Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Poly[methanoltetrakis[μ_3-5-(4-methoxyphenyl)pyrazole-3-carboxylato(2−)]tricopper(II)disodium(I)]

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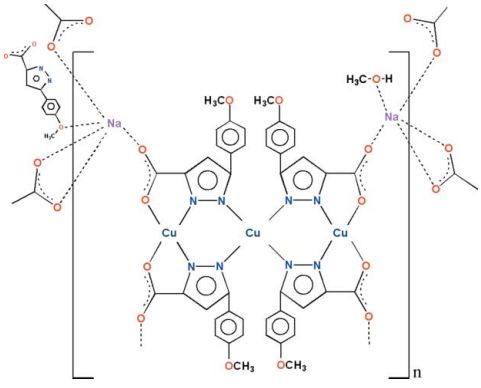
Received 9 November 2007; accepted 28 November 2007

Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.006 Å; R factor = 0.050; wR factor = 0.129; data-to-parameter ratio = 16.3.

The asymmetric unit of the polymeric title complex, $[Cu_3Na_2(C_{11}H_8N_2O_3)_4(CH_4O)]_n$, consists of two Na^I atoms, three Cu^{II} atoms, four 5-(4-methoxyphenyl)pyrazole-3-carboxylate ligands and one methanol molecule. The central Cu^{II} atom is coordinated by four N atoms from four pyrazole-3-carboxylate ligands, forming a distorted tetrahedral (CuN_4) geometry, while each of the other two Cu^{II} atoms is coordinated by two O atoms and two N atoms from the two ligands, forming a slightly distorted square-planar (CuN_2O_2) geometry. Each of the two Na^I atoms is coordinated by five O atoms, forming a distorted octahedral geometry; four O atoms are from the carboxylate groups of the three ligands and the remaining O atom is from the methoxy group of the ligand or from the methanol molecule.

Related literature

For related literature, see: Fujisawa *et al.* (2004); Mezei *et al.* (2004); Omary *et al.* (2003); Spiccia *et al.* (1997); Trofimenko (1972); Zhou *et al.* (2007).



Experimental

Crystal data

$[Cu_3Na_2(C_{11}H_8N_2O_3)_4(CH_4O)]$
M_r = 1133.42
Monoclinic, $P2_1/n$
a = 14.9392 (19) Å
b = 11.2721 (14) Å
c = 28.030 (4) Å
β = 103.259 (2)°
V = 4594.3 (10) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.47 mm^{-1}
T = 293 (2) K
0.20 × 0.18 × 0.18 mm

Data collection

Bruker APEXII diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.758, T_{max} = 0.778
27017 measured reflections
10442 independent reflections
5736 reflections with $I > 2\sigma(I)$
R_{int} = 0.060

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.129
S = 1.02
10442 reflections
640 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.63 e Å^{-3}
$\Delta\rho_{min}$ = −0.46 e Å^{-3}

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *APEX2* (Bruker, 2005); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*) and *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXTL*.

The authors are grateful to Dr Tian Yunqi for his selfless help with our work.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS2241).

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supporting information

Acta Cryst. (2008). E**64**, m114 [https://doi.org/10.1107/S1600536807064008]

Poly[methanoltetrakis[μ_3-5-(4-methoxyphenyl)pyrazole-3-carboxylato(2−)]tricopper(II)disodium(I)

Yue An, Guang-Hua Zhou, Ping-Ping Mu, Xiao-Xia Zhou and Yong-Heng Xing

S1. Comment

Due to their significant interest, the synthesis, structure and properties of copper pyrazolates (Trofimenko, 1972; Omary *et al.*, 2003; Fujisawa *et al.*, 2004), especially, trinuclear copper complexes (Mezei *et al.*, 2004; Spiccia *et al.*, 1997), have been extensively studied. For this kind of complexes have been found to exhibit a variety of structures ranging from polymers to trimers. Besides, the trinuclear copper complexes are known to be important models for the study of testing magnetic exchange models as well as spinfrustration. As a part of our ongoing study of different environment where the reaction of copper (II) with 5-aryl-1*H*-pyrazole-3-carboxylic acid (Zhou *et al.*, 2007). In this work, we describe the reaction of copper (II) with the ligand (5-(4-methoxyphenyl)-1*H*-pyrazole-3-carboxylic acid) in the presence of NaOH, which was used to deprotonate the ligand so as to improve the coordination capability of the ligand.

As can be seen from the crystal structure in Fig.1, the unit of the crystal is mainly made up of the sodium cations part and the anion part. The anion consists of three Cu(II) ions and four ligands. The X-ray analysis reveals that not all the coordination modes of copper(II) ions are the same. The central copper(II), Cu1, is coordinated by four N atoms, which are from four ligands, forming a distorted tetrahedral (CuN_4) geometry. On the other hand, the Cu2 and Cu3 have the similar coordination modes, coordinated by two O atoms and two N atoms of two ligands, respectively, forming a slightly distorted square planar (CuN_2O_2) geometry. In the cations, the coordination modes of the two sodium ions are similar in general, however, Na1 is coordinated by five O atoms, four of which are from three ligands, the other from the methoxy group of the 5-position substituted group of the pyrazole; Na2 is coordinated by five O atoms too, four of which are from three ligands, but the other from the methanol molecule. The cations connect the anions each other, forming a three-dimensional structure in the crystal (Fig. 2).

S2. Experimental

5-(4-Methoxyphenyl)-1*H*-pyrazole-3-carboxylic acid (0.044 g, 0.2 mmol) was added to a solution of copper acetate dihydrate (0.040 g, 0.2 mmol) in methanol (15 ml), the resulting mixture was treated with a solution of NaOH until the pH value come rise to be about 8. The mixture was then stirred continuously for 7 h, and the filtrate was kept in conical flask for about 40 days and some brown block crystals were obtained from the solution, dried in vacuum. Yield: 37.6%. Crystal of the title compound suitable for single-crystal X-ray diffraction was selected directly from the sample as prepared.

