Structures of Tetrakis(1,2-dimethylimidazole)M^{II} Diperchlorates (M^{II} = Ni, Cu)

By Marc N. Potenza, Joseph A. Potenza and Harvey J. Schugar

Department of Chemistry, Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08903, *USA*

Abstract. $[Ni(C_5H_8N_2)_4]^{2+}.2ClO_4^-$, $M_r = 642.14$, monoclinic, $P2_1/n$, $a = 17.938$ (2), $b = 14.438$ (2), $c = 11.336$ (2) Å, $\beta = 93.38$ (1)°, $V = 2931$ (1) Å^3, $Z = 4$, $D_m = 1.44$ (1), $D_x = 1.455$ Mg m^{-3}, μ(Mo $K\alpha$, $\lambda = 0.71073$ Å) = 0.90 mm^{-1}, $F(000) = 1336$, $T = 297$ (1) K, $R_F = 0.061$, $wR_F = 0.076$ for 2676 reflections. $[Cu(C_5H_8N_2)_4]^{2+}.2ClO_4^-$, $M_r = 646.97$, monoclinic, $P2_1/n$, $a = 15.9011$ (7), $b = 16.730$ (3), $c = 10.919$ (1) Å, $\beta = 98.413$ (7)°, $V = 2873$ (1) Å^3, $Z = 4$, $D_m = 1.47$ (1), $D_x = 1.496$ Mg m^{-3}, μ(Mo $K\alpha$, $\lambda = 0.71073$ Å) = 1.00 mm^{-1}, $F(000) = 1340$, $T = 297$ (1) K, $R_F = 0.053$, $wR_F = 0.069$ for 2889 reflections. Three of the four ClO_4 groups in both structures showed disorder; they were modeled as single-site Cl atoms with unrestrained low-occupancy O atoms. Each Ni^{II} ion is coordinated in a distorted square-planar fashion by four N donor atoms from the dimethylimidazole groups. The Ni—N distances are typical. In the Cu complex, one ligand showed an approximate twofold disorder about the Cu—N(im) direction. Each Cu^{II} ion also has four square-planar equatorial Cu—N(im) bonds and, in addition, shows unusually weak axial coordination by two O(ClO_4) atoms. The Cu—O(ClO_4) distances are substantially longer than those found for typical tetragonal $CuN_4O_2(ClO_4)$ coordination, and the observed Cu—O—Cl angles are much larger than usual.

Introduction. The binding sites of nearly all copper-containing proteins are known or thought to contain one or more histidine ligands (Bernarducci, Bharadwaj, Krogh-Jespersen, Potenza & Schugar, 1983). To help understand these sites, model low-molecular-weight complexes of copper and other metals with appropriate ligand sets have been studied by many research groups. As part of a project designed to elucidate the nature of metal–imidazole bonding and to facilitate assignments of the spectra of copper-containing proteins, we have prepared and characterized a variety of M^{II} complexes containing substituted imidazole ligands (Schugar, 1983). The ligand 1,2-dimethylimidazole (1,2-dmi) forms tetrakis diperchlorate complexes with Co^{II}, Ni^{II}, Cu^{II} and Zn^{II}. Preliminary spectroscopic results for these systems have been reported (Bernarducci *et al.*, 1983; Schugar, 1983) as have structural results for the isomorphous Co^{II} and Zn^{II} systems (Bernarducci,

Bharadwaj, Potenza & Schugar, 1987) which contain distorted tetrahedral $[M^{II}(1,2\text{-}dmi)_4]$ chromophores. We report here the structure of the Cu^{II} complex, $[Cu(1,2\text{-}dmi)_4](ClO_4)_2$, as well as that of its Ni^{II} analog, which may serve as a useful diamagnetic host lattice for Cu^{II} EPR studies.

Experimental. Preparation of the title complexes, originally described by Reedijk (1972), has been reported previously (Bernarducci *et al.*, 1983). Crystals of $[Ni(1,2\text{-}dmi)_4](ClO_4)_2$ (1) were obtained as yellow plates from acetone/methanol (30/5 *v/v*). Blue-purple prisms of $[Cu(1,2\text{-}dmi)_4](ClO_4)_2$ (2) were obtained from dry methanol. Caution! These compounds may explode if heated when dry.

