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Two 2,5-Dihydroxy-1,4-benzoquinonate-*O*,*O*′-Containing Mononuclear Complexes: $[Cu(C_6H_2O_4)(C_8H_6N_4)(H_2O)].5H_2O$ and $[Ni(C_6H_2O_4)(C_{12}H_{12}N_2)_2].H_2O$ ($C_8H_6N_4$ = 2,2′-Bipyrimidine, $C_{12}H_{12}N_2$ = 4,4′-Dimethyl-2,2′-bipyridine)

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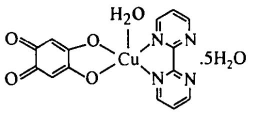
Abstract

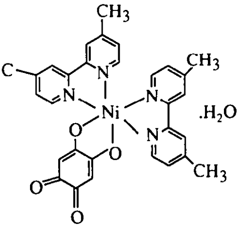
The crystal structures of aqua(2,2′-bipyrimidine-*N*,*N*′)(4,5-dihydroxy-1,2-benzoquinonato-*O*,*O*′)copper(II) pentahydrate, $[Cu(C_6H_2O_4)(C_8H_6N_4)(H_2O)].5H_2O$, containing five-coordinate copper(II) with slightly distorted square-pyramidal geometry, and bis(4,4′-dimethyl-2,2′-bipyridine-*N*,*N*′)(4,5-dihydroxy-1,2-benzoquinonato-*O*,*O*′)nickel(II) monohydrate, $[Ni(C_6H_2O_4)(C_{12}H_{12}N_2)_2].H_2O$, comprising six-coordinate nickel(II) with distorted octahedral geometry, are reported. In both complexes, the dianion of 2,5-dihydroxy-1,4-benzoquinone occurs in the bidentate *o*-benzoquinone form which chelates through the 1,2 O atoms.

Comment

Only a limited number of crystal structures have been reported of coordination compounds containing the dianion of 2,5-dihydroxy-1,4-benzoquinone ($DHBQH_2$). These include $Na_2(H_2O)_{24}[M_2(DHBQ)_3]$, M = Mn^{II}, Cd^{II} (Weiss, Riegler & Robl, 1986), and $[(C_4H_9)_4N]_2[Mo_4O_{10}(DHBQ)_2]$ (Liu, Shaikh & Zubieta, 1989). The dianion of dihydroxybenzoquinone, consisting of two allyl systems interlinked by two long C—C distances corresponding to C_{sp^2}—C_{sp^2} single bonds, acts as a chelating ligand and potentially as a bridging unit. In both respects, it exhibits a striking similarity with the dianion of oxalic acid. Because of our interest in the magnetic properties of polymeric three-dimensionally linked complexes with chelating oxalate ions as bridging ligands (Decurtins, Schmalle, Schneuwly, Ensling & Gütlich, 1994), further studies have been extended to the synthesis of transition metal compounds containing $DHBQ^{2-}$ and its derivatives. Along this line, a chain compound $[Cu(CA)(DCMB)]_n$ (where DCMB = 3,3′-dimethoxycarbonyl-2,2′-bipyridyl, CA = dianion of 3,6-dichloro-2,5-dihydroxy-1,4-benzoquinone) exhibiting weak antiferromagnetic properties has been reported recently (Decurtins, Schmalle, Zheng & Ensling, 1995). During our attempts to synthesize a polymeric copper(II) compound with alternating N and O coordinations from 2,2′-bipyrimidine and $DHBQ^{2-}$, respectively, a neutral mononuclear compound, aqua(2,2′-bipyrimidine-*N*,*N*′)(4,5-dihydroxy-1,2-benzoquinonato-*O*,*O*′)copper(II) pentahydrate, (I), was obtained. The second title compound, bis(4,4′-dimethyl-2,2′-bipyridine-*N*,*N*′)(4,5-dihydroxy-1,2-benzoquinonato-*O*,*O*′)nickel(II) monohydrate, (II), is a product of ligand-exchange reactions, following a synthetic route to construct three-dimensional bridged polymers with $DHBQ^{2-}$, similar to the oxalate networks.



(I)



(II)

The crystal structure of (I) consists of neutral mononuclear $[Cu(DHBQ)(bipym)(H_2O)]$ (bipym = 2,2′-bipyrimidine) units (Fig. 1) and five water molecules of crystallization (Fig. 2). The Cu atom of the five-coordinate CuN_2O_3 chromophore shows slightly distorted square-pyramidal coordination geometry. It is bound to two N atoms from the bipym ligand [at 1.983 (3) and 2.004 (3) Å] and two O atoms from $DHBQ^{2-}$ [1.928 (3) and 1.947 (3) Å] in the basal plane. The apical site is occupied by O1*W* [2.317 (4) Å]. The

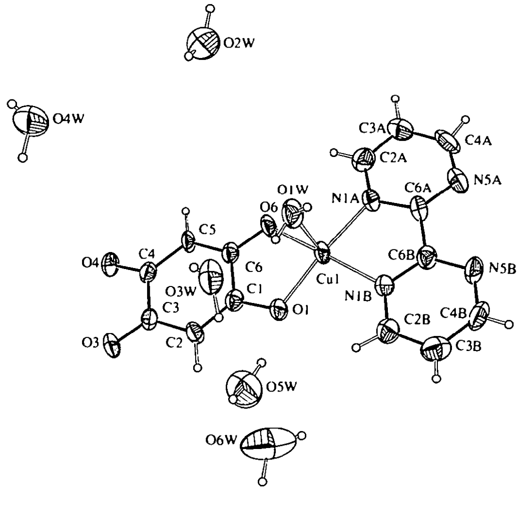


Fig. 1. *ORTEP* (Johnson, 1971) view of (I) with the atom-numbering scheme. The anisotropic displacement ellipsoids are drawn at the 50% probability level. H-atoms are shown as small spheres of arbitrary size.

