	0.0311 (3)	0.1528 (6)	0.121 (3)*	0.90
Cl(11)	0.6705 (2)	0.0448 (4)	0.1532 (7)	0.158 (3)*	0.90
Cl(12)	0.5860 (3)	0.1290 (5)	−0.0029 (5)	0.152 (4)*	0.90
Cl(101)	0.701 (1)	0.056 (1)	0.686 (2)	0.141 (8)	0.25
Cl(102)	0.630 (1)	0.009 (2)	0.481 (3)	0.17 (1)	0.25
Cl(103)	0.587 (1)	0.071 (2)	0.676 (2)	0.16 (1)	0.25
Cl(201)	0.554 (1)	0.483 (1)	0.552 (2)	0.115 (7)	0.25
Cl(202)	0.6753 (9)	0.469 (1)	0.622 (2)	0.106 (6)	0.25
Cl(203)	0.573 (1)	0.385 (2)	0.734 (3)	0.17 (1)	0.25
Cl(301)	0.7041 (7)	0.4746 (9)	0.198 (1)	0.093 (4)	0.30
Cl(302)	0.5740 (9)	0.488 (1)	0.192 (2)	0.129 (6)	0.30
Cl(303)	0.631 (1)	0.395 (1)	0.026 (2)	0.160 (8)	0.30
Cl(401)	0.549 (2)	0.064 (3)	0.057 (4)	0.09 (1)	0.10
Cl(402)	0.669 (2)	0.029 (3)	0.223 (4)	0.09 (1)	0.10
Cl(403)	0.628 (4)	0.118 (6)	0.012 (9)	0.23 (4)	0.10
C(60)	0.9058 (9)	0.205 (1)	0.102 (2)	0.121 (9)*	
C(61)	0.942 (2)	0.261 (2)	0.146 (3)	0.12 (2)*	0.50
C(62)	0.926 (1)	0.334 (2)	0.200 (2)	0.18 (2)*	
C(63)	0.856 (2)	0.336 (3)	0.183 (3)	0.15 (2)*	0.50
C(64)	0.820 (1)	0.286 (1)	0.141 (2)	0.13 (1)*	
C(65)	0.835 (2)	0.216 (2)	0.081 (3)	0.12 (2)*	0.50
C(66)	0.800 (1)	0.163 (2)	0.045 (2)	0.21 (2)*	
C(67)	0.783 (2)	0.232 (2)	0.095 (3)	0.13 (2)*	0.50
C(68)	0.889 (2)	0.276 (2)	0.147 (2)	0.10 (2)*	0.50
C(69)	0.869 (2)	0.158 (2)	0.053 (3)	0.11 (2)*	0.50
(III)					
Cu(1)	0.21086 (5)	0.26118 (6)	0.13173 (9)	0.0584 (4)*	
Cu(2)	0.05206 (5)	0.26038 (7)	0.06569 (9)	0.0691 (5)*	
O(11)	0.1702 (3)	0.3221 (3)	−0.0124 (5)	0.068 (2)*	
O(12)	0.2028 (3)	0.3398 (3)	0.2348 (5)	0.068 (2)*	
O(13)	0.1641 (2)	0.1904 (3)	0.2437 (5)	0.063 (2)*	
O(14)	0.2097 (2)	0.1813 (3)	0.0293 (4)	0.060 (2)*	
N(1)	0.3037 (3)	0.2381 (3)	0.2243 (5)	0.048 (2)*	
O(21)	0.0590 (3)	0.3235 (3)	−0.0628 (5)	0.076 (3)*	
O(22)	0.0921 (3)	0.3369 (3)	0.1849 (5)	0.078 (3)*	
O(23)	0.0527 (2)	0.1944 (3)	0.1910 (5)	0.070 (2)*	
O(24)	0.0987 (2)	0.1776 (3)	−0.0223 (5)	0.064 (2)*	
N(2)	−0.0431 (3)	0.2398 (5)	−0.0118 (5)	0.081 (3)*	
C(1)	0.1150 (4)	0.3393 (5)	−0.0751 (7)	0.066 (4)*	
C(2)	0.1457 (4)	0.3619 (5)	0.2360 (7)	0.063 (4)*	
C(3)	0.1089 (4)	0.1730 (4)	0.2526 (7)	0.062 (4)*	
C(4)	0.1540 (4)	0.1569 (4)	−0.0233 (6)	0.055 (3)*	
C(5)	0.1135 (4)	0.3858 (5)	−0.1851 (9)	0.087 (5)*	
C(6)	0.1440 (4)	0.4280 (5)	0.3132 (8)	0.074 (4)*	
C(7)	0.1058 (4)	0.1247 (5)	0.3586 (9)	0.077 (4)*	
C(8)	0.1559 (4)	0.0923 (5)	−0.1071 (8)	0.072 (4)*	
C(11)	0.3538 (4)	0.2870 (5)	0.2307 (7)	0.063 (4)*	
C(12)	0.4185 (4)	0.2651 (5)	0.2955 (8)	0.079 (4)*	
C(13)	0.4294 (4)	0.1992 (5)	0.3504 (8)	0.083 (4)*	
C(14)	0.3783 (4)	0.1515 (5)	0.3440 (7)	0.068 (4)*	
C(15)	0.3156 (4)	0.1742 (4)	0.2772 (7)	0.056 (3)*	
C(16)	0.3373 (5)	0.3589 (4)	0.1712 (8)	0.075 (4)*	
C(17)	0.3891 (5)	0.0796 (5)	0.4055 (9)	0.102 (5)*	
C(21)	−0.0895 (4)	0.2960 (7)	−0.0138 (8)	0.125 (6)*	
C(22)	−0.1563 (5)	0.2717 (8)	−0.071 (1)	0.159 (8)*	
C(23)	−0.1685 (5)	0.2033 (9)	−0.1199 (9)	0.155 (7)*	
C(24)	−0.1224 (5)	0.1486 (8)	−0.1198 (9)	0.130 (6)*	
C(25)	−0.0557 (5)	0.1715 (6)	−0.0579 (8)	0.101 (5)*	
C(26)	−0.0704 (7)	0.3650 (7)	0.037 (1)	0.140 (7)*	

Table 3 (*cont.*)

	x	*y*	*z*	*U*	Occupancy
C(27)	−0.1336 (7)	0.075 (1)	−0.173 (1)	0.20 (1)*	
Cl(1)	0.1803 (2)	0.4429 (3)	−0.1676 (5)	0.109 (2)*	0.60
Cl(2)	0.0402 (2)	0.4271 (3)	−0.2443 (6)	0.160 (3)*	0.60
Cl(3)	0.1303 (3)	0.3174 (3)	−0.2930 (4)	0.148 (3)*	0.60
Cl(4)	0.2218 (2)	0.4749 (2)	0.3534 (5)	0.112 (3)*	0.60
Cl(5)	0.1248 (4)	0.4020 (3)	0.4389 (5)	0.175 (4)*	0.60
Cl(6)	0.0894 (4)	0.4906 (3)	0.2315 (8)	0.212 (5)*	0.60
Cl(7)	0.0352 (2)	0.0676 (2)	0.3275 (4)	0.076 (2)*	0.60
Cl(8)	0.1759 (2)	0.0737 (2)	0.4134 (4)	0.079 (2)*	0.60
Cl(9)	0.0954 (2)	0.1856 (2)	0.4751 (3)	0.082 (2)*	0.60
Cl(10)	0.0836 (2)	0.0409 (2)	−0.1416 (4)	0.096 (2)*	0.60
Cl(11)	0.2229 (2)	0.0352 (2)	−0.0387 (4)	0.081 (2)*	0.60
Cl(12)	0.1747 (3)	0.1242 (3)	−0.2385 (3)	0.121 (3)*	0.60
Cl(011)	0.0951 (7)	0.4787 (7)	−0.110 (1)	0.092 (4)	0.20
Cl(21)	0.1840 (7)	0.4013 (8)	−0.215 (1)	0.100 (5)	0.20
Cl(31)	0.0587 (9)	0.3675 (9)	−0.303 (2)	0.132 (6)	0.20
Cl(41)	0.2156 (8)	0.4476 (9)	0.426 (1)	0.126 (6)	0.20
Cl(51)	0.0759 (6)	0.4332 (6)	0.371 (1)	0.069 (3)	0.20
Cl(61)	0.1305 (9)	0.4985 (9)	0.207 (2)	0.128 (6)	0.20
Cl(71)	0.043 (1)	0.086 (1)	0.363 (2)	0.171 (8)	0.20
Cl(81)	0.1775 (8)	0.0604 (8)	0.355 (1)	0.115 (5)	0.20
Cl(91)	0.096 (1)	0.200 (1)	0.466 (2)	0.170 (8)	0.20
Cl(101)	0.2178 (9)	0.0204 (9)	−0.042 (2)	0.138 (6)	0.20
Cl(111)	0.0857 (9)	0.0678 (9)	−0.194 (2)	0.134 (6)	0.20
Cl(121)	0.173 (1)	0.147 (1)	−0.232 (2)	0.171 (8)	0.20
Cl(012)	0.156 (1)	0.456 (1)	−0.129 (2)	0.187 (9)	0.20
Cl(22)	0.0441 (5)	0.3997 (5)	−0.2864 (9)	0.051 (3)	0.20
Cl(32)	0.156 (1)	0.348 (1)	−0.280 (2)	0.175 (8)	0.20
Cl(42)	0.1909 (8)	0.4887 (9)	0.281 (1)	0.121 (6)	0.20
Cl(52)	0.1739 (8)	0.4089 (8)	0.465 (1)	0.115 (5)	0.20
Cl(62)	0.0683 (8)	0.4622 (9)	0.286 (1)	0.123 (6)	0.20
Cl(72)	0.0426 (8)	0.0537 (8)	0.258 (1)	0.110 (5)	0.20
Cl(82)	0.1790 (8)	0.0898 (9)	0.440 (1)	0.119 (5)	0.20
Cl(92)	0.0945 (9)	0.143 (1)	0.465 (2)	0.137 (6)	0.20
Cl(102)	0.225 (1)	0.059 (1)	−0.094 (2)	0.183 (9)	0.20
Cl(112)	0.095 (1)	0.032 (1)	−0.080 (2)	0.167 (8)	0.20
Cl(122)	0.143 (1)	0.106 (1)	−0.244 (2)	0.165 (8)	0.20
C(31)	−0.0919 (9)	0.2765 (9)	−0.333 (1)	0.22 (1)*	
C(32)	−0.170 (1)	0.2427 (8)	−0.432 (2)	0.35 (2)*	
C(33)	−0.1647 (7)	0.1853 (7)	−0.472 (1)	0.143 (7)*	
C(34)	−0.1141 (8)	0.137 (1)	−0.470 (1)	0.23 (1)*	
C(35)	−0.0512 (7)	0.1435 (9)	−0.406 (1)	0.19 (1)*	
C(36)	−0.053 (1)	0.217 (1)	−0.347 (1)	0.26 (1)*	
C(37)	−0.1954 (9)	0.2999 (8)	−0.406 (1)	0.22 (1)*	
(IV)					
Cu(1)	0.19291 (5)	0.1134 (1)	0.47365 (6)	0.0465 (4)*	
Cu(2)	0.30715 (5)	0.2683 (1)	0.42348 (6)	0.0489 (5)*	
O(11)	0.1344 (3)	0.1495 (5)	0.3716 (3)	0.051 (2)*	
O(12)	0.1939 (3)	0.3092 (5)	0.4954 (3)	0.051 (3)*	
O(13)	0.2562 (3)	0.0886 (6)	0.5714 (3)	0.054 (3)*	
O(14)	0.2533 (3)	−0.0059 (5)	0.4185 (3)	0.048 (3)*	
O(21)	0.2154 (2)	0.2591 (6)	0.3391 (3)	0.050 (2)*	
O(22)	0.2743 (3)	0.4207 (5)	0.4625 (3)	0.051 (3)*	
O(23)	0.3424 (3)	0.1855 (5)	0.5411 (3)	0.049 (2)*	
O(24)	0.3313 (3)	0.1108 (6)	0.3825 (3)	0.052 (3)*	
N(1)	0.1282 (3)	−0.0168 (6)	0.4965 (4)	0.036 (3)*	
N(2)	0.3952 (3)	0.3492 (7)	0.4219 (4)	0.040 (3)*	
C(1)	0.1590 (4)	0.2115 (8)	0.3275 (4)	0.036 (4)*	
C(2)	0.2236 (4)	0.4081 (9)	0.4859 (5)	0.042 (4)*	
C(3)	0.3157 (4)	0.1303 (9)	0.5831 (5)	0.044 (4)*	
C(4)	0.2972 (4)	0.0106 (9)	0.3859 (5)	0.043 (4)*	
C(5)	0.1096 (3)	0.2321 (8)	0.2470 (4)	0.045 (3)*	
C(6)	0.1909 (4)	0.5344 (8)	0.5028 (5)	0.054 (4)*	
C(7)	0.3594 (4)	0.1049 (9)	0.6685 (4)	0.055 (4)*	
C(8)	0.3178 (5)	−0.1022 (9)	0.3423 (6)	0.073 (5)*	
C(11)	0.1367 (4)	−0.0594 (8)	0.5690 (4)	0.035 (3)*	
C(12)	0.0935 (4)	−0.1430 (8)	0.5888 (5)	0.042 (4)*	
C(13)	0.0382 (4)	−0.1912 (8)	0.5326 (6)	0.050 (4)*	
C(14)	0.0303 (4)	−0.1469 (9)	0.4595 (5)	0.058 (4)*	
C(15)	0.0743 (4)	−0.0633 (8)	0.4425 (5)	0.048 (4)*	
C(16)	0.1069 (4)	−0.1877 (9)	0.6705 (5)	0.074 (5)*	
C(17)	−0.0097 (4)	−0.2863 (9)	0.5506 (5)	0.074 (5)*	
C(21)	0.4482 (5)	0.2789 (8)	0.4221 (5)	0.057 (4)*	
C(22)	0.5066 (5)	0.325 (1)	0.4083 (6)	0.073 (5)*	
C(23)	0.5107 (5)	0.454 (1)	0.3945 (5)	0.063 (5)*	
C(24)	0.4566 (5)	0.5278 (9)	0.3964 (5)	0.064 (5)*	
C(25)	0.4004 (4)	0.474 (1)	0.4099 (5)	0.048 (4)*	
C(26)	0.5651 (6)	0.240 (1)	0.408 (1)	0.21 (1)*	
C(27)	0.5721 (5)	0.516 (1)	0.3782 (5)	0.106 (6)*	
Cl(1)	0.1513 (1)	0.2772 (3)	0.1804 (1)	0.073 (1)*	
Cl(2)	−0.0633 (1)	−0.4096 (3)	0.2853 (1)	0.089 (1)*	
Cl(3)	0.0531 (1)	0.3535 (3)	0.2556 (1)	0.094 (1)*	
Cl(4)	0.2493 (1)	0.6588 (3)	0.5327 (2)	0.095 (1)*	
Cl(5)	0.1456 (1)	0.5143 (3)	0.5693 (2)	0.095 (1)*	
Cl(6)	0.1329 (2)	0.5819 (3)	0.4143 (2)	0.118 (2)*	
Cl(7)	0.4458 (1)	0.1011 (3)	0.6750 (1)	0.082 (1)*	
Cl(8)	0.3423 (1)	0.2337 (3)	0.7224 (1)	0.082 (1)*	
Cl(9)	0.3360 (1)	−0.0411 (3)	0.7031 (1)	0.090 (1)*	
Cl(10)	0.2833 (4)	−0.2488 (5)	0.3578 (4)	0.084 (3)*	0.80
Cl(11)	0.2774 (3)	−0.0632 (4)	0.2419 (2)	0.131 (3)*	0.80
Cl(12)	0.4020 (2)	−0.1134 (4)	0.3510 (4)	0.146 (3)*	0.80
Cl(81)	0.3992 (9)	−0.150 (2)	0.437 (1)	0.138 (7)	0.20
Cl(82)	0.358 (1)	−0.074 (2)	0.288 (1)	0.102 (6)	0.20
Cl(83)	0.266 (2)	−0.223 (3)	0.334 (2)	0.10 (1)	0.20
(V)					
Cu(1)	0.1290 (2)	0.2658 (2)	0.1629 (2)	0.0374 (8)*	
Cu(2)	0.3266 (5)	0.1770 (2)	0.2943 (2)	0.0351 (8)*	
O(11)	0.1327 (7)	0.3849 (8)	0.278 (1)	0.039 (2)*	
O(21)	0.1286 (7)	0.1393 (7)	0.062 (1)	0.044 (2)*	
O(31)	0.1125 (7)	0.2021 (8)	0.352 (1)	0.038 (2)*	
O(41)	0.2415 (7)	0.2891 (8)	0.058 (1)	0.041 (2)*	
N(1)	−0.0274 (8)	0.3007 (9)	0.132 (1)	0.034 (2)*	
O(12)	0.2785 (7)	0.3241 (7)	0.379 (1)	0.039 (2)*	
O(22)	0.2727 (8)	0.0772 (8)	0.161 (1)	0.049 (2)*	
O(32)	0.2617 (7)	0.1413 (8)	0.442 (1)	0.041 (2)*	
O(42)	0.3866 (7)	0.2229 (8)	0.148 (1)	0.049 (2)*	
N(51)	0.4651 (8)	0.171 (1)	0.407 (1)	0.040 (2)*	
C(11)	0.207 (1)	0.392 (1)	0.363 (1)	0.038 (2)*	
C(21)	0.196 (1)	0.073 (1)	0.085 (1)	0.046 (2)*	
C(31)	0.169 (1)	0.164 (1)	0.442 (1)	0.043 (2)*	
C(41)	0.332 (1)	0.276 (1)	0.070 (2)	0.045 (2)*	
C(13)	0.200 (1)	0.480 (1)	0.469 (1)	0.038 (2)*	
C(23)	0.193 (1)	−0.028 (1)	0.007 (2)	0.051 (2)*	
C(33)	0.122 (1)	0.133 (1)	0.556 (1)	0.040 (2)*	
C(43)	0.394 (1)	0.328 (1)	−0.013 (2)	0.049 (2)*	
Cl(11)	0.1271 (4)	0.4624 (5)	0.6048 (5)	0.080 (2)*	
Cl(12)	0.1396 (4)	0.5827 (4)	0.3985 (6)	0.069 (2)*	
Cl(13)	0.3167 (3)	0.5011 (4)	0.5304 (5)	0.059 (2)*	
Cl(21)	0.1599 (6)	−0.0982 (5)	0.1322 (7)	0.089 (2)*	
Cl(22)	0.0989 (4)	−0.0310 (4)	−0.1226 (5)	0.061 (2)*	
Cl(23)	0.3047 (4)	−0.0804 (5)	−0.0617 (8)	0.128 (2)*	
Cl(31)	−0.0042 (3)	0.1923 (4)	0.5805 (5)	0.065 (2)*	
Cl(32)	0.1248 (3)	0.0098 (3)	0.5341 (5)	0.057 (1)*	
Cl(33)	0.1881 (4)	0.1688 (4)	0.7181 (5)	0.061 (2)*	
Cl(41)	0.5054 (4)	0.2556 (5)	−0.0624 (6)	0.090 (2)*	
Cl(42)	0.4171 (5)	0.4311 (5)	0.0984 (6)	0.087 (2)*	
Cl(43)	0.3230 (4)	0.3654 (5)	−0.1583 (5)	0.063 (2)*	
O(1)	−0.3461 (8)	0.293 (1)	0.268 (1)	0.069 (2)*	
O(2)	−0.2171 (9)	0.229 (1)	0.382 (1)	0.075 (2)*	
N(2)	−0.256 (1)	0.274 (1)	0.290 (1)	0.057 (2)*	
C(2)	−0.066 (1)	0.351 (1)	0.027 (2)	0.040 (2)*	
C(3)	−0.168 (1)	0.376 (1)	0.004 (2)	0.045 (2)*	
C(4)	−0.231 (1)	0.350 (1)	0.091 (2)	0.048 (2)*	
C(5)	−0.193 (1)	0.301 (1)	0.195 (2)	0.045 (2)*	
C(6)	−0.090 (1)	0.278 (1)	0.219 (2)	0.039 (2)*	
Cl(1)	0.0187 (3)	0.3732 (4)	−0.0779 (5)	0.055 (2)	
O(51)	0.6748 (9)	0.309 (1)	0.739 (1)	0.067 (2)	
O(52)	0.541 (1)	0.396 (1)	0.672 (1)	0.077 (2)*	
N(52)	0.596 (1)	0.318 (1)	0.664 (1)	0.060 (2)*	
C(52)	0.528 (1)	0.088 (1)	0.390 (2)	0.048 (2)*	
C(53)	0.621 (1)	0.076 (1)	0.467 (2)	0.058 (2)*	
C(54)	0.642 (1)	0.151 (1)	0.558 (2)	0.055 (2)*	
C(55)	0.576 (1)	0.234 (1)	0.575 (2)	0.046 (2)*	
C(56)	0.485 (1)	0.244 (1)	0.496 (1)	0.040 (2)*	
Cl(51)	0.5009 (3)	−0.0021 (4)	0.2676 (6)	0.071 (2)*	
(VI)					
Cu	0.06203 (2)	0.23095 (2)	0.20030 (3)	0.0292 (1)*	
O(1)	0.1008 (1)	0.3033 (1)	0.3198 (2)	0.0392 (8)*	
O(2)	0.0148 (1)	0.1590 (1)	0.0842 (2)	0.0352 (8)*	
O(3)	0.0708 (1)	0.1477 (1)	0.3329 (2)	0.0382 (8)*	
O(4)	−0.0052 (1)	0.3091 (1)	0.1202 (2)	0.0391 (8)*	
C(1)	0.0651 (2)	0.3269 (2)	0.3813 (3)	0.032 (1)*	
C(3)	0.0995 (2)	0.3882 (2)	0.4688 (3)	0.043 (1)*	
C(21)	0.0435 (2)	0.1375 (2)	0.4095 (3)	0.028 (1)*	
C(23)	0.0901 (2)	0.0965 (2)	0.5146 (3)	0.034 (1)*	
N(9)	0.1568 (1)	0.1990 (1)	0.1838 (2)	0.0275 (8)*	
C(8)	0.1748 (2)	0.1253 (2)	0.2003 (3)	0.031 (1)*	
N(7)	0.2382 (1)	0.1118 (1)	0.1908 (2)	0.0309 (9)*	
C(5)	0.2644 (2)	0.1810 (2)	0.1670 (3)	0.030 (1)*	
C(6)	0.3299 (2)	0.2002 (2)	0.1494 (3)	0.038 (1)*	
N(1)	0.3343 (1)	0.2786 (2)	0.1307 (2)	0.039 (1)*	
C(2)	0.2833 (2)	0.3331 (2)	0.1239 (3)	0.041 (1)*	
N(3)	0.2205 (1)	0.3084 (2)	0.1388 (2)	0.0329 (9)*	
C(4)	0.2134 (1)	0.2330 (2)	0.1630 (2)	0.0259 (9)*	
C(14)	0.2722 (2)	0.0374 (2)	0.2030 (3)	0.047 (1)*	
O(10)	0.3769 (1)	0.1562 (2)	0.1492 (2)	0.055 (1)*	
C(11)	0.4017 (2)	0.3063 (3)	0.1190 (3)	0.062 (2)*	