Structure solution; values for complex (2) are given in parentheses. D_m by flotation; crystal $0.13 \times 0.25 \times 0.35$ mm ($0.28 \times 0.35 \times 0.45$ mm); Enraf–Nonius CAD-4 diffractometer; graphite-monochromated Mo $K\alpha$ radiation; θ–2θ scan. Reciprocal-lattice symmetry and systematic absences consistent with monoclinic space group $P2_1/n$. Cell constants from setting angles of 25 reflections with $9.51 \le \theta \le 21.03°$ ($14.32 \le \theta \le 19.35°$); data corrected for Lorentz, polarization and absorption (empirical) effects; min., max. absorption correction 0.96 (1.00), 0.66 (0.79). Variation in intensity of 3 standard reflections < 0.9% (0.3%); 4974 (4846) unique reflections measured with $2 \le 2\theta \le 50°$ ($4 \le 2\theta \le 50°$); 2672 (2889) with $I \ge 3\sigma(I)$ used in refinement. Data collected: $h,k,\pm l$; h 0–21 (0–18), k 0–17 (0–19), l 0–13 (0–12).

Structures solved by direct methods (*MULTAN*82; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and difference Fourier techniques; H atoms at calculated positions; C—H distance = 0.95 Å; H atoms not refined. Full-matrix least-squares refinement on F; all atoms anisotropic except for disordered perchlorate O atoms [(1),(2)] and disordered 1,2-dmi atoms (2) on partially occupied sites; $w = 4F_o^2/[\sigma^2(F_o^2) + 0.0016F_o^4]$. In (1), Cl atoms were treated as single-site atoms while O atoms were assigned fractional occupancies (3 sets) from difference Fourier peak heights. Unrestrained refinement gave a broad range of Cl—O distances [1.31 (2) to 1.62 (3) Å, av. 1.43 Å] and O—Cl—O angles [57 (1) to 154 (2)°, av. 108°] with

Table 1. *Fractional atomic coordinates and isotropic thermal parameters for tetrakis(1,2-dimethylimidazole)nickel(II) diperchlorate*