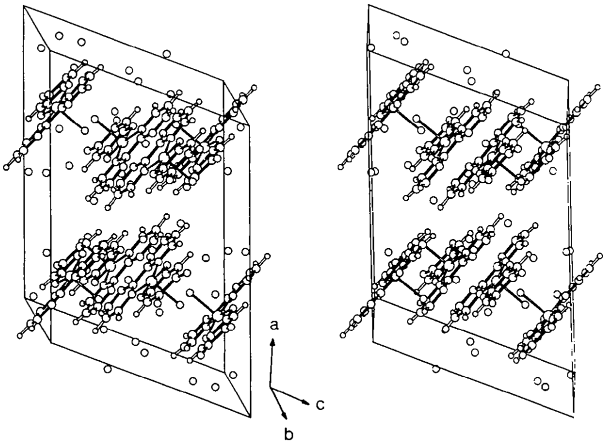


Fig. 2. A *SCHAKAL* (Keller, 1986) stereoview of a packing diagram of compound (I).

deviations from a least-squares plane through N1*A*, N1*B*, O1 and O6 are ±0.004 (2) Å for all four atoms, and the Cu atom lies 0.150 (2) Å out of this plane toward the axial O1*W* atom. The Cu—N bond lengths and N—Cu—N angle [82.1 (1)°] are in agreement with those of $[Cu(C_5O_5)(bipym)(H_2O)_2].H_2O$ [1.978 (1), 2.000 (1) Å and 81.36 (5)°] (Castro, Sletten, Glaerum, Lloret, Faus & Julve, 1994) and $[Cu(C_2O_4)(bipym)(H_2O)].5H_2O$ [1.976 (6), 2.002 (6) Å, 81.5 (3)°] (De Munno *et al.*, 1993). The reduced bond angles N1*A*—C6*A*—C6*B* and N1*B*—C6*B*—C6*A* [average 115.1 (4)°], compared with N5*A*—C6*A*—C6*B* and N5*B*—C6*B*—C6*A* [average 119.6 (4)°], reveal the degree of distortion of the bipym ligand due to the coordination. The dihedral angle between the planar pyrimidine rings is 2.47°. $DHBQ^{2-}$ acts as a bidentate terminal ligand. The Cu—O bond lengths (Table 2) are shorter than the Cu—O distances [2.041 (2), 2.054 (2) Å] in mononuclear $Cu(CA)(terpy).H_2O$ (CA = dianion of 3,6-dichloro-2,5-dihydroxy-1,4-benzoquinone, terpy = 2,2′:6′,2″-terpyridine) (Folgado, Ibañez, Coronado, Beltran, Savirault & Galy, 1988) and the Mn—O distances [2.168 (3) Å] in $[Na_2(H_2O)_{24}\{Mn_2(DHBQ)_3\}]$ (Weiss, Riegler & Robl, 1986) where $DHBQ^{2-}$ bridges two metal ions.

The crystal structure of compound (II) is made up of a neutral $[Ni(DHBQ)(Me_2bpy)_2]$ (Me_2bpy = 4,4′-dimethyl-2,2′-bipyridine) molecule and one water molecule of crystallization in the asymmetric unit. The Ni atom has a distorted octahedral coordination environment, made up by four N atoms from the Me_2bpy ligands and two O atoms from $DHBQ^{2-}$ (Fig. 3). The average Ni—N bond length of 2.057 (8) Å is comparable to those reported for $Ni(EXAN)_2(Me_2bpy)$ [2.073 (9), 2.068 (8) Å] (where exan = ethyl xanthate) (Pang, Lucken & Bernardinelli, 1990). The distances from Ni to the two N atoms N1*B* and N1*D* located *trans* to the O atoms are longer than the distances to N1*A* and N1*C*, which results in slight asymmetric coordination. The two pyridine rings in Me_2bpy are coplanar. The Ni—O bond lengths in compound (II) (Table 5) are longer than the corresponding Cu—O distances in compound (I), while the O1—Ni—O6 angle [80.1 (3)°] is significantly smaller than that of the Cu complex [85.1 (1)°]. A stereoview showing the 6_1 screw axis of the structure is given in Fig. 4.

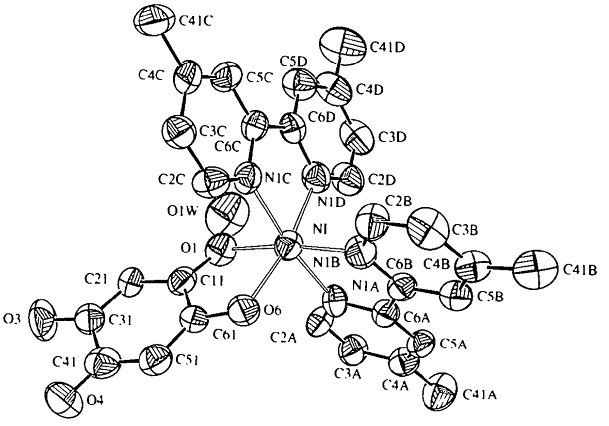


Fig. 3. *ORTEP* (Johnson, 1971) view of (II) with the atom-numbering scheme. The anisotropic displacement ellipsoids are drawn at the 50% probability level.