Table 3 (*cont.*)

	x	y	z	U	Occupancy
O(12)	0.2920 (1)	0.3996 (2)	0.1052 (2)	0.060 (1)*	
C(13)	0.1639 (2)	0.3635 (2)	0.1259 (3)	0.045 (1)*	
Cl(1)	0.07080 (6)	0.38031 (8)	0.59011 (9)	0.0755 (5)*	
Cl(2)	0.19067 (5)	0.38077 (8)	0.5072 (1)	0.0731 (5)*	
Cl(3)	0.07599 (7)	0.47707 (6)	0.4041 (1)	0.0828 (6)*	
Cl(21)	0.15295 (5)	0.16524 (7)	0.58284 (9)	0.0629 (4)*	
Cl(22)	0.13251 (5)	0.01897 (5)	0.47172 (8)	0.0498 (3)*	
Cl(23)	0.04539 (5)	0.06474 (6)	0.61016 (8)	0.0528 (4)*	
(VII)					
Cu(1)	0.11523 (9)	0.25903 (6)	0.31590 (9)	0.0398 (4)*	
Cu(2)	0.2032 (1)	0.23235 (7)	0.04538 (9)	0.0471 (5)*	
O(11)	0.2317 (5)	0.1436 (3)	0.3172 (5)	0.040 (2)*	
O(12)	0.2693 (5)	0.3057 (3)	0.3380 (5)	0.043 (2)*	
O(13)	0.0030 (5)	0.3730 (3)	0.3068 (5)	0.055 (3)*	
O(14)	0.0008 (5)	0.1920 (3)	0.1514 (5)	0.048 (3)*	
O(21)	0.2992 (5)	0.1235 (3)	0.1184 (5)	0.044 (2)*	
O(22)	0.3270 (5)	0.2896 (4)	0.1369 (5)	0.061 (3)*	
O(23)	0.0536 (5)	0.3580 (3)	0.1065 (6)	0.062 (3)*	
O(24)	0.0768 (5)	0.1775 (4)	−0.0383 (5)	0.051 (3)*	
N(1)	−0.0099 (6)	0.2476 (4)	0.4327 (6)	0.039 (3)*	
N(2)	0.2658 (6)	0.2325 (4)	−0.1275 (6)	0.032 (3)*	
C(1)	0.3035 (7)	0.1045 (5)	0.2206 (9)	0.041 (4)*	
C(2)	0.3366 (8)	0.3127 (5)	0.2586 (8)	0.043 (4)*	
C(3)	−0.0051 (8)	0.3957 (5)	0.2086 (9)	0.049 (4)*	
C(4)	−0.0009 (8)	0.1713 (5)	0.0295 (8)	0.041 (4)*	
C(5)	0.4182 (7)	0.0225 (5)	0.2463 (7)	0.046 (4)*	
C(6)	0.4450 (9)	0.3542 (6)	0.3109 (8)	0.060 (5)*	
C(7)	−0.107 (1)	0.4873 (6)	0.203 (1)	0.077 (5)*	
C(8)	−0.1141 (8)	0.1384 (6)	−0.0380 (8)	0.053 (4)*	
C(11)	−0.0308 (7)	0.1687 (6)	0.4156 (8)	0.039 (4)*	
C(12)	−0.1191 (7)	0.1576 (6)	0.4841 (8)	0.046 (4)*	
C(13)	−0.1866 (9)	0.2314 (8)	0.577 (1)	0.071 (6)*	
C(14)	−0.167 (1)	0.3111 (8)	0.592 (1)	0.077 (6)*	
C(15)	−0.0804 (9)	0.3193 (6)	0.5186 (9)	0.057 (5)*	
C(16)	−0.1387 (8)	0.0709 (7)	0.4608 (8)	0.052 (5)*	
N(3)	−0.1558 (7)	0.0036 (6)	0.4399 (8)	0.072 (4)*	
C(21)	0.3474 (8)	0.2771 (5)	−0.1279 (8)	0.036 (4)*	
C(22)	0.3959 (7)	0.2767 (5)	−0.2423 (8)	0.038 (4)*	
C(23)	0.3547 (9)	0.2278 (6)	−0.3563 (9)	0.053 (5)*	
C(24)	0.2724 (9)	0.1802 (6)	−0.3574 (8)	0.052 (4)*	
C(25)	0.2271 (8)	0.1842 (5)	−0.2395 (8)	0.040 (4)*	
C(26)	0.4865 (8)	0.3251 (5)	−0.2349 (8)	0.043 (4)*	
N(4)	0.5601 (7)	0.3631 (5)	−0.2260 (7)	0.064 (4)*	
Cl(1)	0.3783 (2)	−0.0253 (2)	0.3528 (3)	0.086 (1)*	
Cl(2)	0.4631 (2)	−0.0588 (2)	0.1009 (2)	0.086 (1)*	
Cl(3)	0.5442 (2)	0.0676 (2)	0.3110 (3)	0.096 (2)*	
Cl(4)	0.4665 (3)	0.3794 (3)	0.4776 (3)	0.097 (2)*	0.90
Cl(5)	0.4255 (4)	0.4475 (2)	0.2543 (3)	0.100 (2)*	0.90
Cl(6)	0.5941 (3)	0.2750 (3)	0.2489 (4)	0.110 (2)*	0.90
Cl(7)	−0.0292 (5)	0.5579 (3)	0.1687 (4)	0.096 (2)*	0.90
Cl(8)	−0.2209 (3)	0.4695 (2)	0.0830 (4)	0.116 (2)*	0.90
Cl(9)	−0.1786 (6)	0.5397 (4)	0.3515 (6)	0.155 (3)*	0.90
Cl(10)	−0.1661 (2)	0.0792 (2)	0.0448 (3)	0.091 (2)*	
Cl(11)	−0.2395 (2)	0.2352 (2)	−0.0512 (3)	0.083 (1)*	
Cl(12)	−0.0764 (3)	0.0712 (2)	−0.1971 (2)	0.089 (1)*	
Cl(61)	0.521 (4)	0.372 (3)	0.220 (4)	0.14 (1)	0.10
Cl(62)	0.356 (4)	0.468 (3)	0.411 (4)	0.16 (2)	0.10
Cl(63)	0.525 (5)	0.317 (4)	0.391 (6)	0.20 (2)	0.10
Cl(71)	−0.164 (3)	0.552 (2)	0.379 (3)	0.018 (5)	0.10
Cl(72)	−0.053 (4)	0.561 (3)	0.217 (3)	0.07 (1)	0.10
Cl(73)	−0.249 (4)	0.460 (2)	0.181 (4)	0.11 (1)	0.10
(VIII)					
Cu(1)	0.20722 (9)	0.2405 (1)	0.1390 (1)	0.0557 (7)*	
Cu(2)	0.05206 (9)	0.2485 (1)	0.0858 (1)	0.0590 (7)*	
O(11)	0.2134 (4)	0.3186 (5)	0.0307 (7)	0.060 (4)*	
O(12)	0.1621 (4)	0.3186 (5)	0.2540 (7)	0.060 (4)*	
O(13)	0.1928 (4)	0.1653 (5)	0.2499 (8)	0.068 (4)*	
O(14)	0.1717 (5)	0.1736 (5)	0.0049 (8)	0.068 (4)*	
N(1)	0.3023 (4)	0.2642 (5)	0.2300 (8)	0.038 (4)*	
O(21)	0.1011 (4)	0.3296 (5)	−0.0092 (8)	0.061 (4)*	
O(22)	0.0507 (4)	0.3173 (5)	0.2151 (7)	0.058 (4)*	
O(23)	0.0814 (5)	0.1697 (5)	0.2062 (8)	0.067 (4)*	
O(24)	0.0600 (5)	0.1825 (5)	−0.0395 (8)	0.070 (4)*	
N(2)	−0.0400 (5)	0.2865 (7)	0.0012 (8)	0.069 (5)*	
C(1)	0.1588 (7)	0.3433 (7)	−0.021 (1)	0.060 (6)*	
C(2)	0.1073 (7)	0.3349 (7)	0.273 (1)	0.056 (6)*	
C(3)	0.1355 (8)	0.1446 (7)	0.255 (1)	0.068 (7)*	
C(4)	0.1158 (7)	0.1581 (8)	−0.052 (1)	0.069 (7)*	
C(5)	0.1666 (8)	0.3978 (9)	−0.127 (1)	0.079 (7)*	
C(6)	0.1036 (8)	0.3771 (9)	0.386 (1)	0.086 (8)*	
C(7)	0.1295 (7)	0.0760 (8)	0.328 (1)	0.068 (6)*	
C(8)	0.1139 (7)	0.1060 (9)	−0.154 (1)	0.085 (7)*	
C(11)	0.3508 (6)	0.2161 (7)	0.246 (1)	0.044 (5)*	
C(12)	0.4130 (7)	0.2276 (7)	0.308 (1)	0.070 (7)*	
C(13)	0.4272 (7)	0.2978 (8)	0.358 (1)	0.068 (7)*	
C(14)	0.3754 (6)	0.3487 (7)	0.345 (1)	0.052 (6)*	
C(15)	0.3126 (6)	0.3309 (7)	0.276 (1)	0.050 (5)*	
C(21)	−0.0940 (8)	0.245 (1)	−0.023 (1)	0.093 (8)*	
C(22)	−0.1596 (7)	0.266 (1)	−0.080 (1)	0.13 (1)*	
C(23)	−0.161 (1)	0.339 (2)	−0.111 (1)	0.18 (1)*	
C(24)	−0.1087 (9)	0.385 (1)	−0.094 (1)	0.12 (1)*	
C(25)	−0.0468 (9)	0.357 (1)	−0.034 (1)	0.11 (1)*	
Cl(1)	0.2268 (3)	0.4630 (3)	−0.0695 (6)	0.157 (3)*	
Cl(2)	0.1962 (4)	0.3510 (4)	−0.2304 (5)	0.200 (5)*	
Cl(3)	0.0930 (3)	0.4405 (3)	−0.1856 (5)	0.137 (3)*	
Cl(4)	0.1772 (2)	0.4251 (3)	0.4381 (4)	0.114 (2)*	
Cl(5)	0.0345 (3)	0.4357 (3)	0.3723 (5)	0.125 (3)*	
Cl(6)	0.0929 (3)	0.3091 (3)	0.4918 (4)	0.124 (3)*	
Cl(7)	0.0616 (4)	0.0677 (4)	0.3880 (7)	0.095 (2)*	0.60
Cl(8)	0.1239 (6)	−0.0020 (4)	0.2289 (9)	0.159 (2)*	0.60
Cl(9)	0.2051 (4)	0.0536 (6)	0.423 (1)	0.216 (3)*	0.60
Cl(10)	0.0400 (4)	0.0712 (7)	−0.216 (1)	0.226 (5)*	0.60
Cl(11)	0.1763 (5)	0.0384 (5)	−0.1296 (8)	0.122 (4)*	0.60
Cl(12)	0.1416 (8)	0.1587 (7)	−0.2712 (8)	0.213 (6)*	0.60
Cl(13)	0.3344 (2)	0.1303 (2)	0.1881 (4)	0.079 (6)*	
Cl(14)	0.3861 (2)	0.4339 (2)	0.4065 (4)	0.088 (8)*	
Cl(15)	−0.0841 (3)	0.1550 (3)	0.0311 (5)	0.132 (4)*	
Cl(16)	−0.1119 (4)	0.4697 (5)	−0.1410 (6)	0.231 (8)*	
Cl(71)	0.1400 (8)	0.1126 (9)	0.475 (1)	0.143 (5)	0.40
Cl(81)	0.0579 (8)	0.0352 (8)	0.290 (1)	0.149 (6)	0.40
Cl(91)	0.1908 (7)	0.0225 (7)	0.329 (1)	0.119 (5)	0.40
Cl(101)	0.0848 (7)	0.0202 (8)	−0.084 (1)	0.130 (5)	0.40
Cl(111)	0.0567 (5)	0.1211 (6)	−0.2694 (9)	0.084 (3)	0.40
Cl(121)	0.1871 (6)	0.0832 (7)	−0.184 (1)	0.110 (4)	0.40
C(31)	−0.0597 (9)	0.2684 (9)	−0.326 (1)	0.099 (6)	
C(32)	−0.082 (1)	0.337 (1)	−0.379 (2)	0.132 (8)	
C(33)	−0.150 (1)	0.339 (1)	−0.444 (2)	0.136 (8)	
C(34)	−0.190 (1)	0.277 (1)	−0.447 (2)	0.124 (7)	
C(35)	−0.168 (1)	0.213 (1)	−0.387 (2)	0.125 (7)	
C(36)	−0.101 (1)	0.210 (1)	−0.331 (2)	0.118 (7)	
(IX)					
Cu(1)	0.20737 (6)	0.17264 (4)	1.00774 (8)	0.0359 (3)*	
Cu(2)	0.31860 (6)	0.30928 (4)	0.92979 (7)	0.0346 (3)*	
O(11)	0.3716 (3)	0.1604 (2)	1.1108 (4)	0.046 (2)*	
O(12)	0.2052 (3)	0.2666 (2)	1.1717 (4)	0.041 (2)*	
O(13)	0.0480 (3)	0.1969 (2)	0.9035 (4)	0.039 (2)*	
O(14)	0.2493 (3)	0.1388 (2)	0.8159 (4)	0.045 (2)*	
O(21)	0.4528 (3)	0.2689 (2)	1.0667 (4)	0.050 (2)*	
O(22)	0.2836 (3)	0.3689 (2)	1.1017 (4)	0.040 (2)*	
O(23)	0.1315 (3)	0.2984 (2)	0.8323 (4)	0.041 (2)*	
O(24)	0.3471 (3)	0.2416 (2)	0.7656 (4)	0.049 (2)*	
N(1)	0.1279 (4)	0.1007 (3)	1.1294 (5)	0.033 (2)*	
N(2)	0.3498 (4)	0.4084 (3)	0.8386 (5)	0.035 (2)*	
C(1)	0.4554 (5)	0.2077 (4)	1.1152 (6)	0.041 (2)*	
C(2)	0.2397 (5)	0.3349 (3)	1.1873 (6)	0.036 (2)*	
C(3)	0.0466 (5)	0.2577 (3)	0.8476 (6)	0.037 (2)*	
C(4)	0.3119 (5)	0.1731 (4)	0.7468 (6)	0.041 (2)*	
C(5)	0.5847 (5)	0.1898 (4)	1.1997 (7)	0.050 (3)*	
C(6)	0.2341 (6)	0.3816 (3)	1.3359 (6)	0.046 (3)*	
C(7)	−0.0817 (5)	0.2880 (3)	0.7976 (6)	0.043 (2)*	
C(8)	0.3576 (5)	0.1244 (3)	0.6236 (6)	0.046 (2)*	
C(11)	0.1428 (5)	0.0274 (3)	1.1264 (6)	0.041 (2)*	
C(12)	0.0844 (7)	−0.0185 (4)	1.1998 (8)	0.055 (3)*	
C(13)	0.0129 (7)	0.0117 (4)	1.2875 (8)	0.059 (3)*	
C(14)	0.0015 (5)	0.0886 (4)	1.2989 (6)	0.046 (3)*	
C(15)	0.0585 (6)	0.1306 (4)	1.2179 (7)	0.042 (3)*	
C(21)	0.4579 (5)	0.4352 (3)	0.8269 (6)	0.041 (2)*	
C(22)	0.4783 (7)	0.5057 (4)	0.7839 (8)	0.055 (3)*	
C(23)	0.3845 (7)	0.5478 (4)	0.7473 (8)	0.059 (3)*	
C(24)	0.2702 (6)	0.5197 (3)	0.7532 (7)	0.049 (3)*	
C(25)	0.2569 (6)	0.4511 (3)	0.8000 (7)	0.041 (2)*	
Cl(1)	0.5877 (2)	0.0954 (1)	1.2250 (3)	0.090 (1)*	
Cl(2)	0.6914 (2)	0.2113 (1)	1.0965 (2)	0.0800 (9)*	
Cl(3)	0.6216 (2)	0.2471 (1)	1.3729 (2)	0.0791 (9)*	
Cl(4)	0.1259 (2)	0.3422 (1)	1.4198 (2)	0.0705 (8)*	
Cl(5)	0.1989 (2)	0.4748 (1)	1.3112 (2)	0.080 (1)*	
Cl(6)	0.3789 (2)	0.3828 (1)	1.4526 (2)	0.0716 (8)*	
Cl(7)	−0.1988 (1)	0.2144 (1)	0.7487 (2)	0.0746 (8)*	
Cl(8)	−0.0907 (2)	0.3386 (1)	0.6503 (2)	0.0714 (8)*	
Cl(9)	−0.1002 (2)	0.3461 (1)	0.9576 (2)	0.094 (1)*	
Cl(10)	0.2757 (2)	0.0358 (1)	0.5689 (2)	0.0681 (8)*	
Cl(11)	0.3436 (2)	0.1693 (1)	0.4668 (2)	0.099 (1)*	
Cl(12)	0.5084 (2)	0.1099 (1)	0.7013 (3)	0.110 (1)*	
Cl(13)	0.2363 (2)	−0.00949 (9)	1.0189 (2)	0.0616 (7)*	
Cl(14)	−0.0799 (2)	0.1324 (1)	1.4166 (2)	0.0784 (9)*	
Cl(15)	0.5753 (1)	0.3784 (1)	0.8670 (2)	0.0637 (8)*	
Cl(16)	0.1446 (2)	0.5690 (1)	0.7020 (2)	0.085 (1)*	