	x	y	z	B or $B_{eq}(\text{Å}^2)$†	Mult.‡
Ni	0.25377 (5)	0.47032 (6)	1.00001 (8)	3.60 (2)	
Cl(1)	0.4185 (1)	1.0974 (2)	1.1968 (2)	6.54 (6)	
Cl(2)	0.0638 (1)	0.8850 (2)	0.7989 (2)	6.75 (6)	
N(1)	0.1962 (3)	0.3607 (4)	1.0107 (5)	4.2 (1)	
N(2)	0.1592 (3)	0.2176 (4)	1.0069 (5)	5.0 (2)	
N(3)	0.1998 (3)	0.4964 (4)	0.8558 (5)	4.1 (1)	
N(4)	0.1200 (3)	0.5542 (4)	0.7259 (5)	4.1 (1)	
N(5)	0.3082 (3)	0.5831 (4)	0.9859 (5)	3.8 (1)	
N(6)	0.3610 (3)	0.7173 (4)	1.0139 (5)	4.8 (1)	
N(7)	0.3063 (3)	0.4373 (4)	1.1446 (5)	4.1 (1)	
N(8)	0.3895 (3)	0.3890 (4)	1.2769 (5)	4.8 (1)	
C(1)	0.2156 (4)	0.2749 (5)	0.9856 (6)	4.2 (2)	
C(2)	0.1013 (4)	0.2699 (6)	1.0470 (7)	6.2 (2)	
C(3)	0.1246 (4)	0.3578 (5)	1.0493 (7)	5.4 (2)	
C(4)	0.1434 (4)	0.5538 (5)	0.8399 (6)	4.0 (2)	
C(5)	0.1631 (5)	0.4941 (6)	0.6667 (7)	5.9 (2)	
C(6)	0.2133 (4)	0.4575 (5)	0.7481 (6)	5.4 (2)	
C(7)	0.3222 (4)	0.6499 (5)	1.0632 (6)	4.1 (2)	
C(8)	0.3706 (4)	0.6930 (5)	0.8983 (7)	5.6 (2)	
C(9)	0.3384 (4)	0.6103 (5)	0.8812 (6)	5.1 (2)	
C(10)	0.3772 (4)	0.4149 (5)	1.1648 (6)	4.1 (2)	
C(11)	0.3235 (4)	0.3946 (5)	1.3307 (6)	5.3 (2)	
C(12)	0.2721 (4)	0.4235 (5)	1.2505 (6)	4.8 (2)	
C(13)	0.2871 (5)	0.2457 (6)	0.9406 (8)	7.1 (2)	
C(14)	0.1568 (5)	0.1171 (6)	0.9923 (8)	7.0 (2)	
C(15)	0.1103 (5)	0.6084 (6)	0.9304 (7)	6.8 (2)	
C(16)	0.0571 (4)	0.6068 (6)	0.6703 (7)	6.4 (2)	
C(17)	0.3014 (5)	0.6541 (6)	1.1865 (7)	7.1 (2)	
C(18)	0.3898 (5)	0.8023 (6)	1.0705 (8)	7.1 (2)	
C(19)	0.4333 (4)	0.4164 (7)	1.0779 (7)	6.3 (2)	
C(20)	0.4599 (5)	0.3554 (7)	1.3313 (7)	7.1 (2)	
O(1)	0.3939 (5)	1.0229 (7)	1.1245 (9)	9.1 (3)*	0.67
O(1')	0.360 (1)	1.056 (1)	1.110 (2)	7.9 (5)*	0.33
O(2)	0.3680 (6)	1.1747 (8)	1.200 (1)	11.6 (3)*	0.67
O(2')	0.377 (1)	1.154 (1)	1.270 (2)	8.5 (5)*	0.33
O(3)	0.4860 (6)	1.1227 (8)	1.148 (1)	10.4 (3)*	0.67
O(3')	0.461 (1)	1.161 (2)	1.136 (2)	10.2 (6)*	0.33
O(4)	0.4559 (6)	1.0607 (9)	1.302 (1)	11.8 (3)*	0.67
O(4')	0.407 (1)	1.034 (1)	1.285 (2)	8.1 (5)*	0.33
O(5)	0.0919 (8)	0.948 (1)	0.726 (1)	9.4 (4)*	0.50
O(5')	0.101 (1)	0.957 (2)	0.868 (2)	9.2 (6)*	0.30
O(5")	0.076 (1)	0.983 (2)	0.790 (2)	5.0 (5)*	0.20
O(6)	0.031 (1)	0.832 (2)	0.718 (2)	16.5 (7)*	0.50
O(6')	0.060 (1)	0.818 (1)	0.882 (2)	7.9 (5)*	0.30
O(6")	-0.012 (2)	0.870 (2)	0.715 (3)	8.2 (8)*	0.20
O(7)	0.025 (1)	0.928 (1)	0.888 (2)	15.6 (6)*	0.50
O(7')	-0.015 (2)	0.907 (3)	0.820 (3)	16 (1)*	0.30
O(7")	0.015 (1)	0.812 (2)	0.814 (2)	6.4 (7)*	0.20
O(8)	0.1257 (9)	0.839 (1)	0.869 (1)	11.5 (4)*	0.50
O(8')	0.107 (1)	0.871 (1)	0.698 (2)	6.6 (4)*	0.30
O(8")	0.128 (2)	0.814 (3)	0.778 (3)	10 (1)*	0.20

† Starred atoms were refined isotropically. $B_{eq} = 4(\sum_i \sum_j \beta_{ij} a_i a_j)/3$.

‡ Atom multipliers for the disordered perchlorate O atoms.

Table 2. *Fractional atomic coordinates and isotropic thermal parameters for tetrakis(1,2-dimethylimidazole)copper(II) diperchlorate*