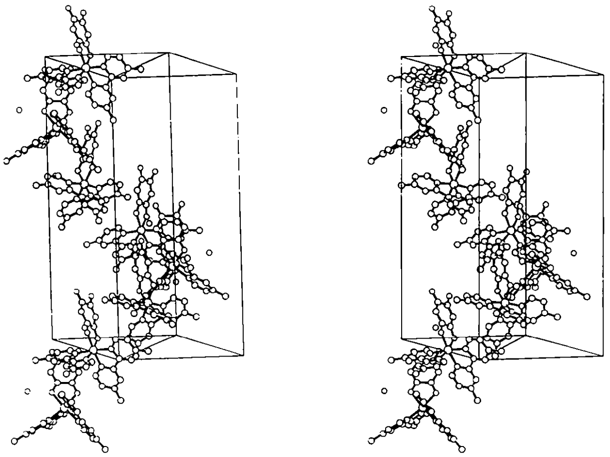


Fig. 4. A *SCHAKAL* (Keller, 1986) stereoview showing the 6_1 screw axis of compound (II).

In both complexes, the $DHBQ^{2-}$ ring is planar, with the largest deviation of 0.025 (3) Å at C3 in compound (I) and 0.052 (6) Å at C61 in compound (II). The pattern of bond lengths is consistent with the localization of single-bond character in the C1—C6 and C3—C4 bonds [1.508 (6) and 1.530 (6) Å, respectively] in (I) or in the C11—C61 and C31—C41 bonds [1.531 (13) and 1.55 (2) Å, respectively] in (II). Furthermore, the remaining C—C bonds are significantly shorter (compare Tables 2 and 5), indicating some degree of conjugation. The C3—O3 and C4—O4 distances [average 1.245 (5) Å] in (I), or C31—O3 and C41—O4 lengths [average 1.245 (14) Å] in (II), are in agreement with double-bond localization in the carbonyl group [mean value 1.222 (13) Å (Kulpe & Dähne, 1978; Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1992)]. DHBQ^{2-} shows an obviously bidentate *o*-quinone form.

Hydrogen-bonding contacts are observed in both structures. In (I), the C—H distances show reasonable values between 0.81 and 1.07 Å, whereas the O—H distances of the water molecules are in a wide range between 0.48 and 1.15 Å (see Table 3), reflecting the relatively large number of unobserved data: about 49% of the reflections have intensities $\leq 2\sigma(I)$. In (II), 56% of the data belong to weak reflections with $I \leq 2\sigma(I)$. For this reason, all the H atoms of the ligands were refined as riding. The residual electron densities near the water O atoms, interpreted as H atoms, were not stable in the refinement. Thus, only one acceptable position of a residual electron-density peak was finally used in Table 6 and Fig. 3 to demonstrate the O1*W*—H11*W*···O1 hydrogen bond. A second water H-atom position could not be identified among other residual electron density peaks near O1*W*. However, the O1*W*···O3$^{\text{i}}$ distance of 3.00 (2) Å may indicate its possible site of occupation.

Experimental

Crystals of compound (I) were prepared by placing a mixture containing 8 mmol of $CuCl_2$ and 8 mmol of 2,2′-bipyrimidine on the top of an Agar gel containing 4 mmol of $DHBQH_2$. Dark red single crystals were grown in several days. Analysis: found C 36.10, H 4.40, N 11.80, Cu 13.85%; $C_{14}H_{20}N_4O_{10}Cu$ requires C 35.94, H 4.31, N 11.97, Cu 13.58%. The density D_m was measured by flotation in toluene/methylene iodide.

Compound (II) was obtained by placing a mixture of 10 mmol of $[Ni(Me_2bpy)_3]Cl_2$ and 10 mmol of $MnCl_2$ on the top of a sodium metasilica gel containing 4 mmol of $DHBQH_2$. Dark red single crystals were produced after several days. Analysis: found C 59.55, H 4.85, N 9.40%; $C_{30}H_{28}N_4O_5Ni$ requires C 61.77, H 4.84, N 9.61%. The density D_m was measured by flotation in toluene/methylene iodide.

Compound (I)

Crystal data

$[Cu(C_6H_2O_4)(C_8H_6N_4)(H_2O)].5H_2O$
$M_r = 467.88$
Monoclinic
$C2/c$
$a = 18.326(4)$ Å
$b = 16.953(3)$ Å
$c = 13.516(3)$ Å
$\beta = 111.25(3)°$
$V = 3913.6(14)$ Å^3
$Z = 8$
$D_x = 1.588$ Mg m^{-3}
$D_m = 1.58$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 4.7–12.4°$
$\mu = 1.177$ mm^{-1}
$T = 295(2)$ K
Plate
0.30 × 0.28 × 0.08 mm
Dark red

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: analytical
$T_{\min} = 0.639$, $T_{\max} = 0.900$
8464 measured reflections (including 90 standards)
3850 independent reflections

1975 observed reflections $[I > 2\sigma(I)]$
$R_{\text{int}} = 0.0873$
$\theta_{\max} = 25.98°$
$h = 0 \rightarrow 22$
$k = 0 \rightarrow 20$
$l = -16 \rightarrow 15$
3 standard reflections
frequency: 180 min
intensity decay: 0.9%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0481$
$wR(F^2) = 0.1055$
$S = 1.091$
3850 reflections
343 parameters
H-atom positions and U_{iso}'s refined
$w = 1/[\sigma^2(F_o^2) + (0.0550P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.621$

$\Delta\rho_{\max} = 0.575$ e Å^{-3}
$\Delta\rho_{\min} = -1.104$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.00020 (6)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (I)*