Table 3 (*cont.*)

	x	*y*	*z*	*U*	Occupancy
(X)					
Cu	0.00470 (5)	0.38479 (5)	0.04711 (5)	0.0302 (2)*	
O(1)	0.2197 (3)	0.3641 (3)	0.1442 (3)	0.048 (1)*	
O(2)	−0.0592 (3)	0.5238 (3)	0.2109 (3)	0.046 (2)*	
O(3)	−0.2154 (3)	0.4513 (3)	−0.0698 (3)	0.045 (1)*	
O(4)	0.0602 (3)	0.2912 (3)	−0.1391 (3)	0.045 (2)*	
N	0.0418 (3)	0.2021 (3)	0.1330 (3)	0.033 (2)*	
C(1)	0.2781 (4)	0.4360 (4)	0.1299 (4)	0.037 (2)*	
C(2)	−0.0744 (4)	0.6469 (4)	0.2243 (4)	0.037 (2)*	
C(3)	0.4568 (5)	0.3711 (5)	0.1915 (6)	0.058 (2)*	
C(4)	−0.1038 (5)	0.7330 (4)	0.3715 (5)	0.047 (2)*	
C(11)	0.1834 (5)	0.1110 (4)	0.1958 (5)	0.040 (2)*	
C(12)	0.2145 (5)	−0.0120 (4)	0.2503 (5)	0.046 (2)*	
C(13)	0.0940 (6)	−0.0421 (5)	0.2372 (5)	0.054 (3)*	
C(14)	−0.0510 (6)	0.0524 (5)	0.1737 (5)	0.054 (3)*	
C(15)	−0.0753 (5)	0.1727 (5)	0.1224 (5)	0.043 (2)*	
Cl(7)	0.4037 (2)	−0.1233 (1)	0.3301 (2)	0.0814 (8)*	
Cl(1)	0.5329 (3)	0.4901 (3)	0.2164 (4)	0.099 (1)*	0.90
Cl(2)	0.5249 (2)	0.2836 (2)	0.3513 (2)	0.099 (1)*	0.90
Cl(3)	0.5150 (2)	0.2419 (2)	0.0421 (3)	0.105 (1)*	0.90
Cl(4)	−0.1864 (2)	0.6673 (1)	0.4527 (1)	0.0650 (7)*	
Cl(5)	−0.2263 (2)	0.9112 (1)	0.3410 (2)	0.0775 (8)*	
Cl(6)	0.0795 (2)	0.7160 (2)	0.4939 (1)	0.0857 (9)*	
Cl(31)	0.470 (2)	0.403 (2)	0.407 (2)	0.078 (4)*	0.10
Cl(32)	0.543 (2)	0.217 (2)	0.171 (2)	0.093 (5)*	0.10
Cl(33)	0.554 (2)	0.489 (1)	0.215 (1)	0.020 (3)*	0.10
(XI)					
Cu	0.05772 (2)	*x*	0.02471 (8)	0.0478 (3)*	
O(1)	0.0877 (5)	−0.0331 (4)	0.0892 (3)	0.074 (3)*	
O(2)	−0.0058 (5)	−0.1296 (4)	0.0480 (3)	0.073 (3)*	
C(1)	0.0504 (6)	−0.1029 (7)	0.0877 (5)	0.064 (4)*	
C(3)	0.0778 (8)	−0.1698 (8)	0.1450 (7)	0.102 (6)*	
N(9)	0.1516 (2)	*x*	0.042 (1)	0.040 (6)	0.50
O(10)	0.3561 (2)	*x*	0.071 (1)	0.12 (1)	0.50
C(8)	0.1830 (2)	*x*	−0.027 (1)	0.049 (8)	0.50
C(14)	0.2904 (2)	*x*	−0.074 (1)	0.07 (1)	0.50
N(3)	0.19672 (7)	*x*	0.1585 (5)	0.050 (3)	
C(4)	0.19746 (8)	*x*	0.0879 (6)	0.045 (4)	
C(13)	0.1396 (1)	*x*	0.1979 (9)	0.096 (6)	
O(12)	¼	¼	0.260 (1)	0.116 (6)	
N(7)	¼	¼	−0.0177 (9)	0.060 (5)	
C(2)	¼	¼	0.194 (1)	0.075 (7)	
C(5)	¼	¼	0.0557 (9)	0.039 (5)	
Cl(1)	−0.0158 (4)	−0.2107 (3)	0.1856 (2)	0.089 (2)*	0.60
Cl(2)	0.1462 (4)	−0.1307 (4)	0.2072 (3)	0.108 (3)*	0.60
Cl(3)	0.1350 (5)	−0.2553 (5)	0.0921 (4)	0.171 (4)*	0.60
Cl(11)	−0.006 (2)	−0.163 (2)	0.209 (1)	0.164 (9)	0.20
Cl(12)	0.010 (1)	−0.243 (1)	0.1599 (8)	0.069 (4)	0.20
Cl(21)	0.183 (1)	−0.148 (1)	0.1805 (8)	0.087 (6)	0.20
Cl(22)	0.098 (1)	−0.098 (1)	0.2310 (9)	0.096 (6)	0.20
Cl(31)	0.090 (1)	−0.258 (1)	0.122 (1)	0.121 (7)	0.20
Cl(32)	0.150 (1)	−0.221 (1)	0.1267 (9)	0.104 (6)	0.20
C(15)	0.027 (1)	0.352 (1)	0.0369 (9)	0.203 (9)	
C(16)	0.033 (1)	0.351 (1)	0.1137 (9)	0.189 (8)	
C(17)	0.089 (1)	$-x+\frac{1}{2}$	0.135 (1)	0.15 (1)	
C(18)	0.08957 (7)	$-x+\frac{1}{2}$	0.004 (1)	0.16 (1)	
C(19)	0.0818 (1)	$-x+\frac{1}{2}$	−0.059 (2)	0.32 (2)	
(XII)					
Cu(1)	0.22434 (5)	0.52772 (6)	0.6754 (1)	0.0444 (4)*	
Cu(2)	0.30064 (5)	0.63030 (6)	0.8417 (1)	0.0463 (4)*	
O(11)	0.2877 (3)	0.4559 (3)	0.7748 (6)	0.065 (3)*	
O(12)	0.2881 (3)	0.5489 (3)	0.5497 (6)	0.060 (3)*	
O(13)	0.1778 (3)	0.6217 (3)	0.6144 (6)	0.064 (3)*	
O(14)	0.1761 (2)	0.5221 (3)	0.8353 (6)	0.057 (3)*	
O(21)	0.3497 (3)	0.5399 (3)	0.9061 (6)	0.064 (3)*	
O(22)	0.3481 (3)	0.6340 (3)	0.6811 (6)	0.066 (3)*	
O(23)	0.2396 (3)	0.7052 (3)	0.7457 (6)	0.066 (3)*	
O(24)	0.2360 (3)	0.6079 (3)	0.9640 (6)	0.054 (3)*	
N(1)	0.1623 (3)	0.4567 (4)	0.5339 (7)	0.044 (3)*	
N(2)	0.3534 (3)	0.7071 (3)	0.9844 (7)	0.040 (3)*	
C(1)	0.3359 (4)	0.4766 (5)	0.8628 (9)	0.053 (4)*	
C(2)	0.3336 (4)	0.5948 (5)	0.5774 (9)	0.053 (4)*	
C(3)	0.1941 (4)	0.6855 (4)	0.6577 (9)	0.050 (4)*	
C(4)	0.1922 (4)	0.5622 (5)	0.9420 (9)	0.047 (4)*	
C(5)	0.3866 (4)	0.4150 (5)	0.911 (1)	0.065 (4)*	
C(6)	0.3749 (5)	0.6034 (6)	0.457 (1)	0.086 (5)*	
C(7)	0.1461 (5)	0.7482 (5)	0.591 (1)	0.076 (5)*	
C(8)	0.1533 (4)	0.5449 (5)	1.061 (1)	0.069 (4)*	
C(11)	0.1056 (4)	0.4839 (5)	0.4667 (8)	0.049 (4)*	
C(12)	0.0648 (4)	0.4410 (5)	0.3673 (9)	0.060 (4)*	
C(13)	0.0874 (4)	0.3700 (5)	0.3436 (9)	0.061 (4)*	
C(14)	0.1459 (4)	0.3401 (5)	0.413 (1)	0.072 (5)*	
C(15)	0.1829 (4)	0.3849 (5)	0.510 (1)	0.063 (4)*	
C(16)	0.0478 (5)	0.3238 (6)	0.240 (1)	0.094 (6)*	
N(3)	0.0152 (5)	0.2893 (6)	0.154 (1)	0.149 (6)*	
C(21)	0.4147 (4)	0.6910 (5)	1.0452 (9)	0.054 (4)*	
C(22)	0.4499 (4)	0.7417 (5)	1.137 (1)	0.055 (4)*	
C(23)	0.4174 (4)	0.8065 (4)	1.1634 (9)	0.050 (4)*	
C(24)	0.3536 (4)	0.8221 (5)	1.1043 (9)	0.057 (4)*	
C(25)	0.3217 (4)	0.7702 (4)	1.0121 (9)	0.053 (4)*	
C(26)	0.4539 (4)	0.8617 (5)	1.259 (1)	0.066 (4)*	
N(4)	0.4820 (4)	0.9058 (5)	1.331 (1)	0.104 (5)*	
Cl(1)	0.4380 (1)	0.4150 (2)	0.7780 (3)	0.094 (1)*	
Cl(2)	0.3516 (2)	0.3275 (1)	0.9152 (3)	0.097 (1)*	
Cl(3)	0.4344 (1)	0.4360 (2)	1.0696 (3)	0.101 (1)*	
Cl(4)	0.4475 (2)	0.6490 (2)	0.5138 (4)	0.125 (2)*	0.90
Cl(5)	0.3883 (2)	0.5202 (2)	0.3839 (5)	0.178 (3)*	0.90
Cl(6)	0.3264 (2)	0.6644 (3)	0.3353 (4)	0.169 (3)*	0.90
Cl(7)	0.1827 (4)	0.7582 (3)	0.4181 (7)	0.079 (3)*	0.40
Cl(8)	0.1626 (5)	0.8314 (4)	0.647 (1)	0.161 (5)*	0.40
Cl(9)	0.0685 (3)	0.7196 (5)	0.552 (1)	0.151 (5)*	0.40
Cl(10)	0.0809 (1)	0.4988 (2)	1.0100 (3)	0.083 (1)*	0.90
Cl(11)	0.2045 (2)	0.4760 (2)	1.1660 (4)	0.117 (2)*	0.90
Cl(12)	0.1485 (2)	0.6207 (2)	1.1656 (4)	0.134 (2)*	0.90
Cl(61)	0.417 (2)	0.669 (2)	0.484 (4)	0.13 (1)	0.10
Cl(62)	0.437 (2)	0.535 (2)	0.489 (4)	0.15 (1)	0.10
Cl(63)	0.335 (1)	0.597 (1)	0.298 (3)	0.063 (8)	0.10
Cl(71)	0.0826 (4)	0.7416 (5)	0.690 (1)	0.076 (3)	0.30
Cl(72)	0.1310 (5)	0.7458 (6)	0.425 (1)	0.111 (4)	0.30
Cl(73)	0.1828 (4)	0.8437 (5)	0.669 (1)	0.086 (3)	0.30
Cl(74)	0.0862 (7)	0.7158 (8)	0.457 (2)	0.046 (4)	0.15
Cl(75)	0.184 (1)	0.812 (1)	0.521 (3)	0.136 (9)	0.15
Cl(76)	0.1109 (8)	0.791 (1)	0.718 (2)	0.078 (6)	0.15
Cl(77)	0.0619 (7)	0.7045 (8)	0.504 (2)	0.043 (4)	0.15
Cl(78)	0.1666 (6)	0.7796 (7)	0.442 (1)	0.036 (4)	0.15
Cl(79)	0.1356 (8)	0.8192 (9)	0.690 (2)	0.071 (5)	0.15
Cl(81)	0.092 (1)	0.641 (1)	1.020 (3)	0.063 (8)	0.10
Cl(82)	0.189 (1)	0.553 (1)	1.213 (3)	0.064 (8)	0.10
Cl(83)	0.078 (1)	0.541 (2)	1.003 (3)	0.10 (1)	0.10
(XIII)					
Cu	0.49163 (5)	0.39085 (4)	0.02556 (5)	0.0270 (1)*	
O(1)	0.3931 (3)	0.3595 (3)	−0.1807 (3)	0.042 (1)*	
O(2)	0.3149 (3)	0.4924 (3)	0.1004 (3)	0.042 (1)*	
O(3)	0.5868 (3)	0.4663 (3)	0.2191 (3)	0.045 (1)*	
O(4)	0.6661 (3)	0.3325 (3)	−0.0642 (3)	0.043 (1)*	
N	0.4725 (3)	0.2324 (3)	0.0872 (3)	0.030 (1)*	
C(1)	0.3754 (4)	0.4355 (3)	−0.2545 (4)	0.032 (1)*	
C(2)	0.2771 (4)	0.6029 (4)	0.1051 (4)	0.033 (1)*	
C(3)	0.2943 (5)	0.4086 (5)	−0.4132 (5)	0.050 (2)*	
C(4)	0.1398 (4)	0.6747 (4)	0.1738 (5)	0.045 (2)*	
Cl(1)	0.2155 (2)	0.2860 (2)	−0.4522 (2)	0.0465 (7)*	0.60
Cl(2)	0.4204 (5)	0.3751 (5)	−0.5410 (3)	0.179 (3)*	0.60
Cl(3)	0.1721 (5)	0.5335 (3)	−0.4359 (6)	0.189 (3)*	0.60
Cl(4)	0.1788 (2)	0.7722 (2)	0.3506 (2)	0.0712 (7)*	0.90
Cl(5)	0.0482 (1)	0.5755 (2)	0.1976 (2)	0.0677 (7)*	0.90
Cl(6)	0.0388 (2)	0.7627 (2)	0.0522 (2)	0.095 (1)*	0.90
C(11)	0.3464 (4)	0.2177 (3)	0.0675 (5)	0.037 (2)*	
C(12)	0.3067 (4)	0.1323 (4)	0.1188 (5)	0.041 (2)*	
C(13)	0.4038 (4)	0.0593 (3)	0.1942 (5)	0.038 (2)*	
C(14)	0.5420 (4)	0.0678 (3)	0.2179 (5)	0.034 (1)*	
C(15)	0.6493 (5)	−0.0055 (4)	0.2926 (5)	0.045 (2)*	
C(16)	0.7792 (5)	0.0074 (4)	0.3113 (5)	0.048 (2)*	
C(17)	0.8083 (4)	0.0958 (4)	0.2553 (5)	0.041 (2)*	
C(18)	0.7084 (4)	0.1703 (4)	0.1818 (5)	0.035 (1)*	
C(19)	0.5720 (4)	0.1574 (3)	0.1609 (4)	0.031 (1)*	
Cl(7)	0.3580 (1)	−0.0448 (1)	0.2611 (2)	0.0619 (6)*	
Cl(8)	0.9759 (1)	0.1115 (1)	0.2815 (2)	0.0642 (6)*	
Cl(11)	0.2554 (4)	0.2629 (3)	−0.4661 (4)	0.0650 (9)*	0.40
Cl(12)	0.3754 (4)	0.4139 (3)	−0.5522 (4)	0.0653 (9)*	0.40
Cl(13)	0.1422 (3)	0.5371 (3)	−0.3935 (4)	0.0613 (8)*	0.40
Cl(14)	0.221 (2)	0.739 (2)	0.364 (2)	0.086 (5)*	0.10
Cl(15)	0.026 (2)	0.602 (2)	0.148 (2)	0.085 (5)*	0.10
Cl(16)	0.068 (2)	0.802 (2)	0.069 (2)	0.080 (4)*	0.10
(XIV)					
Cu	0.53802 (6)	0.09252 (6)	0.46632 (7)	0.0407 (2)*	
O(1)	0.3661 (4)	0.2253 (3)	0.5885 (4)	0.056 (2)*	
O(2)	0.6417 (4)	0.0862 (4)	0.6529 (4)	0.060 (2)*	
O(3)	0.6944 (4)	−0.0744 (3)	0.3574 (4)	0.055 (2)*	
O(4)	0.4178 (4)	0.0657 (4)	0.2953 (4)	0.058 (2)*	
N	0.6131 (4)	0.2216 (4)	0.4011 (5)	0.045 (2)*	
C(1)	0.2880 (5)	0.1894 (5)	0.6463 (5)	0.042 (2)*	
C(2)	0.6445 (5)	0.0117 (5)	0.7274 (6)	0.046 (2)*	
C(3)	0.1556 (5)	0.3021 (5)	0.7353 (7)	0.056 (3)*	
C(4)	0.7370 (6)	0.0129 (6)	0.8646 (6)	0.063 (3)*	
S	0.7856 (2)	0.3150 (2)	0.3384 (2)	0.0759 (9)*	