S3. Refinement

All H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93 Å for aromatic H atoms, 0.96 Å for methyl H atoms, respectively, and with U_{iso}(H) = 1.2U_{eq}(C) for aromatic and methylene H atoms, U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms.

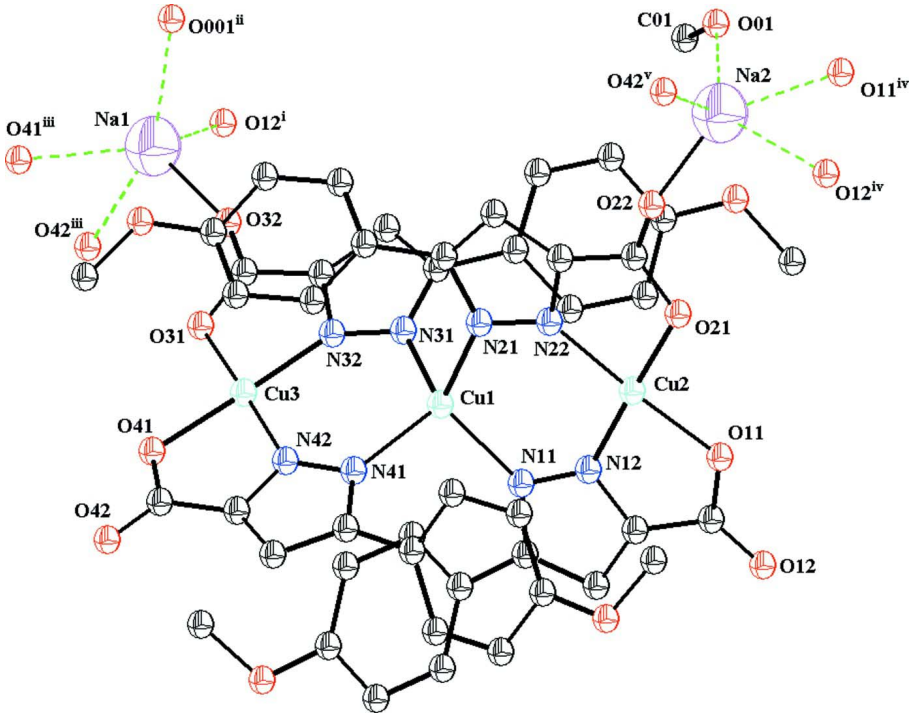

Figure 1

The molecular structure of the title compound, showing displacement ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity [symmetry codes: (i) -*x*, -*y* + 2, -*z*; (ii) *x*, *y* + 1, *z*; (iii) -*x* + 1/2, *y* + 1/2,-*z* + 1/2; (iv) -*x* + 1/2, *y* + 1/2, -*z* - 1/2; (v) -*x* + 1, -*y* + 2, -*z*].

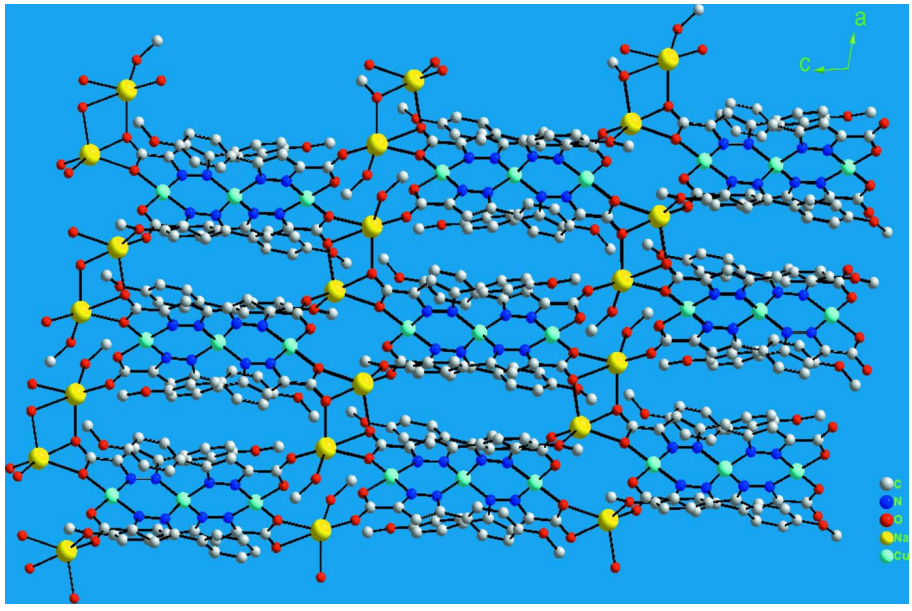

Figure 2

A packing diagram of the title compound, viewed along the *b* axis.