$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
Cu1	0.26327 (3)	0.35890 (3)	0.38280 (4)	0.03171 (14)
O1	0.1783 (2)	0.2875 (2)	0.3129 (2)	0.0354 (8)
O3	0.1468 (2)	0.0147 (2)	0.2503 (3)	0.0432 (9)
O4	0.2872 (2)	−0.0101 (2)	0.4019 (3)	0.0422 (9)
O6	0.3210 (2)	0.2644 (2)	0.4482 (2)	0.0335 (8)
C1	0.2008 (2)	0.2141 (3)	0.3274 (3)	0.0300 (10)
C2	0.1541 (2)	0.1519 (2)	0.2756 (3)	0.0319 (11)
C3	0.1842 (2)	0.0730 (2)	0.2975 (3)	0.0309 (11)
C4	0.2654 (3)	0.0600 (2)	0.3825 (4)	0.0288 (10)
C5	0.3112 (2)	0.1258 (2)	0.4336 (3)	0.0305 (11)
C6	0.2824 (2)	0.2016 (3)	0.4072 (3)	0.0280 (10)
N1*A*	0.3421 (2)	0.4357 (2)	0.4699 (3)	0.0295 (9)
C2*A*	0.4147 (3)	0.4222 (3)	0.5397 (4)	0.0430 (13)
C3*A*	0.4621 (3)	0.4821 (3)	0.5962 (4)	0.0481 (14)
C4*A*	0.4298 (3)	0.5584 (3)	0.5737 (4)	0.052 (2)
N5*A*	0.3593 (2)	0.5736 (2)	0.5048 (3)	0.0448 (11)
C6*A*	0.3182 (3)	0.5119 (2)	0.4555 (3)	0.0315 (11)
N1*B*	0.1989 (2)	0.4570 (2)	0.3354 (3)	0.0306 (9)
C2*B*	0.1263 (3)	0.4629 (3)	0.2652 (4)	0.0395 (13)
C3*B*	0.0921 (3)	0.5351 (3)	0.2381 (4)	0.0493 (15)
C4*B*	0.1365 (3)	0.6006 (3)	0.2862 (4)	0.0466 (14)
N5*B*	0.2089 (2)	0.5956 (2)	0.3560 (3)	0.0421 (11)
C6*B*	0.2374 (3)	0.5231 (3)	0.3792 (3)	0.0336 (11)
O1*W*	0.3070 (2)	0.3541 (2)	0.2421 (3)	0.0429 (9)
O2*W*	0.5442 (3)	0.2797 (3)	0.1883 (4)	0.0703 (14)
O3*W*	0.2138 (3)	0.2523 (2)	0.0774 (3)	0.0592 (13)
O4*W*	0.4430 (2)	0.0495 (3)	0.0164 (4)	0.0716 (14)
O5*W*	0.0512 (3)	0.2885 (3)	0.0071 (4)	0.085 (2)
O6*W*	0.9742 (3)	0.2734 (5)	0.1410 (5)	0.131 (3)

Table 2. *Selected geometric parameters (Å, °) for (I)*

Cu1—O1	1.928 (3)	C5—C6	1.386 (6)
Cu1—O6	1.947 (3)	N1*A*—C2*A*	1.343 (6)
Cu1—N1*A*	1.983 (3)	N1*A*—C6*A*	1.356 (5)
Cu1—N1*B*	2.004 (3)	C2*A*—C3*A*	1.373 (7)
Cu1—O1*W*	2.317 (4)	C3*A*—C4*A*	1.410 (7)
O1—C1	1.304 (5)	C4*A*—N5*A*	1.316 (6)
O3—C3	1.239 (5)	N5*A*—C6*A*	1.320 (5)
O4—C4	1.251 (5)	C6*A*—C6*B*	1.477 (6)
O6—C6	1.287 (5)	N1*B*—C2*B*	1.329 (5)
C1—C2	1.379 (6)	N1*B*—C6*B*	1.343 (6)
C1—C6	1.508 (6)	C2*B*—C3*B*	1.364 (7)
C2—C3	1.436 (6)	C3*B*—C4*B*	1.391 (7)
C3—C4	1.530 (6)	C4*B*—N5*B*	1.323 (6)
C4—C5	1.415 (5)	N5*B*—C6*B*	1.327 (6)
O1—Cu1—O6	85.14 (12)	O6—C6—C5	123.9 (4)
O1—Cu1—N1*A*	171.10 (15)	O6—C6—C1	116.0 (3)
O6—Cu1—N1*A*	96.44 (13)	C5—C6—C1	120.1 (4)
O1—Cu1—N1*B*	94.98 (13)	C2*A*—N1*A*—C6*A*	116.7 (4)
O6—Cu1—N1*B*	171.00 (14)	C2*A*—N1*A*—Cu1	128.9 (3)
N1*A*—Cu1—N1*B*	82.09 (14)	C6*A*—N1*A*—Cu1	114.4 (3)
O1—Cu1—O1*W*	91.97 (13)	N1*A*—C2*A*—C3*A*	122.0 (5)
O6—Cu1—O1*W*	92.94 (13)	C2*A*—C3*A*—C4*A*	115.3 (4)
N1*A*—Cu1—O1*W*	96.69 (14)	N5*A*—C4*A*—C3*A*	124.1 (5)
N1*B*—Cu1—O1*W*	96.05 (14)	C4*A*—N5*A*—C6*A*	115.8 (4)
C1—O1—Cu1	111.7 (2)	N5*A*—C6*A*—N1*A*	126.0 (4)
C6—O6—Cu1	111.2 (2)	N5*A*—C6*A*—C6*B*	119.6 (4)
O1—C1—C2	123.3 (4)	N1*A*—C6*A*—C6*B*	114.4 (4)
O1—C1—C6	114.9 (4)	C2*B*—N1*B*—C6*B*	118.8 (4)
C2—C1—C6	121.8 (4)	C2*B*—N1*B*—Cu1	127.7 (3)
C1—C2—C3	119.1 (4)	C6*B*—N1*B*—Cu1	113.4 (3)
O3—C3—C2	122.4 (4)	N1*B*—C2*B*—C3*B*	120.2 (5)
O3—C3—C4	118.6 (4)	C2*B*—C3*B*—C4*B*	117.2 (4)
C2—C3—C4	119.0 (4)	N5*B*—C4*B*—C3*B*	123.2 (5)
O4—C4—C5	123.9 (4)	C4*B*—N5*B*—C6*B*	115.8 (4)
O4—C4—C3	116.3 (4)	N5*B*—C6*B*—N1*B*	124.7 (4)
C5—C4—C3	119.8 (3)	N5*B*—C6*B*—C6*A*	119.5 (4)
C6—C5—C4	120.0 (4)	N1*B*—C6*B*—C6*A*	115.7 (4)