Table 3 (*cont.*)

	x	*y*	*z*	*U*	Occupancy
F	0.8423 (3)	0.1137 (3)	0.4480 (5)	0.080 (2)*	
C(11)	0.7411 (6)	0.2090 (5)	0.4015 (6)	0.055 (3)*	
C(12)	0.6086 (6)	0.3925 (5)	0.3043 (6)	0.058 (3)*	
C(13)	0.5416 (8)	0.5005 (6)	0.2469 (8)	0.083 (4)*	
C(14)	0.4007 (8)	0.5441 (6)	0.2309 (8)	0.085 (4)*	
C(15)	0.3245 (7)	0.4820 (6)	0.2695 (8)	0.075 (3)*	
C(16)	0.3879 (6)	0.3735 (6)	0.3263 (7)	0.058 (3)*	
C(17)	0.5312 (6)	0.3298 (5)	0.3443 (6)	0.047 (2)*	
Cl(1)	0.0275 (2)	0.2443 (2)	0.7580 (3)	0.084 (1)*	0.90
Cl(2)	0.0850 (2)	0.4327 (2)	0.6519 (3)	0.094 (1)*	0.90
Cl(3)	0.2148 (2)	0.3646 (2)	0.9171 (2)	0.097 (1)*	0.90
Cl(4)	0.8480 (3)	0.0934 (4)	0.8778 (4)	0.097 (2)*	0.55
Cl(5)	0.6365 (4)	0.0588 (5)	1.0280 (3)	0.128 (3)*	0.55
Cl(6)	0.8535 (4)	−0.1673 (4)	0.8440 (6)	0.122 (2)*	0.55
Cl(11)	0.051 (2)	0.272 (2)	0.815 (2)	0.098 (6)	0.10
Cl(21)	0.066 (2)	0.374 (2)	0.584 (2)	0.080 (5)	0.10
Cl(31)	0.176 (2)	0.436 (2)	0.860 (3)	0.104 (6)	0.10
Cl(41)	0.8907 (9)	0.0244 (9)	0.812 (1)	0.102 (2)	0.25
Cl(42)	0.770 (1)	0.159 (1)	0.931 (1)	0.111 (3)	0.20
Cl(51)	0.621 (1)	0.171 (1)	0.993 (1)	0.121 (3)	0.25
Cl(52)	0.692 (1)	−0.016 (1)	1.006 (1)	0.093 (3)	0.20
Cl(61)	0.7724 (8)	−0.1078 (8)	0.936 (1)	0.096 (2)	0.25
Cl(62)	0.891 (1)	−0.122 (1)	0.809 (1)	0.113 (3)	0.20
(XV)					
Cu(1)	0.09929 (9)	0.28147 (5)	0.11321 (8)	0.0532 (4)*	
Cu(2)	0.1118 (1)	0.28286 (5)	0.41184 (8)	0.0543 (4)*	
O(11)	−0.0223 (5)	0.3650 (3)	0.1203 (4)	0.065 (2)*	
O(12)	0.2289 (5)	0.3354 (3)	0.1969 (4)	0.064 (2)*	
O(13)	0.2199 (5)	0.1963 (3)	0.1137 (4)	0.054 (2)*	
O(14)	−0.0288 (5)	0.2153 (3)	0.1964 (4)	0.059 (2)*	
O(21)	−0.0143 (5)	0.3605 (3)	0.3309 (4)	0.065 (2)*	
O(22)	0.2392 (5)	0.3416 (3)	0.4095 (4)	0.062 (2)*	
O(23)	0.2402 (5)	0.1926 (3)	0.3249 (4)	0.062 (2)*	
O(24)	−0.0088 (5)	0.2203 (3)	0.4082 (4)	0.056 (2)*	
N(1)	0.0100 (5)	0.2562 (3)	−0.0574 (5)	0.047 (2)*	
N(2)	0.1954 (5)	0.2445 (3)	0.5823 (5)	0.046 (2)*	
C(1)	−0.0484 (7)	0.3879 (4)	0.2249 (7)	0.055 (3)*	
C(2)	0.2716 (7)	0.3543 (4)	0.3039 (7)	0.059 (3)*	
C(3)	0.2602 (7)	0.1690 (4)	0.2209 (6)	0.051 (3)*	
C(4)	−0.0489 (7)	0.1977 (4)	0.3012 (7)	0.050 (3)*	
C(5)	−0.1324 (8)	0.4610 (4)	0.2236 (7)	0.068 (3)*	
C(6)	0.3785 (9)	0.3978 (5)	0.3082 (8)	0.077 (4)*	
C(7)	0.3424 (8)	0.0961 (5)	0.2163 (8)	0.070 (4)*	
C(8)	−0.1331 (9)	0.1414 (5)	0.3051 (7)	0.074 (4)*	
C(11)	−0.0343 (7)	0.3067 (4)	−0.1458 (6)	0.054 (3)*	
C(12)	−0.0859 (7)	0.2863 (4)	−0.2651 (6)	0.054 (3)*	
C(13)	−0.0952 (7)	0.2185 (4)	−0.2960 (7)	0.060 (3)*	
C(14)	−0.0492 (7)	0.1685 (4)	−0.2002 (7)	0.059 (3)*	
C(15)	0.0018 (7)	0.1885 (4)	−0.0819 (7)	0.051 (3)*	
C(21)	0.2234 (7)	0.2893 (4)	0.6766 (6)	0.052 (3)*	
C(22)	0.2725 (7)	0.2626 (4)	0.7965 (6)	0.051 (3)*	
C(23)	0.2969 (7)	0.1915 (4)	0.8204 (7)	0.053 (3)*	
C(24)	0.2694 (7)	0.1472 (4)	0.7203 (7)	0.057 (3)*	
C(25)	0.2168 (7)	0.1741 (4)	0.6013 (7)	0.053 (3)*	
C(30)	0.565 (1)	0.2831 (7)	0.692 (1)	0.143 (7)*	
C(31)	0.555 (1)	0.2197 (9)	0.635 (1)	0.159 (8)*	
C(32)	0.591 (1)	0.1586 (8)	0.706 (1)	0.156 (8)*	
C(33)	0.627 (1)	0.1639 (7)	0.833 (1)	0.153 (7)*	
C(34)	0.639 (1)	0.2275 (8)	0.897 (1)	0.163 (8)*	
C(35)	0.606 (1)	0.2870 (8)	0.819 (2)	0.183 (9)*	
C(36)	0.626 (2)	0.346 (1)	0.898 (3)	0.35 (2)*	
Cl(1)	−0.2024 (7)	0.4870 (3)	0.0727 (5)	0.132 (3)*	0.50
Cl(2)	−0.0383 (6)	0.5190 (3)	0.2831 (7)	0.128 (3)*	0.50
Cl(3)	−0.2533 (6)	0.4562 (4)	0.3180 (8)	0.172 (4)*	0.50
Cl(4)	0.3666 (5)	0.4488 (2)	0.1753 (4)	0.144 (2)*	0.75
Cl(5)	0.3973 (5)	0.4460 (3)	0.4425 (4)	0.161 (3)*	0.75
Cl(6)	0.5155 (4)	0.3332 (3)	0.3083 (6)	0.164 (3)*	0.75
Cl(7)	0.4680 (4)	0.1025 (3)	0.1245 (4)	0.110 (2)*	0.60
Cl(8)	0.4199 (5)	0.0668 (2)	0.3658 (4)	0.109 (2)*	0.60
Cl(9)	0.2451 (5)	0.0400 (2)	0.1372 (7)	0.148 (3)*	0.60
Cl(10)	−0.0573 (5)	0.0749 (2)	0.4196 (4)	0.093 (2)*	0.60
Cl(11)	−0.1648 (4)	0.0967 (2)	0.1622 (3)	0.074 (2)*	0.60
Cl(12)	−0.2723 (4)	0.1811 (3)	0.3577 (5)	0.114 (2)*	0.60
Cl(13)	−0.1374 (3)	0.3513 (1)	−0.3782 (2)	0.093 (1)*	
Cl(14)	−0.0559 (3)	0.0812 (1)	−0.2282 (2)	0.097 (1)*	
Cl(15)	0.2999 (2)	0.3223 (1)	0.9155 (2)	0.0743 (9)*	
Cl(16)	0.3014 (3)	0.0580 (1)	0.7398 (2)	0.096 (1)*	
Cl(011)	−0.1122 (8)	0.5100 (5)	0.0892 (8)	0.098 (3)	0.30
Cl(21)	−0.0852 (7)	0.5092 (4)	0.3608 (7)	0.070 (2)	0.30
Cl(31)	−0.279 (1)	0.4513 (6)	0.2204 (9)	0.113 (3)	0.30
Cl(012)	−0.056 (1)	0.5175 (9)	0.139 (1)	0.119 (5)	0.20
Cl(22)	−0.164 (1)	0.4914 (8)	0.365 (1)	0.103 (4)	0.20
Cl(32)	−0.280 (1)	0.4575 (8)	0.132 (1)	0.109 (5)	0.20
Cl(41)	0.493 (1)	0.3870 (8)	0.424 (1)	0.137 (5)	0.25
Cl(51)	0.294 (2)	0.491 (1)	0.312 (2)	0.174 (6)	0.25
Cl(61)	0.445 (1)	0.3994 (8)	0.177 (1)	0.144 (5)	0.25
Cl(71)	0.4820 (9)	0.1099 (5)	0.1822 (9)	0.105 (3)	0.30
Cl(81)	0.3535 (8)	0.0472 (4)	0.3516 (7)	0.081 (2)	0.30
Cl(91)	0.2840 (7)	0.0450 (4)	0.0950 (7)	0.080 (2)	0.30
Cl(72)	0.485 (4)	0.104 (2)	0.293 (4)	0.16 (1)	0.10
Cl(82)	0.283 (2)	0.036 (1)	0.329 (2)	0.075 (6)	0.10
Cl(92)	0.361 (2)	0.058 (1)	0.090 (2)	0.087 (7)	0.10
Cl(101)	−0.141 (1)	0.0981 (7)	0.426 (1)	0.085 (4)	0.20
Cl(111)	−0.128 (1)	0.0911 (6)	0.160 (1)	0.080 (3)	0.20
Cl(121)	−0.299 (1)	0.2096 (8)	0.285 (1)	0.114 (5)	0.20
Cl(102)	−0.001 (1)	0.0682 (7)	0.395 (1)	0.089 (4)	0.20
Cl(112)	−0.193 (1)	0.1163 (7)	0.158 (1)	0.088 (4)	0.20
Cl(122)	−0.242 (1)	0.1498 (7)	0.396 (1)	0.082 (3)	0.20
(XVI)					
Cu	0.43833 (4)	0.69990 (5)	0.67218 (4)	0.0469 (2)*	
O(1)	0.4915 (2)	0.7918 (3)	0.6363 (3)	0.063 (2)*	
O(2)	0.5162 (2)	0.6075 (3)	0.6635 (3)	0.056 (2)*	
O(3)	0.3932 (2)	0.6127 (3)	0.7216 (2)	0.060 (2)*	
O(4)	0.4176 (2)	0.7931 (3)	0.7494 (3)	0.060 (2)*	
N	0.3653 (2)	0.6833 (3)	0.5585 (3)	0.044 (2)*	
C(1)	0.5498 (3)	0.8184 (4)	0.6815 (4)	0.053 (3)*	
C(2)	0.5747 (3)	0.5866 (4)	0.7077 (4)	0.050 (2)*	
C(3)	0.5840 (4)	0.8941 (5)	0.6462 (5)	0.081 (3)*	
C(4)	0.6190 (3)	0.5189 (5)	0.6741 (4)	0.069 (3)*	
C(11)	0.3128 (3)	0.6217 (4)	0.5490 (4)	0.051 (2)*	
C(12)	0.2592 (3)	0.6136 (4)	0.4739 (4)	0.057 (3)*	
C(13)	0.2618 (3)	0.6699 (4)	0.4109 (4)	0.056 (3)*	
C(14)	0.3161 (3)	0.7307 (5)	0.4208 (4)	0.058 (3)*	
C(15)	0.3696 (3)	0.7367 (4)	0.4962 (3)	0.047 (2)*	
C(16)	0.3226 (5)	0.7939 (6)	0.3521 (4)	0.090 (4)*	
C(17)	0.2003 (4)	0.5452 (6)	0.4649 (5)	0.086 (4)*	
Cl(1)	0.5794 (3)	0.8670 (4)	0.5429 (3)	0.137 (3)*	0.60
Cl(2)	0.6669 (2)	0.9230 (4)	0.6962 (3)	0.166 (3)*	0.60
Cl(3)	0.5264 (3)	0.9892 (3)	0.6365 (4)	0.159 (3)*	0.60
Cl(4)	0.5756 (1)	0.4797 (2)	0.5768 (1)	0.092 (1)*	0.90
Cl(5)	0.6400 (2)	0.4264 (2)	0.7399 (2)	0.144 (2)*	0.90
Cl(6)	0.6995 (1)	0.5663 (3)	0.6733 (2)	0.144 (2)*	0.90
Cl(11)	0.6076 (5)	0.9799 (4)	0.7269 (5)	0.144 (4)*	0.40
Cl(21)	0.5345 (3)	0.9444 (5)	0.5657 (4)	0.134 (3)*	0.40
Cl(31)	0.6671 (4)	0.8546 (6)	0.6407 (6)	0.149 (4)*	0.40
Cl(41)	0.695 (1)	0.492 (2)	0.731 (1)	0.077 (7)	0.10
Cl(51)	0.631 (2)	0.582 (2)	0.587 (2)	0.14 (1)	0.10
Cl(61)	0.566 (2)	0.433 (2)	0.631 (2)	0.13 (1)	0.10
C(21)	0.6775 (8)	0.236 (1)	0.8866 (8)	0.184 (8)*	
C(22)	0.6717 (8)	0.3134 (9)	0.9200 (9)	0.186 (8)*	
C(23)	0.605 (1)	0.339 (1)	0.920 (1)	0.25 (1)*	
C(24)	0.548 (1)	0.279 (1)	0.883 (1)	0.28 (2)*	
C(25)	0.561 (1)	0.201 (1)	0.849 (1)	0.26 (1)*	
C(26)	0.6279 (9)	0.1818 (9)	0.8533 (8)	0.20 (1)*	