	x	y	z	B or $B_{eq}(\text{Å}^2)$†	Mult.‡
Cu	0.11909 (4)	0.24377 (4)	0.46826 (6)	3.57 (1)	
Cl(1)	0.0628 (1)	0.3970 (1)	0.7387 (2)	4.85 (4)	
Cl(2)	0.1250 (1)	0.0543 (1)	0.2213 (2)	5.59 (4)	
N(1)	0.2418 (3)	0.2768 (3)	0.4987 (4)	3.5 (1)	
N(2)	0.3709 (3)	0.3161 (3)	0.4834 (4)	3.9 (1)	
N(3)	0.1403 (3)	0.1717 (3)	0.6169 (4)	3.9 (1)	
N(4)	0.1892 (4)	0.0853 (3)	0.7590 (5)	5.7 (1)	
N(5)	0.0977 (3)	0.3123 (3)	0.3181 (4)	3.4 (1)	
N(6)	0.1005 (3)	0.4051 (3)	0.1765 (4)	3.5 (1)	
C(1)	0.2992 (3)	0.2840 (4)	0.4230 (5)	3.5 (1)	
C(2)	0.3574 (4)	0.3296 (4)	0.6033 (5)	4.4 (1)	
C(3)	0.2787 (3)	0.3055 (4)	0.6107 (5)	3.9 (1)	
C(4)	0.1991 (4)	0.1176 (4)	0.6500 (5)	4.1 (1)	
C(5)	0.1199 (4)	0.1215 (5)	0.7974 (6)	6.4 (2)	
C(6)	0.0902 (4)	0.1739 (4)	0.7129 (5)	4.9 (1)	
C(7)	0.1198 (3)	0.3869 (3)	0.2982 (5)	3.2 (1)	
C(8)	0.0641 (4)	0.3388 (4)	0.1176 (5)	4.4 (1)	
C(9)	0.0625 (4)	0.2827 (4)	0.2042 (6)	4.7 (2)	
C(13)	0.2913 (4)	0.2598 (4)	0.2906 (6)	5.5 (2)	
C(14)	0.4479 (4)	0.3351 (4)	0.4328 (6)	5.3 (2)	
C(15)	0.2678 (4)	0.0942 (5)	0.5795 (6)	6.3 (2)	
C(16)	0.2397 (6)	0.0231 (5)	0.8264 (7)	9.3 (2)	
C(17)	0.1574 (4)	0.4453 (4)	0.3919 (6)	4.6 (1)	
C(18)	0.1159 (4)	0.4809 (4)	0.1193 (5)	4.7 (1)	
O(5)	0.1422 (4)	0.1112 (4)	0.3196 (5)	9.0 (2)	
O(6)	0.0363 (4)	0.0515 (5)	0.1902 (7)	11.9 (2)	
O(7)	0.1574 (4)	-0.0191 (3)	0.2632 (6)	8.9 (2)	
O(8)	0.1628 (5)	0.0808 (5)	0.1231 (6)	12.7 (2)	
N(7)	-0.0029 (5)	0.2124 (5)	0.4448 (7)	3.7 (2)*	0.60
N(8)	-0.1432 (5)	0.2208 (5)	0.4543 (7)	3.5 (2)*	0.60
C(10)	-0.0703 (6)	0.2619 (5)	0.4436 (8)	3.3 (2)*	0.60
C(11)	-0.1157 (7)	0.1412 (7)	0.463 (1)	5.3 (2)*	0.60
C(12)	-0.0354 (7)	0.1360 (7)	0.456 (1)	5.8 (3)*	0.60
C(19)	-0.0728 (8)	0.3521 (8)	0.427 (1)	6.3 (3)	0.60
C(20)	-0.2276 (8)	0.2521 (8)	0.457 (1)	6.6 (3)*	0.60
O(1)	0.0981 (5)	0.3673 (5)	0.6401 (7)	5.7 (2)*	0.60
O(2)	-0.0188 (5)	0.3569 (5)	0.7471 (8)	6.5 (2)*	0.60
O(3)	0.1419 (6)	0.3834 (6)	0.8351 (9)	7.7 (2)*	0.60
O(4)	0.0545 (5)	0.4806 (5)	0.7387 (8)	6.7 (2)*	0.60
N(7')	-0.0104 (7)	0.2297 (7)	0.462 (1)	3.3 (2)*	0.40
N(8')	-0.1333 (7)	0.1779 (7)	0.465 (1)	3.7 (2)*	0.40
C(10')	-0.0501 (9)	0.1588 (9)	0.469 (1)	4.0 (3)*	0.40
C(11')	-0.139 (1)	0.260 (1)	0.454 (2)	5.9 (4)*	0.40
C(12')	-0.069 (1)	0.295 (1)	0.446 (1)	4.5 (3)*	0.40
C(19')	-0.018 (1)	0.077 (1)	0.473 (2)	8.0 (5)*	0.40
C(20')	-0.211 (1)	0.131 (1)	0.473 (2)	8.6 (6)*	0.40
O(1')	0.0825 (7)	0.3528 (7)	0.630 (1)	5.5 (2)*	0.40
O(2')	0.0057 (6)	0.3547 (6)	0.8006 (8)	3.8 (2)*	0.40
O(3')	0.107 (1)	0.410 (1)	0.842 (2)	10.5 (5)*	0.40
O(4')	0.0309 (7)	0.4736 (7)	0.679 (1)	5.9 (3)*	0.40

† Starred atoms were refined isotropically. $B_{eq} = 4(\sum_i \sum_j \beta_{ij} a_i a_j)/3$.