Table 3. *Hydrogen-bonding geometry (Å, °) for (I)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3*A*—H3*A*···O3^{i}	1.06 (4)	2.23 (4)	3.26 (9)	165 (4)
C4*A*—H4*A*···O2*W*^{ii}	0.81 (5)	2.68 (5)	3.461 (7)	163 (5)
C3*B*—H3*B*···O4*W*^{iii}	0.87 (4)	2.40 (4)	3.252 (6)	168 (5)
C4*B*—H4*B*···O2*W*^{iii}	0.86 (5)	2.64 (5)	3.494 (7)	171 (5)
O1*W*—H11*W*···O3*W*	0.91 (4)	1.99 (4)	2.845 (5)	156 (4)
O1*W*—H12*W*···O3^{iv}	0.60 (6)	2.36 (6)	2.843 (5)	140 (6)
O1*W*—H12*W*···O4^{iv}	0.60 (6)	2.64 (5)	3.104 (4)	136 (6)
O2*W*—H21*W*···O5*W*^{v}	0.73 (6)	2.11 (6)	2.832 (7)	168 (7)
O2*W*—H22*W*···O1*W*^{vi}	0.92 (6)	1.98 (7)	2.838 (6)	155 (6)
O3*W*—H31*W*···O5*W*	1.08 (7)	1.82 (8)	2.848 (7)	156 (7)
O3*W*—H32*W*···O3*W*^{v}	0.48 (9)	2.57 (9)	2.855 (11)	122 (12)
O3*W*—H32*W*···N5*B*^{vii}	0.48 (9)	2.61 (8)	2.992 (6)	139 (12)
O4*W*—H41*W*···O4*W*^{viii}	0.63 (15)	2.29 (14)	2.838 (10)	147 (14)
O4*W*—H42*W*···O4^{ix}	0.93 (6)	1.87 (6)	2.791 (5)	175 (6)
O5*W*—H51*W*···O2*W*^{v}	0.63 (6)	2.26 (6)	2.832 (7)	152 (9)
O5*W*—H52*W*···O3*W*	1.05 (14)	2.47 (19)	2.848 (7)	100 (12)
O6*W*—H61*W*···O6*W*^{x}	0.90 (4)	2.41 (4)	2.749 (10)	102 (3)
O6*W*—H62*W*···O6^{xi}	1.15 (9)	2.01 (9)	3.128 (6)	163 (9)

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

Compound (II)

Crystal data

[$Ni(C_6H_2O_4)(C_{12}H_{12}N_2)_2$].-
H_2O
$M_r = 583.27$
Hexagonal
$P6_1$
$a = 12.942$ (3) Å
$c = 29.326$ (6) Å
$V = 4253.9$ (13) Å^3
$Z = 6$
$D_x = 1.366$ Mg m^{-3}
$D_m = 1.36$ Mg m^{-3}

Mo *Kα* radiation
$\lambda = 0.71073$ Å
Cell parameters from 25
reflections
$\theta = 4.1–16.9°$
$\mu = 0.730$ mm^{-1}
$T = 295$ (2) K
Hexagonal bipyramid
0.65 × 0.60 × 0.55 mm
Dark red

Data collection

Enraf–Nonius CAD-4
diffractometer
ω–2θ scans
Absorption correction:
analytical
$T_{\min} = 0.699$, $T_{\max} =$
0.858
9041 measured reflections
(including 168 standards)
2837 independent reflections

1596 observed reflections
[$I > 2\sigma(I)$]
$R_{\rm int} = 0.1022$
$\theta_{\max} = 25.95°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 36$
3 standard reflections
frequency: 180 min
intensity decay: 1.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0521$
$wR(F^2) = 0.1259$
$S = 1.215$
2835 reflections
370 parameters
H atoms refined with a
riding model
$w = 1/[\sigma^2(F_o^2) + (0.0853P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.110$
$\Delta\rho_{\max} = 1.023$ e Å^{-3}
$\Delta\rho_{\min} = -0.516$ e Å^{-3}

Extinction correction:
*SHELXL*93 (Sheldrick,
1993)
Extinction coefficient:
0.0016 (7)
Atomic scattering factors
from *International Tables
for Crystallography* (1992,
Vol. C, Tables 4.2.6.8 and
6.1.1.4)
Absolute configuration:
Flack (1983) parameter
= −0.04 (4)