Table 4. *Selected bond lengths* (Å) *and bond angles* (°)

(I)

Cu(1)···Cu(2)	3.261 (1)	O(12)—C(2)	1.242 (6)	Cu(2)—Cu(1)—O(11)	83.6 (1)	O(22)—Cu(2)—O(24)	173.4 (2)
Cu(1)—O(11)	1.944 (3)	O(13)—C(3)	1.264 (6)	Cu(2)—Cu(1)—O(12)	68.5 (1)	O(22)—Cu(2)—N(2)	92.0 (2)
Cu(1)—O(12)	2.012 (4)	O(14)—C(4)	1.224 (6)	Cu(2)—Cu(1)—O(13)	90.5 (1)	O(23)—Cu(2)—O(24)	87.5 (2)
Cu(1)—O(13)	1.927 (3)	O(21)—C(1)	1.234 (6)	Cu(2)—Cu(1)—O(14)	61.31 (9)	O(23)—Cu(2)—N(2)	93.8 (2)
Cu(1)—O(14)	2.328 (4)	O(22)—C(2)	1.247 (6)	Cu(2)—Cu(1)—N(1)	152.6 (1)	O(24)—Cu(2)—N(2)	91.3 (2)
Cu(1)—N(1)	2.031 (4)	O(23)—C(3)	1.222 (6)	O(11)—Cu(1)—O(12)	88.4 (2)	Cu(1)—O(11)—C(1)	119.1 (3)
Cu(2)—O(21)	2.020 (4)	O(24)—C(4)	1.260 (6)	O(11)—Cu(1)—O(13)	174.1 (2)	Cu(1)—O(12)—C(2)	137.8 (4)
Cu(2)—O(22)	1.934 (4)	C(1)—C(5)	1.548 (7)	O(11)—Cu(1)—O(14)	89.6 (1)	Cu(1)—O(13)—C(3)	117.0 (3)
Cu(2)—O(23)	2.284 (3)	C(2)—C(6)	1.551 (9)	O(11)—Cu(1)—N(1)	95.9 (2)	Cu(1)—O(14)—C(4)	141.1 (4)
Cu(2)—O(24)	1.928 (4)	C(3)—C(7)	1.547 (7)	O(12)—Cu(1)—O(13)	90.0 (2)	Cu(2)—O(21)—C(1)	140.5 (3)
Cu(2)—N(2)	2.033 (4)	C(4)—C(8)	1.55 (1)	O(12)—Cu(1)—O(14)	129.7 (1)	Cu(2)—O(22)—C(2)	122.1 (4)
O(11)—C(1)	1.249 (6)			O(12)—Cu(1)—N(1)	138.9 (2)	Cu(2)—O(23)—C(3)	140.0 (3)
				O(13)—Cu(1)—O(14)	87.1 (1)	Cu(2)—O(24)—C(4)	114.8 (4)

Table 4 (*cont.*)

O(13)—Cu(1)—N(1)	89.0 (2)	O(11)—C(1)—O(21)	128.7 (5)
O(14)—Cu(1)—N(1)	91.3 (2)	O(11)—C(1)—C(5)	115.6 (4)
Cu(1)—Cu(2)—O(21)	66.4 (1)	O(21)—C(1)—C(5)	115.5 (4)
Cu(1)—Cu(2)—O(22)	81.9 (1)	O(12)—C(2)—O(22)	129.5 (6)
Cu(1)—Cu(2)—O(23)	62.99 (9)	O(12)—C(2)—C(6)	116.2 (5)
Cu(1)—Cu(2)—O(24)	92.8 (1)	O(22)—C(2)—C(6)	114.2 (5)
Cu(1)—Cu(2)—N(2)	156.1 (1)	O(13)—C(3)—O(23)	129.1 (5)
O(21)—Cu(2)—O(22)	88.6 (2)	O(13)—C(3)—C(7)	112.8 (4)
O(21)—Cu(2)—O(23)	129.4 (1)	O(23)—C(3)—C(7)	118.1 (5)
O(21)—Cu(2)—O(24)	92.8 (2)	O(14)—C(4)—O(24)	129.0 (6)
O(21)—Cu(2)—N(2)	136.8 (2)	O(14)—C(4)—C(8)	117.6 (5)
O(22)—Cu(2)—O(23)	86.6 (2)	O(24)—C(4)—C(8)	113.4 (5)

(II)

Cu(1)···Cu(2)	3.216 (2)	Cu(2)—O(12)	1.950 (9)
Cu(1)—O(11)	2.032 (8)	Cu(2)—O(22)	2.226 (9)
Cu(1)—O(21)	1.915 (9)	Cu(2)—O(32)	1.941 (9)
Cu(1)—O(31)	2.198 (9)	Cu(2)—O(42)	2.016 (8)
Cu(1)—O(41)	1.942 (9)	Cu(2)—N(2)	2.019 (8)
Cu(1)—N(1)	2.019 (8)		

O(11)—Cu(1)—O(21)	90.1 (3)	O(22)—Cu(2)—O(42)	131.7 (3)
O(11)—Cu(1)—O(31)	131.2 (3)	O(22)—Cu(2)—N(2)	97.8 (4)
O(11)—Cu(1)—O(41)	87.3 (3)	O(32)—Cu(2)—O(42)	91.4 (4)
O(11)—Cu(1)—N(1)	131.8 (4)	O(32)—Cu(2)—N(2)	89.8 (4)
O(21)—Cu(1)—O(31)	89.4 (4)	O(42)—Cu(2)—N(2)	130.5 (4)
O(21)—Cu(1)—O(41)	173.9 (3)	Cu(1)—O(11)—C(10)	141.1 (8)
O(21)—Cu(1)—N(1)	91.9 (4)	Cu(2)—O(12)—C(10)	117.1 (7)
O(31)—Cu(1)—O(41)	88.2 (3)	Cu(1)—O(21)—C(20)	117.0 (8)
O(31)—Cu(1)—N(1)	97.0 (3)	Cu(2)—O(22)—C(20)	137.4 (8)
O(41)—Cu(1)—N(1)	93.9 (4)	Cu(1)—O(31)—C(30)	138.8 (8)
O(12)—Cu(2)—O(22)	87.4 (3)	Cu(2)—O(32)—C(30)	118.3 (8)
O(12)—Cu(2)—O(32)	173.8 (3)	Cu(1)—O(41)—C(40)	117.3 (7)
O(12)—Cu(2)—O(42)	88.5 (3)	Cu(2)—O(42)—C(40)	139.5 (9)
O(12)—Cu(2)—N(2)	94.9 (4)		
O(22)—Cu(2)—O(32)	88.1 (4)		

(III)

Cu(1)···Cu(2)	3.226 (1)	Cu(2)—O(21)	1.934 (6)
Cu(1)—O(11)	2.020 (5)	Cu(2)—O(22)	2.017 (6)
Cu(1)—O(12)	1.930 (6)	Cu(2)—O(23)	1.902 (6)
Cu(1)—O(13)	2 248 (6)	Cu(2)—O(24)	2.217 (6)
Cu(1)—O(14)	1.905 (5)	Cu(2)—N(2)	2.007 (6)
Cu(1)—N(1)	2.016 (5)		

O(11)—Cu(1)—O(12)	89.7 (2)	O(22)—Cu(2)—O(24)	131.0 (2)
O(11)—Cu(1)—O(13)	130.9 (2)	O(22)—Cu(2)—N(2)	129.3 (3)
O(11)—Cu(1)—O(14)	89.7 (2)	O(23)—Cu(2)—O(24)	88.8 (2)
O(11)—Cu(1)—N(1)	134.9 (2)	O(23)—Cu(2)—N(2)	91.6 (3)
O(12)—Cu(1)—O(13)	88.4 (2)	O(24)—Cu(2)—N(2)	99.7 (3)
O(12)—Cu(1)—O(14)	174.1 (2)	Cu(1)—O(11)—C(1)	139.6 (6)
O(12)—Cu(1)—N(1)	93.6 (2)	Cu(1)—O(12)—C(2)	119.2 (5)
O(13)—Cu(1)—O(14)	87.6 (2)	Cu(1)—O(13)—C(3)	139.7 (5)
O(13)—Cu(1)—N(1)	94.2 (2)	Cu(1)—O(14)—C(4)	116.6 (5)
O(14)—Cu(1)—N(1)	91.0 (2)	Cu(2)—O(21)—C(1)	119.3 (5)
O(21)—Cu(2)—O(22)	89.5 (2)	Cu(2)—O(22)—C(2)	140.6 (6)
O(21)—Cu(2)—O(23)	174.7 (2)	Cu(2)—O(23)—C(3)	117.0 (5)
O(21)—Cu(2)—O(24)	86.8 (2)	Cu(2)—O(24)—C(4)	139.2 (5)
O(21)—Cu(2)—N(2)	92.1 (3)		
O(22)—Cu(2)—O(23)	91.2 (2)		

(IV)

Cu(1)···Cu(2)	3.186 (2)	Cu(2)—O(21)	2.079 (4)
Cu(1)—O(11)	1.952 (4)	Cu(2)—O(22)	1.936 (6)
Cu(1)—O(12)	2.076 (6)	Cu(2)—O(23)	2.237 (5)
Cu(1)—O(13)	1.909 (4)	Cu(2)—O(24)	1.924 (6)
Cu(1)—O(14)	2.189 (6)	Cu(2)—N(2)	2.005 (7)
Cu(1)—N(1)	2.022 (7)		

O(11)—Cu(1)—O(12)	87.9 (2)	O(22)—Cu(2)—O(24)	174.6 (2)
O(11)—Cu(1)—O(13)	174.7 (2)	O(22)—Cu(2)—N(2)	94.0 (3)
O(11)—Cu(1)—O(14)	87.1 (2)	O(23)—Cu(2)—O(24)	89.7 (2)
O(11)—Cu(1)—N(1)	93.3 (2)	O(23)—Cu(2)—N(2)	97.0 (2)
O(12)—Cu(1)—O(13)	89.2 (2)	O(24)—Cu(2)—N(2)	91.2 (3)
O(12)—Cu(1)—O(14)	131.9 (2)	Cu(1)—O(11)—C(1)	117.5 (4)
O(12)—Cu(1)—N(1)	126.3 (3)	Cu(1)—O(12)—C(2)	140.5 (6)
O(13)—Cu(1)—O(14)	91.4 (2)	Cu(1)—O(13)—C(3)	119.4 (5)
O(13)—Cu(1)—N(1)	92.0 (2)	Cu(1)—O(14)—C(4)	137.2 (6)
O(14)—Cu(1)—N(1)	101.8 (2)	Cu(2)—O(21)—C(1)	140.1 (5)
O(21)—Cu(2)—O(22)	88.4 (2)	Cu(2)—O(22)—C(2)	116.9 (6)
O(21)—Cu(2)—O(23)	132.6 (2)	Cu(2)—O(23)—C(3)	135.2 (5)
O(21)—Cu(2)—O(24)	87.3 (2)	Cu(2)—O(24)—C(4)	118.5 (6)
O(21)—Cu(2)—N(2)	130.3 (2)		
O(22)—Cu(2)—O(23)	91.0 (2)		

(V)

Cu(1)···Cu(2)	3.054 (3)	Cu(2)—O(12)	2.134 (9)
Cu(1)—O(11)	1.89 (1)	Cu(2)—O(22)	1.98 (1)
Cu(1)—O(21)	1.91 (1)	Cu(2)—O(32)	1.91 (1)
Cu(1)—O(31)	2.21 (1)	Cu(2)—O(42)	1.93 (1)
Cu(1)—O(41)	2.00 (1)	Cu(2)—N(51)	2.12 (1)
Cu(1)—N(1)	2.11 (1)		

O(11)—Cu(1)—O(21)	174.5 (5)	O(22)—Cu(2)—O(42)	91.2 (5)
O(11)—Cu(1)—O(31)	87.2 (4)	O(22)—Cu(2)—N(51)	130.4 (5)
O(11)—Cu(1)—O(41)	90.1 (5)	O(32)—Cu(2)—O(42)	175.7 (5)
O(11)—Cu(1)—N(1)	90.9 (4)	O(32)—Cu(2)—N(51)	92.6 (5)
O(21)—Cu(1)—O(31)	87.5 (4)	O(42)—Cu(2)—N(51)	88.8 (5)
O(21)—Cu(1)—O(41)	92.4 (4)	Cu(1)—O(11)—C(11)	118.3 (9)
O(21)—Cu(1)—N(1)	91.1 (4)	Cu(1)—O(21)—C(21)	119.6 (9)
O(31)—Cu(1)—O(41)	136.7 (4)	Cu(1)—O(31)—C(31)	137 (1)
O(31)—Cu(1)—N(1)	91.7 (4)	Cu(1)—O(41)—C(41)	136 (1)
O(41)—Cu(1)—N(1)	131.6 (5)	Cu(2)—O(12)—C(11)	138.5 (9)
O(12)—Cu(2)—O(22)	137.1 (4)	Cu(2)—O(22)—C(21)	137 (1)
O(12)—Cu(2)—O(32)	86.9 (4)	Cu(2)—O(32)—C(31)	116 (1)
O(12)—Cu(2)—O(42)	88.9 (4)	Cu(2)—O(42)—C(41)	119 (1)
O(12)—Cu(2)—N(51)	92.5 (4)		
O(22)—Cu(2)—O(32)	91.0 (5)		

(VI)

Cu···Cu^{i}	3.0622 (7)	O(1)—C(1)	1.248 (4)
Cu—O(1)	1.940 (2)	O(2)—C(21^{i})	1.251 (4)
Cu—O(2)	1.950 (2)	O(3)—C(21^{i})	1.230 (4)
Cu—O(3)	2.167 (2)	O(4)—C(1^{i})	1.237 (4)
Cu—O(4)	1.986 (2)	C(1)—C(3)	1.547 (5)
Cu—N(9)	2.045 (3)	C(21)—C(23)	1.551 (4)

O(1)—Cu—O(2)	174.5 (1)	O(4)—Cu—Cu^{i}	71.64 (8)
O(1)—Cu—O(3)	86.33 (9)	N(9)—Cu—Cu^{i}	156.91 (7)
O(1)—Cu—O(4)	90.00 (9)	Cu—O(1)—C(1)	120.2 (2)
O(1)—Cu—N(9)	93.9 (1)	Cu—O(2)—C(21^{i})	115.0 (2)
O(1)—Cu—Cu^{i}	83.93 (7)	Cu—O(3)—C(21^{i})	136.0 (2)
O(2)—Cu—O(3)	92.27 (9)	Cu—O(4)—C(1^{i})	134.8 (2)
O(2)—Cu—O(4)	87.52 (9)	O(1)—C(1)—C(3)	115.9 (3)
O(2)—Cu—N(9)	91.4 (1)	O(1)—C(1)—O(4^{i})	128.6 (3)
O(2)—Cu—Cu^{i}	90.66 (7)	C(3)—C(1)—O(4^{i})	115.5 (3)
O(3)—Cu—O(4)	138.2 (1)	O(3)—C(21)—C(23)	114.7 (3)
O(3)—Cu—N(9)	90.4 (1)	O(3)—C(21)—O(2^{i})	128.7 (3)
O(3)—Cu—Cu^{i}	66.57 (6)	C(23)—C(21)—O(2^{i})	116.5 (3)
O(4)—Cu—N(9)	131.4 (1)		

(VII)

Cu(1)···Cu(2)	3.066 (1)	Cu(2)—O(21)	2.084 (5)
Cu(1)—O(11)	1.924 (5)	Cu(2)—O(22)	1.902 (6)
Cu(1)—O(12)	2.020 (6)	Cu(2)—O(23)	2.174 (5)
Cu(1)—O(13)	1.908 (5)	Cu(2)—O(24)	1.880 (6)
Cu(1)—O(14)	2.264 (5)	Cu(2)—N(2)	2.072 (7)
Cu(1)—N(1)	2.057 (7)		