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Crystal data

$[Cu_3Na_2(C_{11}H_8N_2O_3)_4(CH_4O)]$
$M_r = 1133.42$
Monoclinic, $P2_1/n$
$a = 14.9392$ (19) Å
$b = 11.2721$ (14) Å
$c = 28.030$ (4) Å
$\beta = 103.259$ (2)°
$V = 4594.3$ (10) Å^3
$Z = 4$
$F(000) = 2300$
$D_x = 1.639$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 1.7$–27.4°
$\mu = 1.47$ mm^{-1}
$T = 293$ K
Block, brown
0.20 × 0.18 × 0.18 mm

Data collection

Bruker APEXII diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min} = 0.758$, $T_{max} = 0.778$
27017 measured reflections
10442 independent reflections
5736 reflections with $I > 2\sigma(I)$
$R_{int} = 0.060$
$\theta_{max} = 27.4°$, $\theta_{min} = 1.7°$
$h = -19 \rightarrow 19$
$k = -7 \rightarrow 14$
$l = -36 \rightarrow 36$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.129$
$S = 1.02$
10442 reflections
640 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0492P)^2 + 0.0446P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.63$ e Å^{-3}
$\Delta\rho_{min} = -0.46$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Cu1	0.24102 (4)	0.89206 (4)	0.007883 (16)	0.03566 (15)
Cu2	0.21995 (4)	0.85438 (5)	−0.127702 (17)	0.03981 (16)
Cu3	0.26870 (4)	0.96721 (5)	0.142677 (17)	0.03766 (15)
Na1	0.09271 (12)	1.38506 (14)	0.20928 (6)	0.0445 (4)
Na2	0.38592 (12)	1.20926 (16)	−0.24191 (6)	0.0491 (5)

N21	0.2942 (2)	0.9926 (3)	−0.03602 (11)	0.0331 (8)
N22	0.2824 (2)	0.9723 (3)	−0.08417 (11)	0.0350 (8)
N31	0.1821 (2)	1.0211 (3)	0.03588 (11)	0.0329 (8)
N32	0.1953 (2)	1.0375 (3)	0.08496 (11)	0.0342 (8)
N41	0.3176 (2)	0.8097 (3)	0.06531 (11)	0.0345 (8)
N42	0.3224 (2)	0.8453 (3)	0.11176 (11)	0.0330 (8)
N11	0.1810 (2)	0.7588 (3)	−0.03323 (10)	0.0334 (8)
N12	0.1743 (2)	0.7580 (3)	−0.08211 (11)	0.0350 (8)
O002	0.4384 (3)	1.2269 (3)	0.17398 (11)	0.0665 (10)
O21	0.2702 (2)	0.9444 (3)	−0.17502 (10)	0.0519 (9)
O22	0.3597 (2)	1.1000 (3)	−0.18099 (11)	0.0604 (10)
O003	0.0353 (3)	1.1325 (3)	−0.19293 (12)	0.0777 (12)
O31	0.2137 (2)	1.0889 (3)	0.17528 (10)	0.0489 (8)
O32	0.1214 (2)	1.2466 (3)	0.15958 (11)	0.0620 (10)
O004	0.3920 (3)	0.5010 (3)	−0.11149 (12)	0.0724 (11)
O42	0.4578 (2)	0.7657 (3)	0.22695 (10)	0.0481 (8)
O41	0.3475 (2)	0.8990 (3)	0.20259 (9)	0.0445 (8)
O001	0.1488 (2)	0.5579 (3)	0.17536 (10)	0.0614 (10)
O12	0.0662 (2)	0.5787 (3)	−0.18083 (10)	0.0461 (8)
O11	0.1564 (2)	0.7383 (3)	−0.17436 (9)	0.0468 (8)
O01	0.2871 (3)	1.3552 (3)	−0.23317 (12)	0.0807 (13)
H01D	0.2857	1.4225	−0.2525	0.097*
C002	0.5032 (4)	1.1562 (5)	0.20906 (19)	0.087 (2)
H00A	0.5106	1.1899	0.2412	0.130*
H00B	0.5614	1.1551	0.2001	0.130*
H00C	0.4803	1.0766	0.2091	0.130*
C27	0.4209 (3)	1.1897 (4)	0.12623 (16)	0.0486 (12)
C28	0.3644 (3)	1.2622 (4)	0.09281 (16)	0.0487 (12)
H28A	0.3412	1.3314	0.1034	0.058*
C29	0.3418 (3)	1.2330 (4)	0.04356 (15)	0.0419 (11)
H29A	0.3034	1.2829	0.0215	0.050*
C24	0.3753 (3)	1.1310 (4)	0.02669 (14)	0.0351 (10)
C25	0.4323 (3)	1.0590 (4)	0.06076 (15)	0.0409 (11)
H25A	0.4556	0.9899	0.0501	0.049*
C26	0.4555 (3)	1.0872 (4)	0.11036 (16)	0.0475 (12)
H26A	0.4939	1.0376	0.1326	0.057*
C23	0.3474 (3)	1.0914 (4)	−0.02513 (14)	0.0346 (10)
C22	0.3686 (3)	1.1343 (4)	−0.06771 (15)	0.0402 (11)
H22A	0.4036	1.2007	−0.0711	0.048*
C21	0.3257 (3)	1.0557 (4)	−0.10412 (14)	0.0349 (10)
C20	0.3193 (3)	1.0359 (4)	−0.15744 (15)	0.0430 (11)
C003	−0.0010 (5)	1.0324 (6)	−0.22134 (19)	0.107 (3)
H00D	−0.0124	1.0522	−0.2555	0.161*
H00E	−0.0575	1.0087	−0.2133	0.161*
H00F	0.0424	0.9683	−0.2145	0.161*
C37	0.0562 (3)	1.1217 (5)	−0.14285 (16)	0.0526 (13)
C38	0.0948 (4)	1.2206 (5)	−0.11655 (17)	0.0584 (14)
H38A	0.1056	1.2888	−0.1330	0.070*