Table 4. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (II)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	$U_{\rm eq}$
Ni	0.04528 (10)	0.47264 (10)	0.99999 (4)	0.0495 (3)
O1	0.0507 (6)	0.5720 (5)	0.9444 (3)	0.057 (2)
O6	0.0206 (6)	0.3551 (6)	0.9489 (3)	0.057 (2)
O3	−0.0603 (7)	0.5087 (8)	0.7904 (3)	0.082 (2)
O4	−0.0503 (8)	0.3054 (8)	0.7925 (3)	0.084 (3)
C11	0.0212 (8)	0.5125 (9)	0.9072 (4)	0.052 (2)
C21	−0.0040 (8)	0.5508 (9)	0.8667 (4)	0.053 (2)
C31	−0.0328 (8)	0.4806 (9)	0.8271 (4)	0.057 (3)
C41	−0.0295 (8)	0.3626 (9)	0.8287 (5)	0.062 (3)
C51	−0.0086 (8)	0.3254 (9)	0.8700 (4)	0.056 (3)
C61	0.0095 (7)	0.3888 (8)	0.9087 (3)	0.045 (2)
N1*A*	0.2236 (6)	0.5329 (6)	1.0029 (3)	0.049 (2)
C2*A*	0.3057 (7)	0.6189 (8)	0.9768 (4)	0.051 (2)
C3*A*	0.4262 (9)	0.6670 (9)	0.9840 (4)	0.061 (3)
C4*A*	0.4650 (8)	0.6200 (8)	1.0182 (4)	0.053 (3)
C5*A*	0.3787 (8)	0.5261 (9)	1.0438 (4)	0.052 (2)
C6*A*	0.2606 (8)	0.4855 (8)	1.0350 (3)	0.047 (2)
C41*A*	0.5977 (9)	0.6721 (12)	1.0277 (5)	0.081 (4)
N1*B*	0.0514 (7)	0.3657 (7)	1.0511 (3)	0.055 (2)
C2*B*	−0.0428 (8)	0.2799 (9)	1.0748 (4)	0.059 (3)
C3*B*	−0.0274 (10)	0.2158 (9)	1.1092 (5)	0.070 (3)
C4*B*	0.0850 (8)	0.2378 (8)	1.1218 (4)	0.052 (3)
C5*B*	0.1790 (8)	0.3241 (8)	1.0969 (4)	0.052 (2)
C6*B*	0.1609 (8)	0.3871 (7)	1.0626 (3)	0.045 (2)
C41*B*	0.0986 (9)	0.1755 (9)	1.1605 (5)	0.069 (3)
N1*C*	−0.1326 (6)	0.4197 (6)	1.0057 (3)	0.047 (2)
C2*C*	−0.2221 (8)	0.3226 (8)	0.9863 (4)	0.055 (3)
C3*C*	−0.3400 (9)	0.2960 (8)	0.9893 (4)	0.055 (3)

C4*C*	−0.3681 (8)	0.3686 (9)	1.0137 (4)	0.056 (3)
C5*C*	−0.2749 (9)	0.4675 (9)	1.0337 (4)	0.054 (3)
C6*C*	−0.1578 (7)	0.4942 (7)	1.0295 (3)	0.043 (2)
C41*C*	−0.4932 (10)	0.3430 (13)	1.0182 (5)	0.094 (5)
N1*D*	0.0537 (7)	0.6036 (7)	1.0430 (3)	0.054 (2)
C2*D*	0.1508 (9)	0.6968 (10)	1.0607 (4)	0.065 (3)
C3*D*	0.1493 (9)	0.7859 (10)	1.0840 (4)	0.071 (3)
C4*D*	0.0448 (11)	0.7882 (9)	1.0900 (4)	0.070 (3)
C5*D*	−0.0588 (10)	0.6895 (9)	1.0711 (4)	0.064 (3)
C6*D*	−0.0513 (8)	0.5998 (7)	1.0492 (4)	0.045 (2)
C41*D*	0.0424 (13)	0.8848 (12)	1.1147 (7)	0.105 (5)
O1*W*	0.1654 (10)	0.8248 (8)	0.9474 (5)	0.121 (4)

Table 5. *Selected geometric parameters (Å, °) for (II)*

Ni—N1*A*	2.035 (7)	C6*A*—C6*B*	1.516 (13)
Ni—O6	2.044 (7)	N1*B*—C6*B*	1.344 (12)
Ni—O1	2.055 (7)	N1*B*—C2*B*	1.361 (13)
Ni—N1*C*	2.054 (7)	C2*B*—C3*B*	1.38 (2)
Ni—N1*B*	2.067 (9)	C3*B*—C4*B*	1.39 (2)
Ni—N1*D*	2.072 (8)	C4*B*—C5*B*	1.380 (13)
O1—C11	1.280 (13)	C4*B*—C41*B*	1.45 (2)
O6—C61	1.289 (12)	C5*B*—C6*B*	1.386 (14)
O3—C31	1.245 (14)	N1*C*—C2*C*	1.337 (12)
O4—C41	1.245 (14)	N1*C*—C6*C*	1.356 (12)
C11—C21	1.389 (15)	C2*C*—C3*C*	1.389 (13)
C11—C61	1.531 (13)	C3*C*—C4*C*	1.366 (14)
C21—C31	1.403 (15)	C4*C*—C5*C*	1.375 (14)
C31—C41	1.55 (2)	C4*C*—C41*C*	1.488 (14)
C41—C51	1.38 (2)	C5*C*—C6*C*	1.382 (12)
C51—C61	1.350 (14)	C6*C*—C6*D*	1.488 (12)
N1*A*—C6*A*	1.336 (12)	N1*D*—C2*D*	1.336 (13)
N1*A*—C2*A*	1.331 (12)	N1*D*—C6*D*	1.347 (12)
C2*A*—C3*A*	1.376 (13)	C2*D*—C3*D*	1.35 (2)
C3*A*—C4*A*	1.391 (15)	C3*D*—C4*D*	1.38 (2)
C4*A*—C5*A*	1.389 (14)	C4*D*—C5*D*	1.422 (15)
C4*A*—C41*A*	1.523 (14)	C4*D*—C41*D*	1.46 (2)
C5*A*—C6*A*	1.370 (12)	C5*D*—C6*D*	1.372 (14)