O(11)—Cu(1)—O(12)	88.3 (2)	O(22)—Cu(2)—O(24)	177.4 (2)
O(11)—Cu(1)—O(13)	177.2 (2)	O(22)—Cu(2)—N(2)	89.9 (3)
O(11)—Cu(1)—O(14)	89.3 (2)	O(23)—Cu(2)—O(24)	89.4 (2)
O(11)—Cu(1)—N(1)	92.2 (2)	O(23)—Cu(2)—N(2)	106.0 (2)
O(12)—Cu(1)—O(13)	90.7 (2)	O(24)—Cu(2)—N(2)	92.5 (2)
O(12)—Cu(1)—O(14)	137.5 (2)	Cu(1)—O(11)—C(1)	116.0 (5)
O(12)—Cu(1)—N(1)	137.4 (2)	Cu(1)—O(12)—C(2)	132.2 (5)
O(13)—Cu(1)—O(14)	89.8 (2)	Cu(1)—O(13)—C(3)	119.4 (5)
O(13)—Cu(1)—N(1)	90.3 (3)	Cu(1)—O(14)—C(4)	136.8 (6)
O(14)—Cu(1)—N(1)	85.0 (2)	Cu(2)—O(21)—C(1)	136.2 (4)
O(21)—Cu(2)—O(22)	88.0 (2)	Cu(2)—O(22)—C(2)	122.7 (6)
O(21)—Cu(2)—O(23)	137.3 (2)	Cu(2)—O(23)—C(3)	132.4 (6)
O(21)—Cu(2)—O(24)	91.7 (2)	Cu(2)—O(24)—C(4)	117.7 (5)
O(21)—Cu(2)—N(2)	116.6 (2)		
O(22)—Cu(2)—O(23)	89.1 (2)		

(VIII)

Cu(1)···Cu(2)	3.113 (3)	Cu(2)—O(21)	2.188 (9)
Cu(1)—O(11)	1.914 (9)	Cu(2)—O(22)	1.953 (9)
Cu(1)—O(12)	2.252 (9)	Cu(2)—O(23)	2.014 (9)
Cu(1)—O(13)	1.93 (1)	Cu(2)—O(24)	1.91 (1)
Cu(1)—O(14)	2.001 (9)	Cu(2)—N(2)	2.07 (1)
Cu(1)—N(1)	2.074 (9)		

O(11)—Cu(1)—O(12)	89.4 (4)	O(22)—Cu(2)—O(24)	176.0 (4)
O(11)—Cu(1)—O(13)	174.6 (4)	O(22)—Cu(2)—N(2)	90.3 (4)
O(11)—Cu(1)—O(14)	90.7 (4)	O(23)—Cu(2)—O(24)	90.6 (4)
O(11)—Cu(1)—N(1)	90.4 (4)	O(23)—Cu(2)—N(2)	134.0 (4)
O(12)—Cu(1)—O(13)	86.4 (4)	O(24)—Cu(2)—N(2)	92.8 (4)
O(12)—Cu(1)—O(14)	135.4 (4)	Cu(1)—O(11)—C(1)	115.0 (9)
O(12)—Cu(1)—N(1)	90.7 (3)	Cu(1)—O(12)—C(2)	138.3 (8)
O(13)—Cu(1)—O(14)	89.8 (4)	Cu(1)—O(13)—C(3)	120.3 (8)

Table 4 (*cont.*)

O(13)—Cu(1)—N(1)	93.1 (4)	Cu(1)—O(14)—C(4)	136 (1)	O(13)—Cu(1)—O(14)	89.5 (2)
O(14)—Cu(1)—N(1)	133.8 (4)	Cu(2)—O(21)—C(1)	136.3 (8)	O(13)—Cu(1)—N(1)	95.9 (2)
O(21)—Cu(2)—O(22)	90.8 (4)	Cu(2)—O(22)—C(2)	115.3 (9)	O(14)—Cu(1)—N(1)	98.1 (2)
O(21)—Cu(2)—O(23)	136.4 (4)	Cu(2)—O(23)—C(3)	135 (1)	O(21)—Cu(2)—O(22)	88.8 (3)
O(21)—Cu(2)—O(24)	86.8 (4)	Cu(2)—O(24)—C(4)	121.0 (8)	O(21)—Cu(2)—O(23)	166.7 (2)
O(21)—Cu(2)—N(2)	89.6 (4)			O(21)—Cu(2)—O(24)	90.5 (2)
O(22)—Cu(2)—O(23)	88.9 (4)			O(21)—Cu(2)—N(2)	98.3 (2)
				O(22)—Cu(2)—O(23)	88.4 (2)

O(11)—Cu(1)—O(12)	88.5 (1)	O(22)—Cu(2)—O(24)	174.4 (2)	O(13)—Cu(1)—O(14)	89.5 (2)
O(11)—Cu(1)—O(13)	173.5 (2)	O(22)—Cu(2)—N(2)	90.6 (2)	O(13)—Cu(1)—N(1)	95.9 (2)
O(11)—Cu(1)—O(14)	89.5 (2)	O(23)—Cu(2)—O(24)	90.3 (2)	O(14)—Cu(1)—N(1)	98.1 (2)
O(11)—Cu(1)—N(1)	94.2 (2)	O(23)—Cu(2)—N(2)	93.8 (2)	O(21)—Cu(2)—O(22)	88.8 (3)
O(12)—Cu(1)—O(13)	87.6 (1)	O(24)—Cu(2)—N(2)	94.9 (2)	O(21)—Cu(2)—O(23)	166.7 (2)
O(12)—Cu(1)—O(14)	145.4 (2)	Cu(1)—O(11)—C(1)	121.2 (4)	O(21)—Cu(2)—O(24)	90.5 (2)
O(12)—Cu(1)—N(1)	90.2 (2)	Cu(1)—O(12)—C(2)	133.8 (4)	O(21)—Cu(2)—N(2)	98.3 (2)
O(13)—Cu(1)—O(14)	90.7 (2)	Cu(1)—O(13)—C(3)	115.2 (3)	O(22)—Cu(2)—O(23)	88.4 (2)
O(13)—Cu(1)—N(1)	91.1 (2)	Cu(1)—O(14)—C(4)	129.3 (4)		
O(14)—Cu(1)—N(1)	124.3 (2)	Cu(2)—O(21)—C(1)	129.2 (4)		
O(21)—Cu(2)—O(22)	88.3 (2)	Cu(2)—O(22)—C(2)	117.5 (3)		
O(21)—Cu(2)—O(23)	145.6 (2)	Cu(2)—O(23)—C(3)	133.3 (4)		
O(21)—Cu(2)—O(24)	89.9 (2)	Cu(2)—O(24)—C(4)	120.8 (4)		
O(21)—Cu(2)—N(2)	120.4 (2)				
O(22)—Cu(2)—O(23)	88.1 (1)				

O(1)—Cu—Cu^{ii}	78.3 (1)	O(3)—Cu—N	101.3 (1)	O(1)—Cu—O(2)	89.8 (1)
O(2)—Cu—Cu^{ii}	81.9 (1)	O(4)—Cu—N	97.1 (1)	O(1)—Cu—O(3)	164.3 (1)
O(3)—Cu—Cu^{ii}	85.9 (1)	Cu—O(1)—C(1)	127.5 (2)	O(1)—Cu—O(4)	88.8 (1)
O(4)—Cu—Cu^{ii}	82.6 (1)	Cu—O(2)—C(2)	124.0 (3)	O(1)—Cu—N	94.5 (1)
N—Cu—Cu^{ii}	172.77 (9)	Cu—O(3)—C(1^{ii})	118.2 (3)	O(2)—Cu—O(3)	87.9 (1)
		Cu—O(4)—C(2^{ii})	122.6 (2)	O(2)—Cu—O(4)	164.4 (1)
		O(1)—C(1)—C(3)	113.9 (4)	O(2)—Cu—N	98.5 (1)
		O(1)—C(1)—O(3^{ii})	129.4 (4)	O(3)—Cu—O(4)	89.3 (1)
		C(3)—C(1)—O(3^{ii})	116.6 (5)		
		O(2)—C(2)—C(4)	115.9 (4)		
		O(2)—C(2)—O(4^{ii})	128.8 (4)		
		C(4)—C(2)—O(4^{ii})	115.1 (4)		

Cu···Cu^{v}	2.7364 (9)	Cu—N(9)	2.116 (4)	N(9)—Cu—O(2^{v})	90.0 (4)
Cu—O(1)	1.945 (7)	Cu^{v}—O(10^{iii})	2.11 (1)	O(10^{iii})—Cu^{v}—O(2)	101.2 (5)
Cu—O(2^{iv})	1.968 (7)			O(2^{v})—Cu—O(2^{v})	88.8 (3)
				Cu—O(1)—C(1)	121.3 (6)
O(1)—Cu—N(9)	104.1 (4)			C(1)—O(2)—Cu^{iv}	122.3 (7)
O(1^{iv})—Cu^{v}—O(10^{iii})	92.9 (5)				
O(1)—Cu—O(2^{iv})	90.2 (3)				
O(1)—Cu—O(2^{v})	165.8 (3)				
O(1)—Cu—O(1^{v})	87.4 (3)				

Cu(1)···Cu(2)	2.769 (1)	Cu(2)—O(21)	1.963 (5)	O(11)—Cu(1)—O(12)	88.0 (2)
Cu(1)—O(11)	1.977 (5)	Cu(2)—O(22)	1.976 (6)	O(11)—Cu(1)—O(13)	162.2 (2)
Cu(1)—O(12)	1.979 (6)	Cu(2)—O(23)	1.973 (6)	O(11)—Cu(1)—O(14)	88.2 (2)
Cu(1)—O(13)	1.987 (6)	Cu(2)—O(24)	1.974 (6)	O(11)—Cu(1)—N(1)	101.9 (2)
Cu(1)—O(14)	1.983 (6)	Cu(2)—N(2)	2.126 (6)	O(12)—Cu(1)—O(13)	89.8 (2)
Cu(1)—N(1)	2.142 (6)			O(12)—Cu(1)—O(14)	165.3 (2)
				O(12)—Cu(1)—N(1)	96.5 (2)
				O(22)—Cu(2)—O(24)	163.2 (2)
				O(22)—Cu(2)—N(2)	102.7 (2)
				O(23)—Cu(2)—O(24)	88.5 (2)
				O(23)—Cu(2)—N(2)	95.0 (2)
				O(24)—Cu(2)—N(2)	94.1 (2)
				Cu(1)—O(11)—C(1)	122.0 (5)
				Cu(1)—O(12)—C(2)	123.6 (6)

Cu···Cu^{vii}	2.7856 (9)	O(1)—C(1)	1.235 (6)	O(1)—Cu—O(2)	87.8 (1)
Cu—O(1)	1.977 (3)	O(2)—C(2)	1.232 (5)	O(1)—Cu—O(3)	163.9 (1)
Cu—O(2)	1.981 (3)	O(3)—C(1^{vii})	1.244 (5)	O(1)—Cu—O(4)	89.1 (1)
Cu—O(3)	1.963 (3)	O(4)—C(2^{vii})	1.243 (6)	O(1)—Cu—N	98.8 (1)
Cu—O(4)	1.964 (3)	C(1)—C(3)	1.544 (5)	O(1)—Cu—Cu^{vii}	85.2 (1)
Cu—N	2.161 (4)	C(2)—C(4)	1.559 (5)	O(2)—Cu—O(3)	88.9 (1)
				O(2)—Cu—O(4)	163.8 (1)
				O(2)—Cu—N	92.6 (1)
				O(2)—Cu—Cu^{vii}	83.4 (1)
				O(3)—Cu—O(4)	89.6 (1)
				O(3)—Cu—N	97.1 (1)
				O(3)—Cu—Cu^{vii}	78.8 (1)
				O(4)—Cu—N	103.5 (1)

O(4)—Cu—Cu^{vii}	80.6 (1)	Cu···Cu^{viii}	2.761 (1)	Cu—O(3)	1.979 (3)
N—Cu—Cu^{vii}	174.28 (7)	Cu—O(1)	1.973 (3)	Cu—O(4)	1.961 (4)
Cu—O(1)—C(1)	119.2 (3)	Cu—O(2)	1.965 (4)	Cu—N	2.153 (5)
Cu—O(2)—C(2)	121.3 (3)				
Cu—O(3)—C(1^{vii})	127.7 (3)	O(1)—Cu—O(2)	89.4 (1)	O(3)—Cu—O(4)	89.5 (1)
Cu—O(4)—C(2^{vii})	125.5 (2)	O(1)—Cu—O(3)	164.8 (2)	O(3)—Cu—N	94.4 (2)
O(1)—C(1)—C(3)	117.2 (4)	O(1)—Cu—O(4)	88.2 (1)	O(4)—Cu—N	98.1 (2)
O(1)—C(1)—O(3^{vii})	129.1 (3)	O(1)—Cu—N	100.8 (2)	Cu—O(1)—C(1)	121.1 (3)
C(3)—C(1)—O(3^{vii})	113.7 (4)	O(2)—Cu—O(3)	88.8 (1)	Cu—O(2)—C(2)	122.7 (4)
O(2)—C(2)—C(4)	116.7 (4)	O(2)—Cu—O(4)	164.5 (2)	Cu—O(3)—C(1^{viii})	126.0 (4)
O(2)—C(2)—O(4^{vii})	129.2 (4)	O(2)—Cu—N	97.4 (2)	Cu—O(4)—C(2^{viii})	124.3 (4)
C(4)—C(2)—O(4^{vii})	114.1 (4)				

Cu(1)···Cu(2)	3.177 (1)	Cu(2)—O(21)	1.984 (5)	O(11)—Cu(1)—O(12)	88.0 (2)
Cu(1)—O(11)	1.922 (5)	Cu(2)—O(22)	1.919 (6)	O(11)—Cu(1)—O(13)	177.4 (2)
Cu(1)—O(12)	1.982 (6)	Cu(2)—O(23)	2.317 (5)	O(11)—Cu(1)—O(14)	90.9 (2)
Cu(1)—O(13)	1.931 (5)	Cu(2)—O(24)	1.907 (6)	O(11)—Cu(1)—N(1)	90.7 (2)
Cu(1)—O(14)	2.296 (6)	Cu(2)—N(2)	2.019 (5)	O(12)—Cu(1)—O(13)	92.0 (2)
Cu(1)—N(1)	2.033 (5)			O(12)—Cu(1)—O(14)	130.9 (2)
				O(12)—Cu(1)—N(1)	143.8 (2)
				O(13)—Cu(1)—O(14)	87.1 (2)
				O(13)—Cu(1)—N(1)	90.9 (2)
				O(14)—Cu(1)—N(1)	85.4 (2)
				O(21)—Cu(2)—O(22)	89.0 (2)
				O(21)—Cu(2)—O(23)	131.0 (2)
				O(21)—Cu(2)—O(24)	93.0 (2)
				O(21)—Cu(2)—N(2)	142.2 (2)
				O(22)—Cu(2)—O(23)	89.2 (2)

O(22)—Cu(2)—O(24)	176.4 (2)	Cu(1)—O(13)—C(3)	126.0 (5)	Cu···Cu^{x}	3.035 (1)
O(22)—Cu(2)—N(2)	90.0 (2)	Cu(1)—O(14)—C(4)	120.9 (5)	Cu—O(1)	1.931 (5)
O(23)—Cu(2)—O(24)	87.3 (2)	Cu(2)—O(21)—C(1)	125.2 (5)	Cu—O(2)	2.095 (4)
O(23)—Cu(2)—N(2)	86.8 (2)	Cu(2)—O(22)—C(2)	122.7 (6)	Cu—O(3)	1.909 (5)
O(24)—Cu(2)—N(2)	90.3 (2)	Cu(2)—O(23)—C(3)	119.9 (5)	Cu—O(4)	2.047 (5)
Cu(1)—O(11)—C(1)	119.4 (4)	Cu(2)—O(24)—C(4)	126.5 (6)	Cu—N	2.071 (4)
Cu(1)—O(12)—C(2)	140.5 (6)				
Cu(1)—O(13)—C(3)	115.5 (4)				
Cu(1)—O(14)—C(4)	138.4 (5)				
Cu(2)—O(21)—C(1)	138.9 (5)				
Cu(2)—O(22)—C(2)	118.0 (5)				
Cu(2)—O(23)—C(3)	139.7 (4)				
Cu(2)—O(24)—C(4)	116.5 (5)				

O(1)—Cu—O(2)	88.8 (2)	O(3)—Cu—O(4)	88.5 (2)	O(1)—C(1)	1.235 (6)
O(1)—Cu—O(3)	172.6 (2)	O(3)—Cu—N	93.2 (2)	O(2)—C(2)	1.232 (5)
O(1)—Cu—O(4)	86.9 (2)	O(4)—Cu—N	118.8 (2)	O(3)—C(1^{vii})	1.244 (5)
O(1)—Cu—N	94.1 (2)	Cu—O(1)—C(1)	120.7 (4)	O(4)—C(2^{vii})	1.243 (6)
O(2)—Cu—O(3)	91.1 (2)	Cu—O(2)—C(2)	134.2 (4)	C(1)—C(3)	1.544 (5)
O(2)—Cu—O(4)	141.5 (1)	Cu—O(3)—C(2^{x})	118.5 (4)	C(2)—C(4)	1.559 (5)
O(2)—Cu—N	99.7 (2)	Cu—O(4)—C(1^{x})	133.6 (4)		

Symmetry code: (i) $-x, y, \frac{1}{2}-z$; (ii) $-x, 1-y, -z$; (iii) $-\frac{1}{2}+y, -\frac{1}{2}+x, -z$; (iv) $-y, -x, -z$; (v) y, x, z; (vi) $-x, -y, -z$; (vii) $1-x, 1-y, -z$; (viii) $1-x, -y, 1-z$; (ix) $1-x, y, \frac{3}{2}-z$.

flow cooling unit, the diffraction spots split. This indicates that the crystal had four twin components of different orientation retaining the tetragonal $a+b$ or $a-b$ direction. The low-temperature phase is orthorhombic, *Pccn* (a subgroup of $P4_2/ncm$), $a=16.056\,(3)$, $b=15.085\,(2)$, $c=19.053\,(4)$ Å, $V=4615\,(2)$ Å^3, $Z=4$ at 120 K. The structure analysis was not carried out.