‡ Atom multipliers for the disordered 1,2-dimethylimidazole and perchlorate atoms.

averages close to accepted values. The nine largest positive $\Delta\rho$ peaks (0.35 to 0.46 e Å^{-3}) were 1.25 to 1.61 Å from Cl atoms while the nine largest negative $\Delta\rho$ peaks (−0.31 to −0.37 e Å^{-3}) were 0.60 to 0.96 Å from the Cl atoms. In (2), one ligand showed an approximate twofold disorder about Cu—N(7,7') and a related disorder of the O atoms of one ClO$_4$ group. Two-site occupancies were set at 0.60 and 0.40 with the ClO$_4$ group modeled as in (1) [Cl(1)—O, 1.26 (2) to 1.535 (9) Å, av. 1.43 Å; O—Cl(1)—O, 88.8 (9) to 131 (1)°, av. 109°]. The largest two $\Delta\rho$ peaks (0.43, 0.46 e Å^{-3}) were 1.54 and 1.37 Å from Cl(1) while the largest negative peak (−0.48 e Å^{-3}) was 0.72 Å from Cl(1). Excluding the ClO$_4$ groups and disordered ligand atoms, $\Delta_{max}/\sigma = 0.21$ (0.30). Final $R_F =$

0.061 (0.053), $wR_F = 0.076$ (0.069), $S = 2.10$ (1.59). Scattering factors from *International Tables for X-ray Crystallography* (1974). Programs from Enraf–Nonius (1983) *SDP*.

Discussion. Final positional parameters and their e.s.d.'s are given in Tables 1 and 2.* A view of the Ni-containing cation $[Ni(1,2-dmi)_4]^{2+}$, showing the atom-numbering scheme, is given in Fig. 1. Fig. 2

shows a corresponding view of the [Cu(1,2-dmi)$_4$]-(ClO$_4$)$_2$ complex. Selected bond distances and angles for (1) and (2) are listed in Tables 3 and 4, respectively.

The structure of (1) contains discrete tetrakis(1,2-dmi)nickel(II) cations separated by perchlorate anions. Each Ni^{II} ion is coordinated in a distorted square-planar fashion by four imidazole N donor atoms. The shortest interionic Ni···O(ClO$_4$) contact [3·74 (2) Å] precludes axial coordination by the perchlorate anions. Each imidazole group is planar to within ±0·01 Å while the methyl C atoms deviate from 0·01 to 0·06 Å from these planes. The imidazole planes I–IV make dihedral angles of 79·2 (2), 79·4 (2), 47·5 (2) and 62·6 (2)°, respectively, with the planar (±0·019 Å) NiN$_4$ unit. The four Ni—N distances in (1) are equivalent to each other within ±0·012 Å and are relatively insensitive to the NiN$_4$/im dihedral angle. Their average [1·900 (9) Å] is only slightly larger than the value of 1·881 (3) Å reported for the Ni—N(im)

distance in a related square-planar Ni^{II}N$_4$ complex that contains two imidazole donor groups (Jameson, Potenza, Potenza & Schugar, 1985).
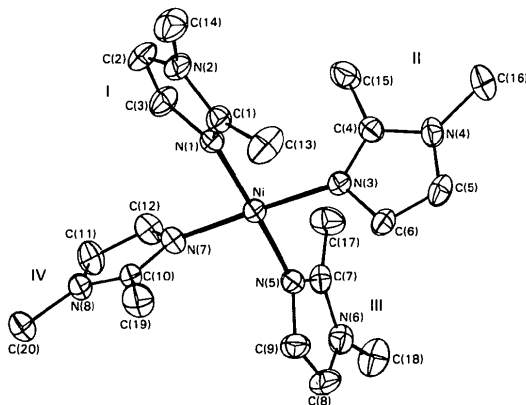