C39	0.1171 (3)	1.2178 (4)	−0.06624 (16)	0.0477 (12)
H39A	0.1431	1.2847	−0.0490	0.057*
C34	0.1016 (3)	1.1171 (4)	−0.04033 (14)	0.0363 (10)
C35	0.0620 (3)	1.0210 (4)	−0.06773 (15)	0.0426 (11)
H35A	0.0502	0.9530	−0.0514	0.051*
C36	0.0388 (3)	1.0215 (4)	−0.11856 (15)	0.0482 (12)
H36A	0.0120	0.9552	−0.1359	0.058*
C33	0.1288 (3)	1.1111 (4)	0.01371 (14)	0.0346 (10)
C32	0.1069 (3)	1.1861 (4)	0.04886 (15)	0.0383 (10)
H32A	0.0711	1.2544	0.0437	0.046*
C31	0.1507 (3)	1.1359 (4)	0.09326 (14)	0.0374 (11)
C30	0.1616 (3)	1.1623 (4)	0.14637 (16)	0.0454 (12)
C004	0.4011 (4)	0.5693 (5)	−0.15262 (18)	0.0808 (19)
H00G	0.3997	0.5177	−0.1800	0.121*
H00H	0.4585	0.6114	−0.1450	0.121*
H00I	0.3514	0.6250	−0.1607	0.121*
C47	0.3925 (3)	0.5600 (4)	−0.06895 (16)	0.0492 (12)
C48	0.4107 (3)	0.6787 (4)	−0.06168 (15)	0.0434 (12)
H48A	0.4244	0.7250	−0.0865	0.052*
C49	0.4081 (3)	0.7290 (4)	−0.01677 (15)	0.0401 (11)
H49A	0.4203	0.8096	−0.0120	0.048*
C44	0.3883 (3)	0.6632 (4)	0.02072 (14)	0.0362 (10)
C45	0.3748 (4)	0.5420 (4)	0.01318 (16)	0.0532 (13)
H45A	0.3640	0.4947	0.0385	0.064*
C46	0.3770 (4)	0.4911 (4)	−0.03111 (18)	0.0641 (16)
H46A	0.3680	0.4098	−0.0355	0.077*
C43	0.3779 (3)	0.7190 (4)	0.06680 (14)	0.0360 (10)
C42	0.4218 (3)	0.6984 (4)	0.11475 (15)	0.0414 (11)
H42A	0.4667	0.6417	0.1263	0.050*
C41	0.3856 (3)	0.7789 (4)	0.14223 (14)	0.0346 (10)
C40	0.3996 (3)	0.8143 (4)	0.19402 (14)	0.0389 (11)
C17	0.1403 (3)	0.5876 (4)	0.12659 (15)	0.0440 (12)
C18	0.1213 (3)	0.6996 (4)	0.10857 (15)	0.0447 (12)
H18A	0.1110	0.7602	0.1292	0.054*
C19	0.1174 (3)	0.7232 (4)	0.05952 (15)	0.0409 (11)
H19A	0.1053	0.7999	0.0476	0.049*
C14	0.1313 (3)	0.6344 (4)	0.02838 (14)	0.0342 (10)
C15	0.1472 (3)	0.5200 (4)	0.04669 (15)	0.0485 (13)
H15A	0.1551	0.4584	0.0259	0.058*
C16	0.1514 (3)	0.4969 (4)	0.09585 (15)	0.0516 (13)
H16A	0.1618	0.4200	0.1079	0.062*
C13	0.1362 (3)	0.6607 (4)	−0.02251 (14)	0.0334 (10)
C12	0.1005 (3)	0.5983 (4)	−0.06540 (14)	0.0393 (11)
H12A	0.0667	0.5283	−0.0687	0.047*
C11	0.1262 (3)	0.6631 (4)	−0.10215 (14)	0.0335 (10)
C10	0.1138 (3)	0.6555 (4)	−0.15602 (15)	0.0398 (11)
C01	0.2282 (5)	1.3529 (7)	−0.2013 (3)	0.128 (3)
H01A	0.1935	1.4253	−0.2044	0.191*