Discussion

Molecular structure

The molecular structures of (I)–(XVI) are shown in Fig. 1 with the atom-numbering schemes. All of the binuclear complexes except (XI) have the discrete cage structure. The compounds (X), (XI), (XIII) and (XIV) possess a crystallographic center of symmetry between the two Cu atoms, and (VI), (XI) and (XVI) possess a crystallographic twofold axis perpendicular to the Cu···Cu axis. The dimer unit in (XI) shares the axial caffeine ligands with adjacent units to form infinite linear chains along the $a\pm b$ directions. The mean bond lengths and bond angles involving the Cu atoms are compared in Table 5. Other copper(II) trichloroacetates, for which the crystal structures have already been reported, are also included in Table 5: $[Cu(Cl_3CCOO)_2(PhCN)]_2$ (Nakashima, Mikuriya & Muto, 1985), $[Cu(Cl_3CCOO)_2(2\text{-Cl-py})]_2$ (Moreland & Doedens, 1978) and $[Cu(Cl_3CCOO)_2(caffeine)]_2.2C_6H_6$ (Horie, Husebye, Kato, Meyers, Muto, Suzuki, Tokii & Zingaro, 1986). The numbering of the compounds is in order of increasing $-2J$ values except for (XV) and (XVI), for which the solvent molecules of crystallization are lost under reduced pressure in the magnetic susceptibility balance. The Cu atoms of (XII)–(XIV) ($-2J=229$–240 cm^{-1}) have typical square-pyramidal (SP) coordination geometry with four O atoms of the four bridging carboxylates on the square-basal plane and an N atom of the monodentate ligand at the apical position. Crystals of those compounds having small $-2J$ values, [(I)–(IV); $-2J=79$–107 cm^{-1}], show approximate trigonal-bipyramidal (TBP) coordination geometries. The basal triangle consists of two O atoms of two carboxylates and an N atom of the monodentate ligand, and the apical positions are occupied by the two O atoms of the other two carboxylates. The z axes of the trigonal bipyramids at the two Cu atoms are perpendicular to each other. Thus, the SP structure may have a crystallographic center of symmetry between two Cu atoms in a cage, but it should be absent in the TBP structure.

The structures of the carboxylate bridges in (I) are shown separately in Fig. 2. A comparison of the normal dimeric SP structures in (XII)–(XIV) with the dimeric TBP complexes in (I)–(IV) reveals the following features of the TBP structure: a longer Cu···Cu distance [*e.g.* 3.261 (1) Å in (I) *versus* 2.761 (3) Å in (XIV)], larger Cu—O_{eq}—C bond angles [*e.g.* 137.8 (4) to 141.1 (4)° in (I) *versus ca* 123° in the SP complexes], smaller Cu—O_{ax}—C bond angles [*e.g.* 114.8 (3) to 122.1 (4)° in (I)], two especially longer Cu—O_{eq} bond lengths [*e.g.* 2.284 (3) and 2.328 (4) Å in (I)], shorter Cu—O_{ax} bond lengths [*e.g.* 1.927 (3) to 1.944 (3) Å in (I)], a larger sum of the bond lengths of the Cu—O—C—O—Cu bridge [*e.g.* 6.740 (6) Å in (I) *versus* 6.442 (8) Å in (XIV)], and large differences in the O_{eq}—Cu—N bond angles. The $-2J$ values of 131 to 220 cm^{-1} for (V)–(XI) indicate that these complexes have intermediate structures between SP and TBP. The coordination geometry around the Cu atoms changes from SP to TBP in a similar way to the Berry twist (Berry, 1960), *i.e.* the Cu···Cu interatomic distance of the $Cu_2(Cl_3CCOO)_4$ cage structure elongates, two bridging carboxylate ions opposite each other move parallel to the Cu···Cu axis, and the other two carboxylate ions move in an antiparallel direction.

Among the large number of dimeric copper(II) carboxylates studied so far, the TBP structure has only been observed for copper(II) trichloroacetates and triphenylacetates as stated in the *Introduction*. The stronger acidity of trichloroacetic acid ($pK_a=0.7$ in aqueous solution) than acetic acid ($pK_a=4.75$) suggests that the Cu—O coordination bond is weaker for the trichloroacetate ion, and the cage structure is more flexible than the corresponding copper(II) acetate complex (Porter *et al.*, 1986). The energy difference between the SP and the TBP molecular structures may be of the same order of magnitude as the intermolecular interactions in the crystals. As a consequence, the cage structure may be deformed by the crystal packing forces. In fact, certain copper(II) trichloroacetate dimers crystallize in several packing modes when different solvents of crysallization are used and yield complexes with a variety of $-2J$ values. For example, the caffeine adduct forms the TBP structure in $[Cu(Cl_3CCOO)_2(caffeine)]_2$ [(VI); $-2J=136$ cm^{-1}] on crystallization from chloroform, and the SP structure in $[Cu(Cl_3CCOO)_2(caffeine)]_2.2C_6H_6$ (Horie *et al.*, 1986; $-2J=203$ cm^{-1}) from benzene. The driving force for the TBP deformation of the copper(II) triphenylacetate dimer may be the intermolecular nonbonded repulsions of the bulky triphenylmethyl groups. The cage structure of this complex is expected to be more flexible than that of the acetates, because of the greater acidity of Ph_3CCOOH compared with CH_3COOH (pK_a values of Ph_3CCOOH and CH_3COOH in dimethyl sulfoxide solutions are 9.29 and 11.41, respectively; Steward, Dziedzic, Johnson & Frohliger, 1971). Thus, the bulkiness of the substituent groups on the bridges and the weak-

ness of the Cu—O coordination bonds make the TBP deformation possible.

Orientational disorder of the trichloromethyl groups is usually observed in dimeric copper(II) trichloroacetates. (VI) is a rare case in which disorder of the Cl atoms was not detected, and the R value of 0.035 is the smallest among the sixteen refinements. 45 independent Cl_3CCOO^- bridges exist in (I)–

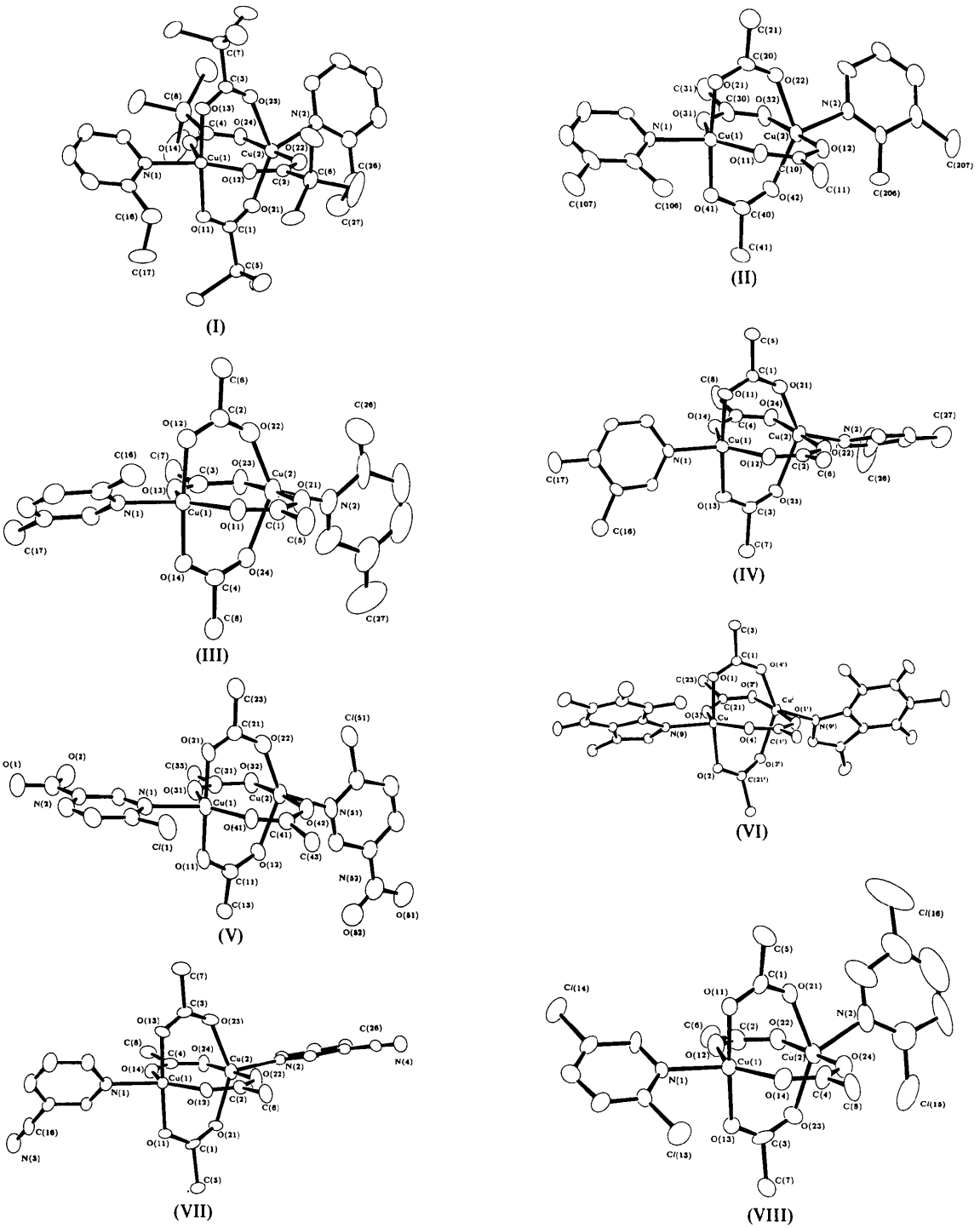


Fig. 1. *ORTEP* drawings (Johnson, 1971) of the dimeric complexes (I)–(VIII) with the numbering schemes. The chlorine atoms of the trichloromethyl groups are omitted for clarity except for (I). The thermal ellipsoids are scaled at the 30% probability level.

(XVI). If we consider the orientations of the 32 trichloromethyl groups with a population of greater than or equal to 80%, 17 bridges have a Cl—C—C—O dihedral angle of *ca* 90°, suggesting that this is the prefered configuration. Orientational disorder of the trifluoromethyl groups was also observed in $[Cu(F_3CCOO)_2(quinoline)]_2$ (Moreland & Doedens, 1975). Fig. 2 indicates that the carboxylate C—O bond distance is longer on the shorter Cu—O bond side. A rough correlation between the Cu—O and C—O bond distances of the Cu—O—C moieties is observed as seen from Fig. 4, in which

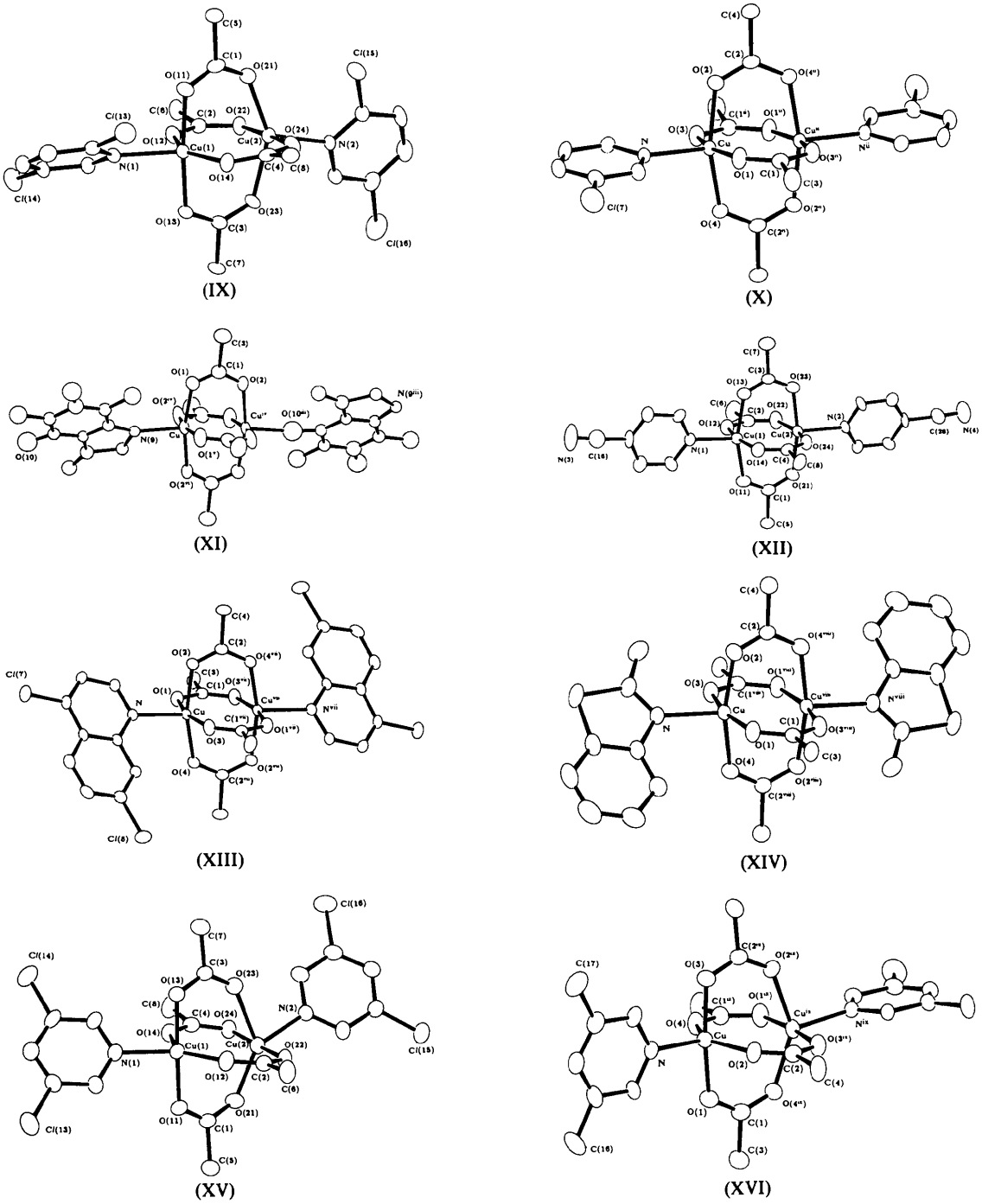


Fig. 1 (*cont.*) *ORTEP* drawings (Johnson, 1971) of the dimeric complexes (IX)–(XVI) with the numbering schemes. The chlorine atoms of the trichloromethyl groups are omitted for clarity. The thermal ellipsoids are scaled at the 30% probability level.

Table 5. *Comparison of the dimensions of the* $[Cu_2(COO)_4]$ *cages in* $[Cu(Cl_3CCOO)_2L]_2.S$ *and their* $-2J$ *values*

	(I)	(II)	(III)	(IV)	(V)	(VI)	(VII)	(VIII)	(IX)	(X)
L	2-Et-py	2,3-Me_2-py	2,5-Me_2-py	3,4-Me_2-py	2-Cl-5-NO_2-py	Caffeine (3)[f]	3-CN-py	2,5-Cl_2-py	2,5-Cl_2-py	3-Cl-py
S		Toluene	Toluene					Benzene		
Cu···Cu (Å)	3.261 (1)	3.216 (2)	3.226 (1)	3.186 (2)	3.054 (3)	3.062 (1)	3.066 (1)	3.113 (3)	2.951 (1)	2.774 (1)
Cu—O (longest) (Å)	2.328 (4)	2.226 (9)	2.248 (6)	2.237 (5)	2.21 (1)	2.167 (2)	2.264 (5)	2.252 (9)	2.130 (4)	1.981 (3)
Cu—O (shortest) (Å)	1.927 (4)	1.915 (9)	1.902 (6)	1.909 (6)	1.89 (1)	1.940 (2)	1.880 (6)	1.915 (13)	1.925 (4)	1.972 (3)
Cu—O—C—O—Cu (longest) (Å)	6.740 (6)	6.609 (10)	6.612 (9)	6.616 (10)	6.61 (1)	6.598 (5)	6.634 (10)	6.682 (15)	6.555 (8)	6.436 (6)
Cu—O—C—O—Cu (average) (Å)	6.580	6.530	6.528	6.551	6.498	6.501	6.528	6.522	6.475	6.430
Cu—O—C (largest) (°)	141.1 (4)	141.1 (8)	140.6 (6)	140.5 (6)	139 (1)	136.0 (2)	136.8 (6)	138.3 (8)	133.8 (4)	127.5 (2)
Cu—O—C (smallest) ( )	114.8 (4)	117.0 (8)	116.6 (5)	116.9 (6)	116 (1)	115.0 (2)	117.7 (5)	115.0 (9)	115.2 (3)	118.2 (3)
⟨123 − ∠Cu—O—C⟩[d] (°)	10.8	10.9	10.9	10.1	9.4	8.9	7.7	9.3	6.4	3.7
φ_{bend}[e] (°)	8.9 (2)	6.8 (6)	2.6 (3)	5.7 (3)	5.6 (5)	12.5 (3)	5.8 (3)	7.3 (5)	9.3 (2)	7.7 (2)
$-2J$ (cm $^{-1}$)	79	95	102	107	131	136	138	141	191	193

	(XI)			(XII)	(XIII)	(XIV)	(XV)	(XVI)
L	Caffeine (1)[a,f]	2-Cl-py[b]	½Caffeine	PhCN[c]	4-CN-py	4,7-Cl_2-quin	2-F-btz[h]	3,5-Cl_2-py	3,5-Me_2-py
S	2Benzene		2Toluene					Toluene	2Benzene
Cu···Cu (Å)	2.852 (2)	2.766 (3)	2.736 (1)	2.732 (1)	2.769 (1)	2.786 (1)	2.761 (3)	3.177 (1)	3.035 (1)
Cu—O (longest) (Å)	1.987 (4)	1.973 (5)	1.968 (7)	1.972 (6)	1.987 (6)	1.981 (3)	1.979 (3)	2.317 (5)	2.095 (4)
Cu—O (shortest) (Å)	1.957 (4)	1.941 (5)	1.945 (7)	1.955 (6)	1.963 (5)	1.963 (3)	1.961 (4)	1.907 (6)	1.909 (4)
Cu—O—C—O—Cu (longest) (Å)	6.406 (5)	6.385 (7)	6.13 (1)	6.43 (1)	6.44 (1)	6.420 (6)	6.442 (8)	6.738 (9)	6.475 (7)
Cu—O—C—O—Cu (average) (Å)	6.406	6.360	6.413	6.410	6.430	6.419	6.425	6.561	6.465
Cu—O—C (largest) ( )	127.7 (4)	126.8 (4)	121.3 (7)	123.8 (6)	126.5 (6)	127.7 (3)	126.0 (4)	140.5 (5)	134.2 (4)
Cu—O—C (smallest) (°)	121.6 (4)	119.9 (4)	122.3 (6)	122.0 (4)	119.9 (5)	119.2 (3)	121.1 (3)	115.5 (5)	118.5 (4)
⟨123 − ∠Cu—O—C⟩[d] ( )	3.1	2.4	1.2	0.5	2.0	3.2	1.6	11.0	7.2
φ_{bend}[e] ( )	2.8 (2)	5.0 (2)	3.0 (4)	5.6 (3)	3.9 (4)	2.2 (2)	2.0 (2)	6.2 (3)	2.4 (2)
$-2J$ (cm $^{-1}$)	195	220	220	224	229	237	240	(g)	(g)

Notes: (*a*) Horie *et al.* (1986). (*b*) Moreland & Doedens (1978). (c) Nakashima *et al.* (1985). (*d*) Deviation of the Cu—O—C bond angles from 123°. (*e*) Average of the dihedral angles between Cu—O···O—Cu and the O—C—O least-squares planes. (*f*) The number in parentheses corresponds to the number used by Horie *et al.* (1986). (XI) is different from the caffeine (2). (*g*) The $-2J$ values of (XV) and (XVI) after removal of the solvent molecules from crystals are 92 and 74 cm $^{-1}$, respectively. (*h*) btz = benzothiazole.

only structural data with R values less than 0.06 are presented.