N1*A*—Ni—O6	92.4 (3)	N1*A*—C6*A*—C5*A*	122.9 (8)
N1*A*—Ni—O1	96.7 (3)	N1*A*—C6*A*—C6*B*	114.3 (8)
O6—Ni—O1	80.1 (3)	C5*A*—C6*A*—C6*B*	122.7 (8)
N1*A*—Ni—N1*C*	172.5 (3)	C6*B*—N1*B*—C2*B*	117.5 (9)
O6—Ni—N1*C*	94.5 (3)	C6*B*—N1*B*—Ni	115.7 (6)
O1—Ni—N1*C*	87.4 (3)	C2*B*—N1*B*—Ni	126.8 (7)
N1*A*—Ni—N1*B*	79.1 (3)	N1*B*—C2*B*—C3*B*	121.6 (9)
O6—Ni—N1*B*	94.4 (3)	C2*B*—C3*B*—C4*B*	121.6 (10)
O1—Ni—N1*B*	173.0 (3)	C5*B*—C4*B*—C3*B*	115.8 (10)
N1*C*—Ni—N1*B*	97.4 (3)	C5*B*—C4*B*—C41*B*	124.1 (9)
N1*A*—Ni—N1*D*	94.3 (3)	C3*B*—C4*B*—C41*B*	120.0 (9)
O6—Ni—N1*D*	168.6 (3)	C6*B*—C5*B*—C4*B*	121.4 (9)
O1—Ni—N1*D*	90.0 (3)	N1*B*—C6*B*—C5*B*	122.2 (8)
N1*C*—Ni—N1*D*	79.4 (3)	N1*B*—C6*B*—C6*A*	113.9 (8)
N1*B*—Ni—N1*D*	95.9 (4)	C5*B*—C6*B*—C6*A*	123.9 (8)
C11—O1—Ni	113.1 (6)	C2*C*—N1*C*—C6*C*	119.0 (8)
C61—O6—Ni	114.9 (6)	C2*C*—N1*C*—Ni	125.3 (6)
O1—C11—C21	124.6 (9)	C6*C*—N1*C*—Ni	115.6 (6)
O1—C11—C61	116.7 (9)	N1*C*—C2*C*—C3*C*	122.2 (9)
C21—C11—C61	118.6 (10)	C4*C*—C3*C*—C2*C*	120.1 (9)
C11—C21—C31	120.7 (10)	C3*C*—C4*C*—C5*C*	116.9 (9)
O3—C31—C21	123.2 (11)	C3*C*—C4*C*—C41*C*	121.9 (9)
O3—C31—C41	117.9 (11)	C5*C*—C4*C*—C41*C*	121.3 (10)
C21—C31—C41	118.9 (10)	C4*C*—C5*C*—C6*C*	122.4 (9)
O4—C41—C51	124.3 (10)	N1*C*—C6*C*—C5*C*	119.4 (8)
O4—C41—C31	117.1 (11)	N1*C*—C6*C*—C6*D*	114.3 (8)
C51—C41—C31	118.5 (11)	C5*C*—C6*C*—C6*D*	126.3 (9)
C61—C51—C41	122.0 (10)	C2*D*—N1*D*—C6*D*	117.2 (9)
O6—C61—C51	125.3 (9)	C2*D*—N1*D*—Ni	128.0 (8)
O6—C61—C11	114.2 (9)	C6*D*—N1*D*—Ni	114.3 (6)
C51—C61—C11	120.6 (10)	N1*D*—C2*D*—C3*D*	124.0 (11)
C6*A*—N1*A*—C2*A*	118.0 (8)	C4*D*—C3*D*—C2*D*	121.0 (10)
C6*A*—N1*A*—Ni	116.9 (6)	C3*D*—C4*D*—C5*D*	115.2 (10)
C2*A*—N1*A*—Ni	125.0 (6)	C3*D*—C4*D*—C41*D*	121.5 (11)
N1*A*—C2*A*—C3*A*	122.7 (10)	C5*D*—C4*D*—C41*D*	123.3 (12)
C4*A*—C3*A*—C2*A*	119.2 (9)	C6*D*—C5*D*—C4*D*	120.6 (10)
C3*A*—C4*A*—C5*A*	117.6 (9)	N1*D*—C6*D*—C5*D*	121.9 (9)
C3*A*—C4*A*—C41*A*	120.8 (10)	N1*D*—C6*D*—C6*C*	115.8 (8)
C5*A*—C4*A*—C41*A*	121.6 (10)	C5*D*—C6*D*—C6*C*	122.3 (9)
C6*A*—C5*A*—C4*A*	119.3 (9)		

Table 6. *Hydrogen-bonding geometry (Å, °) for (II)*

D—H···*A*	*D*···*A*
C3*A*—H3*A*···O4$^{\rm i}$	3.40 (1)
C5*A*—H5*A*···O3$^{\rm ii}$	3.31 (1)
C41*A*—H41*A*···O4$^{\rm ii}$	3.23 (2)
C5*D*—H5*D*···O4$^{\rm iii}$	3.35 (1)
O1*W*—H11*W*···O1	2.84 (1)
O1*W*···O3$^{\rm i}$	3.00 (2)

Symmetry codes: (i) $1 + x - y, 1 + x, \frac{1}{6} + z$; (ii) $1 - y, 1 + x - y, \frac{1}{3} + z$; (iii) $-y, 1 + x - y, \frac{1}{3} + z$.