Fig. 1. View of the tetrakis(1,2-dimethylimidazole)nickel(II) cation showing the atom-numbering scheme.
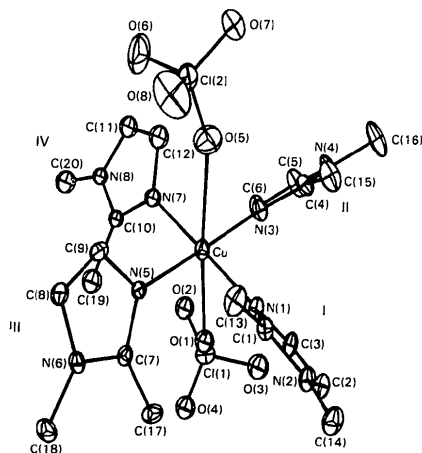

Fig. 2. View of the tetrakis(1,2-dimethylimidazole)copper(II) diperchlorate complex showing the atom-numbering scheme. The disordered perchlorate and 1,2-dimethylimidazole groups have been omitted for clarity.

Table 3. Selected bond lengths (Å) and angles (°) for tetrakis(1,2-dimethylimidazole)nickel(II) diperchlorate

Ni—N(1)	1·898 (4)	N(2)—C(2)	1·382 (8)
Ni—N(3)	1·888 (5)	N(4)—C(5)	1·364 (7)
Ni—N(5)	1·911 (4)	N(6)—C(8)	1·376 (7)
Ni—N(7)	1·903 (4)	N(8)—C(11)	1·365 (7)
N(1)—C(1)	1·321 (6)	C(2)—C(3)	1·337 (7)
N(3)—C(4)	1·321 (6)	C(5)—C(6)	1·358 (7)
N(5)—C(7)	1·316 (6)	C(8)—C(9)	1·335 (7)
N(7)—C(10)	1·320 (6)	C(11)—C(12)	1·324 (7)
N(1)—C(3)	1·382 (6)	N(2)—C(14)	1·460 (7)
N(3)—C(6)	1·378 (6)	N(4)—C(16)	1·471 (6)
N(5)—C(9)	1·390 (6)	N(6)—C(18)	1·466 (7)
N(7)—C(12)	1·394 (6)	N(8)—C(20)	1·456 (7)
N(2)—C(1)	1·341 (6)	C(1)—C(13)	1·470 (8)
N(4)—C(4)	1·336 (6)	C(4)—C(15)	1·449 (7)
N(6)—C(7)	1·339 (6)	C(7)—C(17)	1·469 (7)
N(8)—C(10)	1·331 (6)	C(10)—C(19)	1·448 (7)
N(1)—Ni—N(3)	88·2 (2)	C(1)—N(2)—C(2)	108·2 (5)
N(1)—Ni—N(5)	177·6 (2)	C(4)—N(4)—C(5)	108·5 (4)
N(1)—Ni—N(7)	88·8 (2)	C(7)—N(6)—C(8)	108·0 (4)
N(3)—Ni—N(5)	89·8 (2)	C(10)—N(8)—C(11)	108·2 (4)
N(3)—Ni—N(7)	176·9 (2)	N(2)—C(2)—C(3)	106·6 (5)
N(5)—Ni—N(7)	93·2 (2)	N(4)—C(5)—C(6)	106·6 (6)
C(1)—N(1)—C(3)	107·6 (4)	N(6)—C(8)—C(9)	106·8 (5)
C(4)—N(3)—C(6)	108·1 (4)	N(8)—C(11)—C(12)	107·4 (5)
C(7)—N(5)—C(9)	107·0 (4)	N(1)—C(3)—C(2)	108·6 (5)
C(10)—N(7)—C(12)	106·5 (4)	N(3)—C(6)—C(5)	107·4 (6)
N(1)—C(1)—N(2)	109·2 (5)	N(5)—C(9)—C(8)	108·4 (5)
N(3)—C(4)—N(4)	109·4 (5)	N(7)—C(12)—C(11)	108·2 (5)
N(5)—C(7)—N(6)	109·8 (5)		
N(7)—C(10)—N(8)	109·8 (5)		

Table 4. Selected bond lengths (Å) and angles (°) for tetrakis(1,2-dimethylimidazole)copper(II) diperchlorate