Magneto-structural correlation

The magneto-structural data in Table 5 indicate that the $-2J$ value decreases with deformation of the $Cu_2(Cl_3CCOO)_4$ cage structure, *i.e.*, modification of the coordination geometry from SP to TBP. Deformation of the cage is marked by several geometrical parameters: (*a*) the Cu···Cu distance, (*b*) the average deviation of the Cu—O—C bond angles from 123°, (*c*) the summation of the bond distances in the Cu—O—C—O—Cu bridge, and (*d*) the longest Cu—O bond distance. The correlations are shown in Figs. 3(*a*)–3(*d*). The Cu···Cu distance is the most suitable parameter from a technical point of view, since the coordinates of the Cu atoms are only slightly biased in the least-squares refinement by the disorder of the trichloromethyl groups. Fig. 3(*a*) shows a linear correlation between the $-2J$ values and the Cu···Cu distances, *i.e.* the longer the Cu···Cu distance, the smaller the $-2J$ value. It should be emphasized that the correlation is not the result of the Cu···Cu direct spin-exchange, which seems to be negligibly weak compared to the spin superexchange through the bridging carboxylates (Yamanaka *et al.*, 1991).

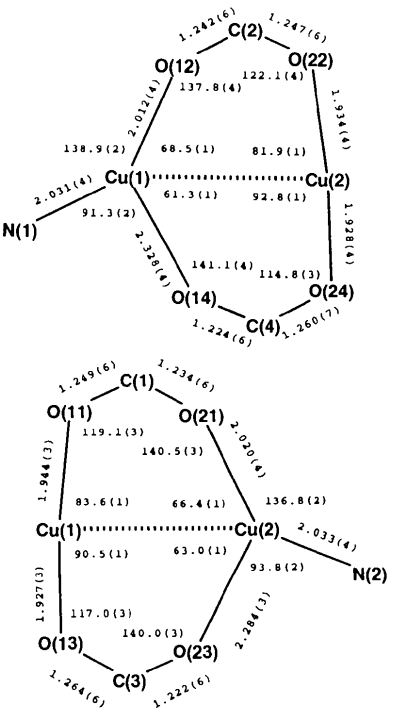


Fig. 2. The structure of the trichloroacetate bridges in (I) with bond lengths (Å) and angles (°).

The spin-exchange interaction in bimetallic systems with two unpaired electrons can be described by the concept of magnetic orbitals (Kahn, 1985). The small $-2J$ values for the TBP structure are related to the magnetic orbitals of the complex (see Fig. 5). In the SP structure, the spin densities of the Cu^{2+} ions are localized in the $d_{x^2-y^2}$ orbitals in a simple approximation, and the magnetic orbitals effectively overlap with each other through the orbitals of the four bridging carboxylates. However, in an ideal TBP structure, the magnetic orbitals consist mainly of d_{z^2} orbitals, which are perpendicular to

each other at the two Cu^{II} sites. These magnetic orbitals only overlap slightly with each other through the orbitals of the bridging groups. Therefore, the spin superexchange interactions are suppressed by the TBP deformation. The TBP coordination geometry can be characterized by the O—Cu—O bond angle between the bridges opposite each other; this angle is larger than 173.4 (2)° for (I)–(IX) and less than 166.7 (2)° for (X)–(XIV). The $-2J$ value for (X), 193 cm^{-1}, is nearly equal to that of (IX), 191 cm^{-1}; however, (X) is classified as SP and (IX) as TBP based on this criterion. A good correlation is observed between the $-2J$ values and the equatorial O—Cu—O bond angles of the TBP complexes as shown in Fig. 3(*f*), indicating that the ideal TBP structure may have $-2J$ value of *ca* 25 cm^{-1}.

The $-2J$ values of the SP complexes which have a Cu···Cu distance of less than 2.8 Å range from 193 to 240 cm^{-1} as shown in Fig. 3(*a*). This observation may be related to bending of the bridges, which is measured by the mean angle φ_{bend}, the dihedral angle between the carboxylate O—C—O and Cu—O···O—Cu least-squares planes. The decrease of the $-2J$ value as φ_{bend} increases has recently been observed for copper(II) benzoate dimers (Kawata, Uekusa, Ohba, Furukawa, Tokii, Muto & Kato, 1992). An explanation of this correlation is that a bent bridge leads to a smaller overlap between the $d_{x^2-y^2}$ orbital of the Cu atom (x and y nearly parallel to the Cu—O directions) and the $2p_x$ orbital of the carboxylate O atom (x along the C—CCl_3 direction) compared to a planar bridge. Therefore, the spin

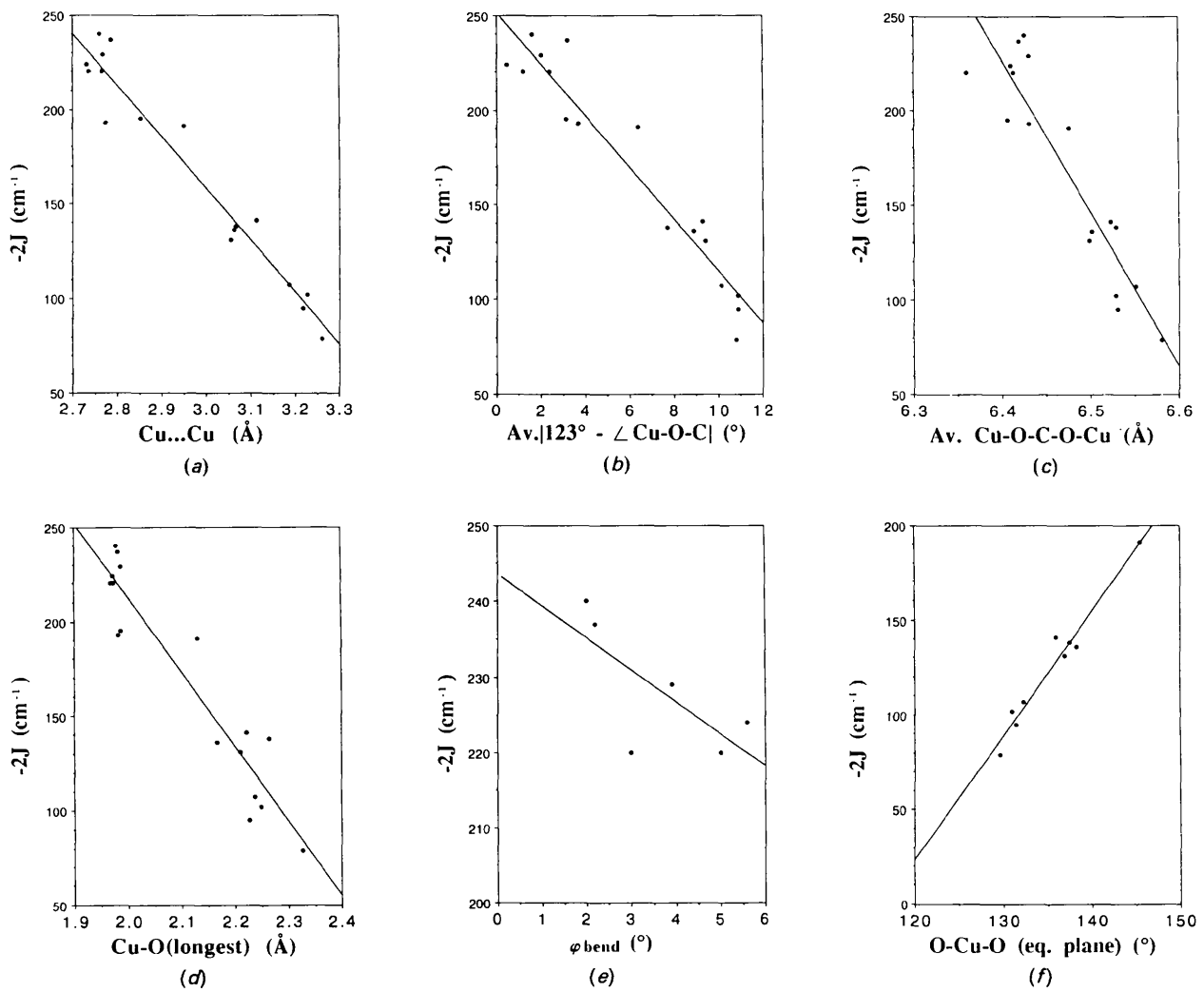


Fig. 3. Linear correlations between the $-2J$ values of the dimeric copper trichloroacetates listed in Table 5 except for (XV) and (XVI), and (*a*) the Cu···Cu distances, (*b*) the mean values of |123° − ∠Cu—O—C|, (*c*) the mean values of the Cu—O—C—O—Cu bridge distances, (*d*) the longest Cu—O bond distance, (*e*) the mean values of φ_{bend} of the SP structure (Cu···Cu < 2.8 Å), and (*f*) the equatorial O—Cu—O bond angle of the TBP structure with axial O—Cu—O bond angles greater than 173°.

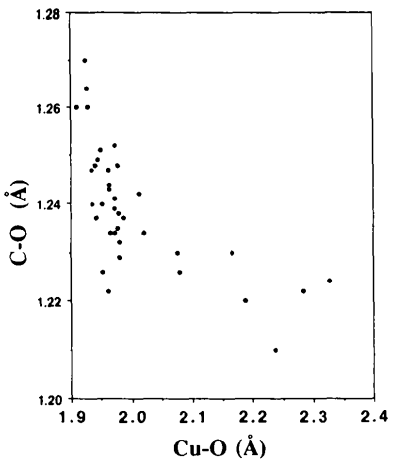


Fig. 4. Correlation between the Cu—O and C—O bond lengths of the independent Cu—O—C moiety in the crystals listed in Table 5 with R values less than 0.06.

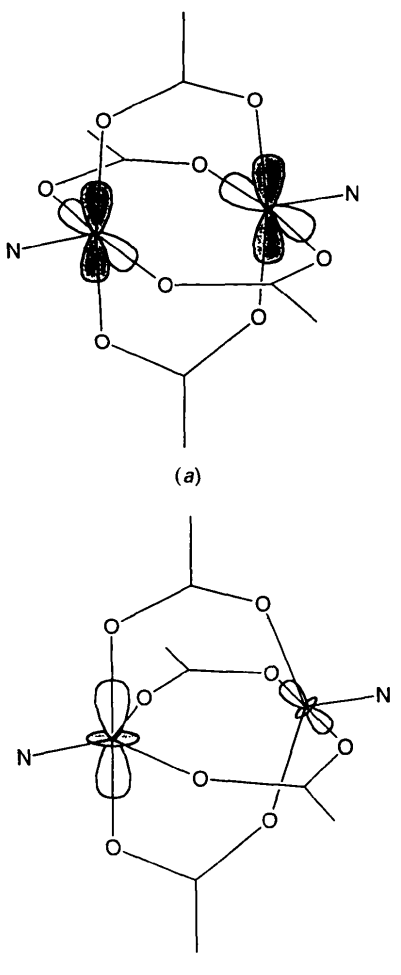


Fig. 5. Schematic drawing of the magnetic orbitals in (*a*) the SP, and (*b*) the TBP structures.

Table 6. *Results of linear-regression analyses carried out on the data shown in Fig.* 3

The equation used is $y = a + bx$, where $y = -2J$ (cm^{-1}) and $x =$ the structure parameter. R^2 is the square of the correlation coefficient. $R = S_{xy}/S_xS_y$, where S_{xy} is the covariance of x and y; S_x and S_y are the standard deviations of the distributions of x and y.

	a	b	R^2
(*a*)	980	−274	0.949
(*b*)	251	13.6	0.923
(*c*)	5400	−808	0.850
(*d*)	1000	−394	0.893
(*e*)	243	−4.20	0.523
(*f*)	−765	6.57	0.960

superexchange through the symmetric HOMO of the carboxylate ion decreases as φ_{bend} increases. A rough correlation between the $-2J$ values and the mean φ_{bend} angles of the SP structures is shown in Fig. 3(*e*). On the other hand, the effect of bridge bending on the $-2J$ value in the TBP structure is unclear. For example, (VI) and (VII) have nearly the same $-2J$ values (136 and 138 cm^{-1}), and the same Cu···Cu distances [3.062 (1) and 3.066 (1) Å], while the mean φ_{bend} angles are 12.5 (3) and 5.8 (3)°, respectively. In the TBP structures other factors such as the size of the equatorial O—Cu—O bond angle may be important. Results of linear-regression analyses for the data in Fig. 3 are given in Table 6.

The structural data for (XV) and (XVI) were not utilized in this investigation of the magneto-structural correlations, because the solvent molecules of crystallization were lost under reduced pressure when the magnetic susceptibilities were measured. Based on the least-squares line of Fig. 3(*f*), the equatorial O—Cu—O bond angles of (XV) 130.9 (2)–131.0 (2) and (XVI) 141.5 (1)° suggest $-2J$ values of (XV) 95 and (XVI) 165 cm^{-1}. The observed $-2J$ values for these compounds are 92 and 74 cm^{-1}, respectively. Therefore, the structure of complex (XV) does not change, but that of complex (XVI) is expected to be changed by removal of solvent molecules from the crystals.

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Electron-Density Distribution in Crystals of *lel*$_3$-[*M*(chxn)$_3$](NO$_3$)$_3$.3H$_2$O (*M* = Cr, Rh; chxn = *trans*-1,2-diaminocyclohexane) at 120 K

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Abstract

The electron-density distributions in non-centrosymmetric crystals containing Cr^{III} or Rh^{III} complexes with *trans*-1,2-diaminocyclohexane (chxn) as a bidentate ligand have been investigated by the multipole expansion method based on X-ray intensities collected at 120 K with Mo $K\alpha$ radiation (λ = 0.71073 Å). Crystals of the Cr^{III} and Rh^{III} complexes are isomorphous and hexagonal $P6_3$, $Z = 2$. (I): $\Delta(\lambda\lambda\lambda)$-tris(*trans*-1,2-diaminocyclohexane)-chromium(III) nitrate trihydrate, [Cr(C$_6$H$_{14}$N$_2$)$_3$](NO$_3$)$_3$.3H$_2$O, M_r = 634.6, $F(000)$ = 678, a = 13.029 (2), c = 10.040 (2) Å, V = 1476.0 (5) Å^3, D_x = 1.43 Mg m^{-3}, μ = 0.444 mm^{-1}, R = 0.041 for 3914 reflections. (II): $\Delta(\lambda\lambda\lambda)$-tris(*trans*-1,2-diaminocyclohexane)rhodium(III) nitrate trihydrate, [Rh(C$_6$H$_{14}$N$_2$)$_3$](NO$_3$)$_3$.3H$_2$O, M_r = 685.5, $F(000)$ = 720, a = 13.101 (2), c = 9.984 (2) Å, V = 1484.0 (5) Å^3, D_x = 1.53 Mg m^{-3}, μ = 0.632 mm^{-1}, R = 0.028 for 4602 reflections. The electron populations of the *d* orbitals of Cr^{III} and Rh^{III} atoms in a chemical D_3 ligand field were estimated and compared with those of the *lel*$_3$-Co^{III} complex. Phase improvement is necessary even when the valence-/core-electron ratio becomes smaller, because the phases based on the independent atom model are poor for one of the hexadecapole densities of the metal atoms in the title crystals.

Introduction

It is well-known that deformation densities of non-centrosymmetric structures suffer from phase error and the features are much smeared if the phase angle of F_o is estimated based on the spherical independent atom model (IAM). This inadequacy can be removed by the aspherical-atom model (Hirshfeld, 1971). In a previous paper (Morooka, Ohba, Saito & Miyamae,

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