Both structures were determined using Patterson interpretation routines. As compound (II) has a polar axis the absolute polarity was determined by Flack's χ-parameter refinement (Flack, 1983; Bernardinelli & Flack, 1985). The H atoms for (I) were refined isotropically, whereas for (II) a riding-model refinement was applied with fixed C—H distances. The H-atom positions of the water molecule for (II) were refined with isotropic displacement parameters, but the resulting O—H distances are not in a chemically meaningful range.

For both compounds, data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ORTEP* (Johnson,1971); *SCHAKAL*86 (Keller, 1986).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1126). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tetrachlorobis(tetrahydrofuran-*O*)-zirconium(IV)

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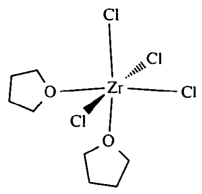
Abstract

The title compound, $[ZrCl_4(C_4H_8O)_2]$, contains zirconium with distorted octahedral coordination geometry, with two tetrahydrofuran ligands *cis* with respect to each other. The difference in *trans* influence of the tetrahydrofuran and chloride ligands leads to two marginally different groups of chloride ligands, with Zr—Cl bond lengths of 2.389 (11)/2.398(8) and 2.422 (8)/2.425(8) Å.

Comment

The X-ray crystal structure of the title compound, (I), was determined for comparison with the data of an EXAFS investigation in tetrahydrofuran solution (Bökman & Bertagnolli, 1994). $ZrCl_4$ is of potential interest as its complexes with Lewis bases are effective Ziegler–Natta catalysts soluble in non-polar solvents (Young, 1988).



(I)

The solid-state structure of the title complex exhibits isolated monomeric $[ZrCl_4(thf)_2]$ units, with zirconium in a distorted octahedral coordination environment. Within experimental error, the Zr—O distances of both the tetrahydrofuran rings [2.23 (1) and 2.24 (1) Å] are similar to the distance found in solution [2.22 (8) Å].

The chloride ligands *trans* to a tetrahydrofuran ligand show shorter Zr—Cl distances [Zr—Cl1 2.389 (11) and Zr—Cl2 2.398 (8) Å] than the two adjacent *cis*-Cl—Zr linkages [Zr—Cl3 2.422 (8) and Zr—Cl4 2.425 (8) Å]. Though these differences are statistically of marginal significance, they are probably real as a similar *trans* influence has been reported for the crystal structure of $[ZrCl_4(pinacolone)_2]$ (Galeffi, Simard & Wuest, 1990). The Zr—Cl bond lengths *trans* to pinacolone are, with an average value of 2.391 (5) Å, slightly shorter than the average [2.42 (2) Å] for the *cis*-Cl—Zr bonds. Furthermore, the isostructural complex $[HfCl_4(thf)_2]$ gives the same trend for *M*—Cl distances. The mean value of 2.370 (7) Å for the *cis*-Cl—Hf bonds is marginally shorter than the average *trans*-Cl—Hf distance [2.395 (7) Å; Duraj, Towns, Baker & Schupp, 1990].

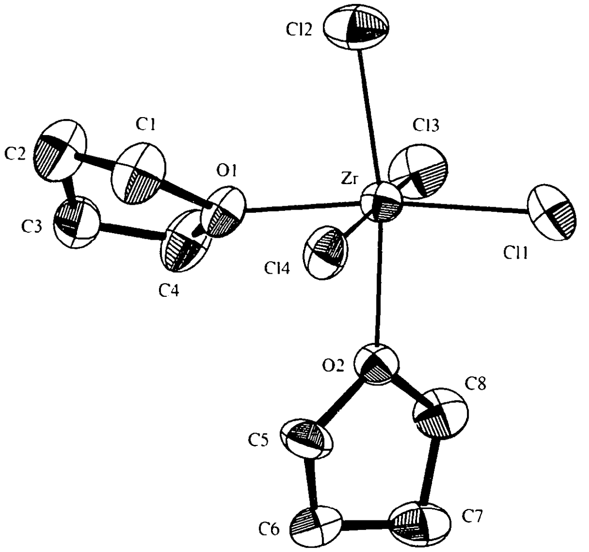


Fig. 1. *ORTEP*II view (Johnson, 1976) of $[ZrCl_4(thf)_2]$ showing the labelling of atoms. Displacement ellipsoids are shown at the 50% probability level and H atoms are omitted.

The EXAFS molecular structure of the adduct $[ZrCl_4(thf)_2]$ in solution (Bökman & Bertagnolli, 1994) is obviously similar to the solid-state molecular structure. The main effect upon dissolving the complex in tetrahydrofuran seems to be an increase of the *cis*-Cl—Zr distance by 0.07 (2) Å, whereas the Zr—O and *trans*-Cl—Zr bonds are not affected within experimental error. A comparison with the crystal structure of the related compound $[ZrCpCl_3(thf)_2]$, where Cp is cyclopentadienyl, shows that all distances are larger in the latter [up to 0.12 Å for the average Zr—O bond; *trans*-Cl—Zr 2.468 (1) Å, *cis*-Cl—Zr 2.492 (1) and 2.511 (1) Å; Erker