Cu—N(1)	2·009 (4)	N(6)—C(7)	1·353 (5)
Cu—N(3)	2·010 (4)	N(8)—C(10)	1·368 (13)
Cu—N(5)	1·988 (4)	N(2)—C(2)	1·376 (6)
Cu—N(7)	1·989 (10)	N(4)—C(5)	1·376 (6)
Cu—N(7')	2·063 (15)	N(6)—C(8)	1·368 (6)
Cu—O(1)	2·843 (11)	N(8)—C(11)	1·400 (15)
Cu—O(1')	2·66 (2)	C(2)—C(3)	1·328 (6)
Cu—O(5)	2·803 (5)	C(5)—C(6)	1·310 (7)
N(1)—C(1)	1·323 (5)	C(8)—C(9)	1·335 (7)
N(3)—C(4)	1·314 (6)	C(11)—C(12)	1·29 (2)
N(5)—C(7)	1·323 (6)	N(2)—C(14)	1·450 (6)
N(7)—C(10)	1·354 (15)	N(4)—C(16)	1·447 (7)
N(1)—C(3)	1·363 (6)	N(6)—C(18)	1·451 (6)
N(3)—C(6)	1·406 (6)	N(8)—C(20)	1·446 (14)
N(5)—C(9)	1·379 (6)	C(1)—C(13)	1·488 (7)
N(7)—C(12)	1·39 (2)	C(4)—C(15)	1·479 (7)
N(2)—C(1)	1·343 (6)	C(7)—C(17)	1·476 (7)
N(4)—C(4)	1·338 (6)	C(10)—C(19)	1·520 (15)
N(1)—Cu—N(3)	89·3 (2)	C(7)—N(5)—C(9)	105·8 (4)
N(1)—Cu—N(5)	91·3 (2)	C(10)—N(7)—C(12)	105 (1)
N(1)—Cu—N(7)	177·7 (3)	N(1)—C(1)—N(2)	110·0 (4)
N(1)—Cu—O(1)	84·0 (2)	N(3)—C(4)—N(4)	110·6 (4)
N(1)—Cu—O(5)	96·2 (2)	N(5)—C(7)—N(6)	110·3 (4)
N(3)—Cu—N(5)	178·4 (2)	N(7)—C(10)—N(8)	112 (1)
N(3)—Cu—N(7)	89·5 (3)	C(1)—N(2)—C(2)	107·1 (4)
N(3)—Cu—O(1)	85·7 (3)	C(4)—N(4)—C(5)	107·2 (4)
N(3)—Cu—O(5)	88·4 (2)	C(7)—N(6)—C(8)	107·4 (4)
N(5)—Cu—N(7)	90·0 (3)	C(10)—N(8)—C(11)	103·0 (9)
N(5)—Cu—O(1)	95·9 (3)	N(2)—C(2)—C(3)	106·7 (4)
N(5)—Cu—O(5)	90·0 (2)	N(4)—C(5)—C(6)	107·6 (5)
N(7)—Cu—O(1)	94·0 (4)	N(6)—C(8)—C(9)	106·7 (4)
N(7)—Cu—O(5)	85·7 (3)	N(8)—C(11)—C(12)	111 (1)
O(1)—Cu—O(5)	174·1 (3)	N(1)—C(3)—C(2)	109·7 (4)
Cu—O(1)—Cl(1)	151·5 (7)	N(3)—C(6)—C(5)	108·8 (4)
Cu—O(1')—Cl(1)	167 (1)	N(5)—C(9)—C(8)	109·9 (4)
Cu—O(5)—Cl(2)	159·0 (3)	N(7)—C(12)—C(11)	109 (1)
C(1)—N(1)—C(3)	106·5 (4)		
C(4)—N(3)—C(6)	105·7 (4)		