H01B	0.2635	1.3448	−0.1683	0.191*
H01C	0.1869	1.2868	−0.2093	0.191*
C001	0.1668 (5)	0.6523 (6)	0.21017 (19)	0.111 (3)
H00J	0.1714	0.6210	0.2425	0.166*
H00K	0.1176	0.7089	0.2028	0.166*
H00L	0.2236	0.6904	0.2087	0.166*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0578 (4)	0.0319 (3)	0.0185 (2)	0.0002 (2)	0.0113 (2)	−0.0008 (2)
Cu2	0.0568 (4)	0.0445 (3)	0.0192 (3)	−0.0096 (3)	0.0109 (2)	−0.0018 (2)
Cu3	0.0532 (4)	0.0396 (3)	0.0204 (3)	0.0049 (3)	0.0088 (2)	−0.0021 (2)
Na1	0.0633 (13)	0.0442 (11)	0.0278 (9)	−0.0025 (9)	0.0141 (9)	−0.0038 (7)
Na2	0.0558 (12)	0.0646 (13)	0.0277 (9)	−0.0015 (9)	0.0109 (8)	0.0135 (8)
N21	0.043 (2)	0.037 (2)	0.0195 (17)	−0.0033 (17)	0.0067 (15)	−0.0025 (14)
N22	0.047 (2)	0.038 (2)	0.0234 (18)	−0.0057 (17)	0.0135 (16)	0.0001 (15)
N31	0.046 (2)	0.033 (2)	0.0209 (17)	0.0039 (16)	0.0096 (16)	0.0016 (14)
N32	0.048 (2)	0.033 (2)	0.0242 (18)	0.0019 (17)	0.0123 (16)	−0.0017 (14)
N41	0.050 (2)	0.034 (2)	0.0218 (18)	0.0012 (17)	0.0114 (16)	−0.0040 (14)
N42	0.042 (2)	0.037 (2)	0.0190 (17)	0.0013 (16)	0.0040 (16)	−0.0016 (14)
N11	0.052 (2)	0.033 (2)	0.0159 (16)	−0.0020 (17)	0.0091 (16)	0.0025 (14)
N12	0.049 (2)	0.035 (2)	0.0204 (17)	−0.0057 (17)	0.0081 (16)	−0.0007 (14)
O002	0.086 (3)	0.077 (3)	0.0336 (19)	−0.010 (2)	0.0095 (19)	−0.0170 (17)
O21	0.076 (2)	0.061 (2)	0.0211 (15)	−0.0183 (18)	0.0158 (16)	−0.0035 (14)
O22	0.086 (3)	0.062 (2)	0.0399 (19)	−0.0145 (19)	0.0266 (19)	0.0114 (16)
O003	0.105 (3)	0.094 (3)	0.030 (2)	−0.001 (2)	0.006 (2)	0.0095 (19)
O31	0.072 (2)	0.050 (2)	0.0249 (16)	0.0097 (17)	0.0106 (16)	−0.0053 (14)
O32	0.095 (3)	0.051 (2)	0.048 (2)	0.0225 (19)	0.032 (2)	−0.0068 (16)
O004	0.110 (3)	0.064 (3)	0.053 (2)	−0.012 (2)	0.038 (2)	−0.0275 (18)
O42	0.051 (2)	0.062 (2)	0.0282 (17)	0.0057 (16)	0.0029 (15)	0.0056 (15)
O41	0.059 (2)	0.049 (2)	0.0250 (16)	0.0092 (16)	0.0082 (15)	−0.0038 (13)
O001	0.095 (3)	0.064 (2)	0.0250 (17)	−0.020 (2)	0.0139 (18)	0.0055 (15)
O12	0.058 (2)	0.044 (2)	0.0318 (17)	−0.0052 (16)	0.0012 (15)	−0.0127 (14)
O11	0.067 (2)	0.053 (2)	0.0201 (15)	−0.0161 (17)	0.0102 (15)	−0.0055 (13)
O01	0.101 (3)	0.108 (3)	0.042 (2)	0.036 (2)	0.035 (2)	0.023 (2)
C002	0.111 (6)	0.101 (5)	0.038 (3)	−0.004 (4)	−0.005 (3)	−0.010 (3)
C27	0.060 (3)	0.054 (3)	0.031 (3)	−0.010 (3)	0.007 (2)	−0.008 (2)
C28	0.063 (3)	0.041 (3)	0.046 (3)	−0.001 (2)	0.021 (3)	−0.019 (2)
C29	0.049 (3)	0.034 (3)	0.043 (3)	0.002 (2)	0.013 (2)	−0.005 (2)
C24	0.040 (3)	0.035 (3)	0.031 (2)	−0.006 (2)	0.011 (2)	−0.0022 (18)
C25	0.051 (3)	0.036 (3)	0.033 (2)	−0.004 (2)	0.006 (2)	−0.0083 (19)
C26	0.052 (3)	0.047 (3)	0.039 (3)	0.000 (2)	0.000 (2)	−0.001 (2)
C23	0.041 (3)	0.034 (3)	0.030 (2)	0.000 (2)	0.011 (2)	−0.0007 (18)
C22	0.048 (3)	0.037 (3)	0.038 (3)	−0.007 (2)	0.014 (2)	0.002 (2)
C21	0.041 (3)	0.035 (3)	0.029 (2)	0.000 (2)	0.010 (2)	0.0053 (18)
C20	0.058 (3)	0.042 (3)	0.031 (2)	0.005 (2)	0.016 (2)	0.007 (2)
C003	0.160 (7)	0.123 (6)	0.032 (3)	−0.012 (5)	0.008 (4)	−0.012 (4)

C37	0.059 (3)	0.070 (4)	0.029 (3)	0.012 (3)	0.008 (2)	0.008 (2)
C38	0.073 (4)	0.066 (4)	0.036 (3)	0.000 (3)	0.010 (3)	0.016 (2)
C39	0.059 (3)	0.044 (3)	0.037 (3)	0.002 (2)	0.005 (2)	0.003 (2)
C34	0.037 (3)	0.042 (3)	0.029 (2)	0.002 (2)	0.006 (2)	0.0067 (19)
C35	0.051 (3)	0.045 (3)	0.030 (2)	−0.002 (2)	0.006 (2)	0.005 (2)
C36	0.052 (3)	0.058 (3)	0.032 (3)	−0.005 (2)	0.005 (2)	−0.005 (2)
C33	0.045 (3)	0.033 (2)	0.027 (2)	0.000 (2)	0.009 (2)	0.0054 (18)
C32	0.046 (3)	0.030 (2)	0.040 (3)	0.004 (2)	0.013 (2)	0.0040 (19)
C31	0.050 (3)	0.034 (3)	0.032 (2)	−0.001 (2)	0.018 (2)	−0.0020 (19)
C30	0.061 (3)	0.043 (3)	0.037 (3)	−0.002 (2)	0.021 (2)	−0.006 (2)
C004	0.113 (6)	0.092 (5)	0.043 (3)	−0.013 (4)	0.030 (3)	−0.021 (3)
C47	0.057 (3)	0.054 (3)	0.040 (3)	−0.001 (2)	0.017 (2)	−0.015 (2)
C48	0.056 (3)	0.044 (3)	0.036 (3)	−0.001 (2)	0.021 (2)	−0.004 (2)
C49	0.046 (3)	0.035 (3)	0.043 (3)	−0.001 (2)	0.019 (2)	−0.009 (2)
C44	0.043 (3)	0.035 (3)	0.031 (2)	0.005 (2)	0.010 (2)	−0.0043 (19)
C45	0.086 (4)	0.044 (3)	0.039 (3)	0.002 (3)	0.031 (3)	0.003 (2)
C46	0.109 (5)	0.031 (3)	0.063 (4)	−0.006 (3)	0.042 (3)	−0.013 (2)
C43	0.046 (3)	0.032 (3)	0.031 (2)	−0.001 (2)	0.010 (2)	−0.0040 (18)
C42	0.045 (3)	0.041 (3)	0.035 (3)	0.008 (2)	0.002 (2)	0.001 (2)
C41	0.041 (3)	0.035 (3)	0.026 (2)	0.002 (2)	0.006 (2)	0.0028 (18)
C40	0.044 (3)	0.047 (3)	0.024 (2)	−0.009 (2)	0.006 (2)	0.001 (2)
C17	0.053 (3)	0.051 (3)	0.030 (2)	−0.010 (2)	0.014 (2)	0.005 (2)
C18	0.061 (3)	0.044 (3)	0.035 (3)	−0.004 (2)	0.023 (2)	−0.008 (2)
C19	0.052 (3)	0.035 (3)	0.040 (3)	0.003 (2)	0.018 (2)	0.002 (2)
C14	0.040 (3)	0.039 (3)	0.024 (2)	−0.002 (2)	0.0093 (19)	0.0046 (18)
C15	0.079 (4)	0.036 (3)	0.035 (3)	−0.008 (2)	0.021 (2)	0.002 (2)
C16	0.082 (4)	0.041 (3)	0.036 (3)	−0.005 (2)	0.020 (3)	0.010 (2)
C13	0.039 (3)	0.034 (3)	0.028 (2)	0.0024 (19)	0.0078 (19)	0.0041 (18)
C12	0.050 (3)	0.034 (3)	0.033 (2)	−0.010 (2)	0.008 (2)	−0.0021 (19)
C11	0.039 (3)	0.036 (3)	0.024 (2)	−0.002 (2)	0.0026 (19)	−0.0061 (18)
C10	0.048 (3)	0.044 (3)	0.026 (2)	0.005 (2)	0.005 (2)	−0.002 (2)
C01	0.114 (7)	0.161 (8)	0.105 (6)	0.016 (5)	0.019 (5)	0.005 (5)
C001	0.187 (8)	0.105 (6)	0.038 (3)	−0.052 (5)	0.022 (4)	−0.002 (3)

Geometric parameters (Å, º)

Cu1—N31	1.955 (3)	C25—H25A	0.9300
Cu1—N21	1.970 (3)	C26—H26A	0.9300
Cu1—N11	1.978 (3)	C23—C22	1.390 (5)
Cu1—N41	1.979 (3)	C22—C21	1.392 (5)
Cu2—N22	1.899 (3)	C22—H22A	0.9300
Cu2—N12	1.917 (3)	C21—C20	1.492 (5)
Cu2—O11	1.938 (3)	C003—H00D	0.9600
Cu2—O21	1.952 (3)	C003—H00E	0.9600
Cu3—N42	1.898 (3)	C003—H00F	0.9600
Cu3—N32	1.906 (3)	C37—C36	1.374 (6)
Cu3—O31	1.932 (3)	C37—C38	1.387 (7)
Cu3—O41	1.973 (3)	C38—C39	1.373 (6)

Na1—O32	2.199 (3)	C38—H38A	0.9300
Na1—O12^{i}	2.360 (4)	C39—C34	1.395 (6)
Na1—O001^{ii}	2.402 (3)	C39—H39A	0.9300
Na1—O41^{iii}	2.431 (3)	C34—C35	1.381 (6)
Na1—O42^{iii}	2.489 (3)	C34—C33	1.477 (5)
Na2—O22	2.212 (3)	C35—C36	1.387 (5)
Na2—O01	2.262 (4)	C35—H35A	0.9300
Na2—O42^{iv}	2.292 (4)	C36—H36A	0.9300
Na2—O11^{v}	2.309 (3)	C33—C32	1.393 (5)
Na2—O12^{v}	2.842 (3)	C32—C31	1.387 (5)
N21—N22	1.340 (4)	C32—H32A	0.9300
N21—C23	1.361 (5)	C31—C30	1.490 (5)
N22—C21	1.335 (5)	C004—H00G	0.9600
N31—C33	1.350 (5)	C004—H00H	0.9600
N31—N32	1.357 (4)	C004—H00I	0.9600
N32—C31	1.341 (5)	C47—C48	1.371 (6)
N41—N42	1.348 (4)	C47—C46	1.377 (6)
N41—C43	1.357 (5)	C48—C49	1.389 (5)
N42—C41	1.345 (5)	C48—H48A	0.9300
N11—N12	1.351 (4)	C49—C44	1.373 (5)
N11—C13	1.361 (5)	C49—H49A	0.9300
N12—C11	1.338 (5)	C44—C45	1.390 (6)
O002—C27	1.369 (5)	C44—C43	1.476 (5)
O002—C002	1.450 (6)	C45—C46	1.375 (6)
O21—C20	1.296 (5)	C45—H45A	0.9300
O22—C20	1.227 (5)	C46—H46A	0.9300
O003—C37	1.372 (5)	C43—C42	1.373 (5)
O003—C003	1.415 (6)	C42—C41	1.378 (5)
O31—C30	1.288 (5)	C42—H42A	0.9300
O32—C30	1.226 (5)	C41—C40	1.473 (5)
O004—C47	1.364 (5)	C17—C18	1.365 (6)
O004—C004	1.419 (6)	C17—C16	1.371 (6)
O42—C40	1.241 (5)	C18—C19	1.389 (5)
O41—C40	1.289 (5)	C18—H18A	0.9300
O001—C17	1.384 (5)	C19—C14	1.375 (5)
O001—C001	1.427 (6)	C19—H19A	0.9300
O12—C10	1.229 (5)	C14—C15	1.389 (5)
O11—C10	1.301 (5)	C14—C13	1.475 (5)
O01—C01	1.389 (7)	C15—C16	1.390 (5)
O01—H01D	0.9300	C15—H15A	0.9300
C002—H00A	0.9600	C16—H16A	0.9300
C002—H00B	0.9600	C13—C12	1.389 (5)
C002—H00C	0.9600	C12—C11	1.387 (5)
C27—C28	1.377 (6)	C12—H12A	0.9300
C27—C26	1.380 (6)	C11—C10	1.481 (5)
C28—C29	1.384 (5)	C01—H01A	0.9600
C28—H28A	0.9300	C01—H01B	0.9600
C29—C24	1.380 (5)	C01—H01C	0.9600