The coordination geometry in (2) is more difficult to describe. Each Cu^{II} ion is coordinated in a distorted square-planar fashion by four 1,2-dmi ligands. The Cu^{II} ions are also nearest neighbours to the perchlorate group O, atoms O(1) and O(5), suggesting the possibility of axial coordination. If axial coordination is present, geometric considerations suggest that it must be very weak. The $Cu–O(ClO_4)$ distances in (2) are substantially longer than those reported for tetragonally coordinated Cu^{II} complexes containing 'semi-coordinated' perchlorate ligands [range 2·495 (6)–2·667 (5) Å; Sekizaki (1981); Fawcett, Rudich, Toby, Lalancette, Potenza & Schugar (1980)]. Moreover, the effectiveness of perchlorate as a ligand should be dependent on the $Cu–O(ClO_4)–Cl$ angle. If one assumes sp^3 hybridization at O, maximum bonding would be expected for angles near 109°. In (2), the $Cu–O–Cl$ angles are far removed from this value while with tetragonal copper complexes known to involve axial coordination by perchlorate, the tetrahedral angle is approached much more closely. For example, in $Cu\{N,N'-bis(2-aminoethyl)-1,3-propanediamine\}$-$(ClO_4)_2$, the $Cu–O(ClO_4)–Cl$ angles were 118·9 (3) and 121·1 (3)° (Fawcett et al., 1980). The apparent weakness of axial coordination in (2) may result in part from the presence of the bulky methyl groups on the 1,2-dmi ligands. In tetrakis(1,4,5-trimethylimidazole)-copper(II) diperchlorate [(3), Bernarducci et al. (1983)], a complex closely related to (2) chemically but with sterically more demanding trimethylated imidazole ligands, all $Cu–O(ClO_4)$ distances were found to be greater than 4 Å and axial coordination was absent.

Excluding the disordered atom N(7'), the Cu–N distances in (2) are equivalent to each other and to the Cu–N lengths reported [2·004 (7), 1·995 (7) Å] for (3). These distances are typical of those observed for Cu–N(azole) ligands. The imidazole groups are planar

to within ±0·01 Å. Their planes (I–IV, Fig. 2) make dihedral angles of 50·0 (2), 50·1 (2), 52·0 (3) and 52·0 (3)°, respectively, with the planar (±0·03 Å) CuN_4 unit; dihedral angles ranging from 18·7 to 85·7° have been observed for tetragonal $Cu^{II}im_4X_2$ complexes, where im = imidazole or substituted imidazole and X is an axial ligand bonded to Cu by means of an O atom (Bernarducci et al., 1983).

References

BERNARDUCCI, E., BHARADWAJ, P. K., KROGH-JESPERSEN, K., POTENZA, J. A. & SCHUGAR, H. J. (1983). J. Am. Chem. Soc. 105, 3860–3866.
BERNARDUCCI, E., BHARADWAJ, P. K., POTENZA, J. A. & SCHUGAR, H. J. (1987). Acta Cryst. C43, 1511–1514.
Enraf–Nonius (1983). Structure Determination Package. Enraf–Nonius, Delft, The Netherlands.
FAWCETT, T. G., RUDICH, S. M., TOBY, B. H., LALANCETTE, R. A., POTENZA, J. A. & SCHUGAR, H. J. (1980). Inorg. Chem. 19, 940–945.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
JAMESON, D., POTENZA, M. N., POTENZA, J. A. & SCHUGAR, H. J. (1985). Acta Cryst. C41, 1736–1738.
MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1982). MULTAN82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data. Univs. of York, England, and Louvain, Belgium.
REEDIJK, J. (1972). Recl Trav. Chim. Pays-Bas, 91, 1373–1382.
SCHUGAR, H. J. (1983). Copper Coordination Chemistry: Biochemical and Inorganic Perspectives, edited by K. D. KARLIN & J. ZUBIETA, pp. 43–74. New York: Adenine Press.
SEKIZAKI, M. (1981). Bull. Chem. Soc. Jpn, 54, 146–149.

Structure of Sodium (−)-Shikimate Dihydrate

BY CHRISTOPHER ABELL, FRANK H. ALLEN,* TIMOTHY D. H. BUGG, MICHAEL J. DOYLE AND PAUL R. RAITHBY

University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England

Abstract. Sodium (−)-3α,4α,5β-trihydroxy-1-cyclohexene-1-carboxylate dihydrate, $Na^+.C_7H_9O_5^-.2H_2O$, $M_r = 232·2$, monoclinic, $C2$, $a = 15·806$ (2), $b = 7·139$ (1), $c = 17·395$ (3) Å, $β = 100·05$ (2)°, $V = 1932·7$ (4) Å³, $Z = 8$, $D_x = 1·595$ Mg m⁻³, Cu $K\alpha$, $\lambda = 1·54178$ Å, $\mu = 1·575$ mm⁻¹, $F(000) = 976$, $T = 293$ K, $R = 0·066$ for 2252 observed reflections [$I > 3\sigma(I)$] and 318 parameters. A clear indication of absolute configuration [$\eta = 1·25$ (23)] is in accord with the chemical assignment. The cyclohexene ring adopts a

* Author for correspondence.