C29—H29A	0.9300	C001—H00J	0.9600
C24—C25	1.387 (6)	C001—H00K	0.9600
C24—C23	1.485 (5)	C001—H00L	0.9600
C25—C26	1.390 (5)		

N31—Cu1—N21	96.08 (13)	C22—C21—C20	138.0 (4)
N31—Cu1—N11	127.78 (14)	O22—C20—O21	124.7 (4)
N21—Cu1—N11	105.49 (12)	O22—C20—C21	121.6 (4)
N31—Cu1—N41	104.58 (13)	O21—C20—C21	113.6 (4)
N21—Cu1—N41	122.51 (14)	O003—C003—H00D	109.5
N11—Cu1—N41	102.60 (13)	O003—C003—H00E	109.5
N22—Cu2—N12	99.55 (13)	H00D—C003—H00E	109.5
N22—Cu2—O11	177.64 (13)	O003—C003—H00F	109.5
N12—Cu2—O11	82.73 (13)	H00D—C003—H00F	109.5
N22—Cu2—O21	82.16 (13)	H00E—C003—H00F	109.5
N12—Cu2—O21	176.68 (14)	O003—C37—C36	123.7 (5)
O11—Cu2—O21	95.61 (12)	O003—C37—C38	116.2 (4)
N42—Cu3—N32	97.74 (13)	C36—C37—C38	120.0 (4)
N42—Cu3—O31	178.72 (13)	C39—C38—C37	120.1 (4)
N32—Cu3—O31	83.24 (13)	C39—C38—H38A	120.0
N42—Cu3—O41	82.78 (13)	C37—C38—H38A	120.0
N32—Cu3—O41	178.06 (14)	C38—C39—C34	121.6 (4)
O31—Cu3—O41	96.28 (12)	C38—C39—H39A	119.2
O32—Na1—O12^{i}	103.65 (13)	C34—C39—H39A	119.2
O32—Na1—O001^{ii}	100.87 (13)	C35—C34—C39	116.7 (4)
O12^{i}—Na1—O001^{ii}	98.11 (13)	C35—C34—C33	121.1 (4)
O32—Na1—O41^{iii}	127.59 (14)	C39—C34—C33	122.1 (4)
O12^{i}—Na1—O41^{iii}	116.02 (12)	C34—C35—C36	122.9 (4)
O001^{ii}—Na1—O41^{iii}	105.64 (12)	C34—C35—H35A	118.6
O32—Na1—O42^{iii}	101.94 (12)	C36—C35—H35A	118.6
O12^{i}—Na1—O42^{iii}	83.62 (11)	C37—C36—C35	118.8 (4)
O001^{ii}—Na1—O42^{iii}	156.02 (12)	C37—C36—H36A	120.6
O41^{iii}—Na1—O42^{iii}	53.59 (10)	C35—C36—H36A	120.6
O22—Na2—O01	94.91 (14)	N31—C33—C32	109.9 (4)
O22—Na2—O42^{iv}	106.28 (13)	N31—C33—C34	120.1 (4)
O01—Na2—O42^{iv}	123.62 (16)	C32—C33—C34	130.0 (4)
O22—Na2—O11^{v}	143.86 (15)	C31—C32—C33	104.3 (4)
O01—Na2—O11^{v}	88.48 (12)	C31—C32—H32A	127.8
O42^{iv}—Na2—O11^{v}	101.47 (12)	C33—C32—H32A	127.8
O22—Na2—O12^{v}	114.85 (12)	N32—C31—C32	109.4 (3)
O01—Na2—O12^{v}	138.08 (12)	N32—C31—C30	113.2 (4)
O42^{iv}—Na2—O12^{v}	77.25 (11)	C32—C31—C30	137.4 (4)
O11^{v}—Na2—O12^{v}	50.01 (10)	O32—C30—O31	125.1 (4)
N22—N21—C23	107.5 (3)	O32—C30—C31	120.5 (4)
N22—N21—Cu1	123.5 (2)	O31—C30—C31	114.3 (4)
C23—N21—Cu1	129.0 (3)	O004—C004—H00G	109.5
C21—N22—N21	109.7 (3)	O004—C004—H00H	109.5
C21—N22—Cu2	116.0 (3)	H00G—C004—H00H	109.5

N21—N22—Cu2	134.3 (3)	O004—C004—H00I	109.5
C33—N31—N32	107.3 (3)	H00G—C004—H00I	109.5
C33—N31—Cu1	130.3 (3)	H00H—C004—H00I	109.5
N32—N31—Cu1	122.3 (2)	O004—C47—C48	124.5 (4)
C31—N32—N31	109.0 (3)	O004—C47—C46	115.5 (4)
C31—N32—Cu3	114.1 (3)	C48—C47—C46	119.9 (4)
N31—N32—Cu3	136.5 (3)	C47—C48—C49	119.2 (4)
N42—N41—C43	107.8 (3)	C47—C48—H48A	120.4
N42—N41—Cu1	122.6 (3)	C49—C48—H48A	120.4
C43—N41—Cu1	129.3 (3)	C44—C49—C48	121.9 (4)
C41—N42—N41	108.8 (3)	C44—C49—H49A	119.0
C41—N42—Cu3	114.9 (3)	C48—C49—H49A	119.0
N41—N42—Cu3	136.2 (3)	C49—C44—C45	117.6 (4)
N12—N11—C13	107.0 (3)	C49—C44—C43	121.6 (4)
N12—N11—Cu1	120.9 (2)	C45—C44—C43	120.7 (4)
C13—N11—Cu1	132.0 (2)	C46—C45—C44	121.0 (4)
C11—N12—N11	109.8 (3)	C46—C45—H45A	119.5
C11—N12—Cu2	114.3 (3)	C44—C45—H45A	119.5
N11—N12—Cu2	135.8 (3)	C45—C46—C47	120.2 (4)
C27—O002—C002	116.3 (4)	C45—C46—H46A	119.9
C20—O21—Cu2	115.3 (3)	C47—C46—H46A	119.9
C20—O22—Na2	159.9 (3)	N41—C43—C42	108.8 (3)
C37—O003—C003	118.2 (4)	N41—C43—C44	119.8 (4)
C30—O31—Cu3	114.8 (3)	C42—C43—C44	131.4 (4)
C30—O32—Na1	157.2 (3)	C43—C42—C41	106.0 (4)
C47—O004—C004	117.6 (4)	C43—C42—H42A	127.0
C40—O42—Na2^{iv}	126.3 (3)	C41—C42—H42A	127.0
C40—O42—Na1^{vi}	91.1 (3)	N42—C41—C42	108.6 (3)
Na2^{iv}—O42—Na1^{vi}	105.43 (13)	N42—C41—C40	113.3 (4)
C40—O41—Cu3	113.5 (2)	C42—C41—C40	138.0 (4)
C40—O41—Na1^{vi}	92.6 (2)	O42—C40—O41	122.6 (4)
Cu3—O41—Na1^{vi}	153.97 (15)	O42—C40—C41	122.0 (4)
C17—O001—C001	117.1 (4)	O41—C40—C41	115.4 (4)
C17—O001—Na1^{vii}	128.7 (3)	C18—C17—C16	120.1 (4)
C001—O001—Na1^{vii}	111.2 (3)	C18—C17—O001	123.6 (4)
C10—O12—Na1^{i}	118.4 (3)	C16—C17—O001	116.3 (4)
C10—O12—Na2^{viii}	81.5 (3)	C17—C18—C19	120.1 (4)
Na1^{i}—O12—Na2^{viii}	93.58 (11)	C17—C18—H18A	119.9
C10—O11—Cu2	115.2 (2)	C19—C18—H18A	120.0
C10—O11—Na2^{viii}	104.8 (2)	C14—C19—C18	120.7 (4)
Cu2—O11—Na2^{viii}	139.39 (15)	C14—C19—H19A	119.6
C01—O01—Na2	125.5 (4)	C18—C19—H19A	119.6
C01—O01—H01D	117.2	C19—C14—C15	118.7 (4)
Na2—O01—H01D	117.2	C19—C14—C13	121.1 (4)
O002—C002—H00A	109.5	C15—C14—C13	120.1 (4)
O002—C002—H00B	109.5	C14—C15—C16	120.3 (4)
H00A—C002—H00B	109.5	C14—C15—H15A	119.8
O002—C002—H00C	109.5	C16—C15—H15A	119.8

H00A—C002—H00C	109.5	C17—C16—C15	119.9 (4)
H00B—C002—H00C	109.5	C17—C16—H16A	120.0
O002—C27—C28	115.7 (4)	C15—C16—H16A	120.0
O002—C27—C26	124.7 (4)	N11—C13—C12	109.3 (3)
C28—C27—C26	119.6 (4)	N11—C13—C14	120.8 (3)
C27—C28—C29	120.6 (4)	C12—C13—C14	129.9 (4)
C27—C28—H28A	119.7	C11—C12—C13	105.0 (4)
C29—C28—H28A	119.7	C11—C12—H12A	127.5
C24—C29—C28	121.0 (4)	C13—C12—H12A	127.5
C24—C29—H29A	119.5	N12—C11—C12	108.8 (3)
C28—C29—H29A	119.5	N12—C11—C10	113.8 (4)
C29—C24—C25	117.7 (4)	C12—C11—C10	137.3 (4)
C29—C24—C23	122.9 (4)	O12—C10—O11	123.6 (4)
C25—C24—C23	119.2 (4)	O12—C10—C11	122.6 (4)
C24—C25—C26	121.9 (4)	O11—C10—C11	113.8 (4)
C24—C25—H25A	119.1	O01—C01—H01A	109.5
C26—C25—H25A	119.1	O01—C01—H01B	109.5
C27—C26—C25	119.2 (4)	H01A—C01—H01B	109.5
C27—C26—H26A	120.4	O01—C01—H01C	109.5
C25—C26—H26A	120.4	H01A—C01—H01C	109.5
N21—C23—C22	109.2 (4)	H01B—C01—H01C	109.5
N21—C23—C24	118.9 (3)	O001—C001—H00J	109.5
C22—C23—C24	131.8 (4)	O001—C001—H00K	109.5
C23—C22—C21	104.5 (4)	H00J—C001—H00K	109.5
C23—C22—H22A	127.7	O001—C001—H00L	109.5
C21—C22—H22A	127.7	H00J—C001—H00L	109.5
N22—C21—C22	109.1 (3)	H00K—C001—H00L	109.5
N22—C21—C20	112.8 (4)		

Symmetry codes: (i) $-x, -y+2, -z$; (ii) $x, y+1, z$; (iii) $-x+1/2, y+1/2, -z+1/2$; (iv) $-x+1, -y+2, -z$; (v) $-x+1/2, y+1/2, -z-1/2$; (vi) $-x+1/2, y-1/2, -z+1/2$; (vii) $x, y-1, z$; (viii) $-x+1/2, y-1/2, -z-1/2$.