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Tris(2,2′-bioxazoline-κ^2N,N')-copper(II) diperchlorate and tris(2,2′-bioxazoline-κ^2N,N') nickel(II) diperchlorate

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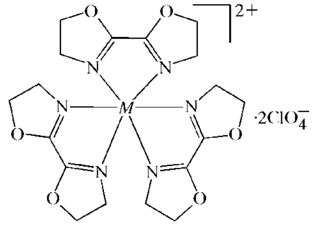
In the two isomorphous title compounds, *viz*. tris[2,2′-bi(4,5-dihydro-1,3-oxazole)-κ^2N,N']copper(II) diperchlorate, $[Cu(C_6H_8N_2O_2)_3](ClO_4)_2$, (I), and tris[2,2′-bi(4,5-dihydro-1,3-oxazole)-κ^2N,N']nickel(II) diperchlorate, $[Ni(C_6H_8N_2O_2)_3](ClO_4)_2$, (II), the M^{II} ions each have a distorted octahedral coordination geometry formed *via* six N atoms from three 2,2′-bioxazoline ligands. For each ligand, the two five-membered rings are nearly coplanar. It is noteworthy that the Jahn–Teller effect is stronger in (I) than in (II). The three-dimensional supramolecular structures of (I) and (II) are formed *via* weak hydrogen-bonding interactions between O atoms from perchlorate anions and H atoms from 2,2′-bioxazoline ligands.

Comment

Recently, studies of transition metal coordination compounds and supramolecules as new hybrid materials based on multifunctional organic ligands have attracted considerable interest due to their potential use in catalysis, magnetism, electrical conductivity and molecular recognition (Hagrman *et al.*, 1999; Inoue *et al.*, 1996; Zaworotko, 1997). At present, the rational design of new compounds and the modification of their structures is still a challenge. A current synthetic strategy widely used in this area is to select organic building blocks that are attractive for assembling functional compounds and supramolecules. 2,2′-Bithiazoline has been used for assembling coordination compounds showing interesting magnetic properties (Liu *et al.*, 2003). As the analogue of 2,2′-bithiazoline, 2,2′-bioxazoline is also a good ligand, used for fabricating novel topologies (Patra *et al.*, 2001; Walther *et al.*, 1999; Ozarowski *et al.*, 1988). It may act as a bidentate terminal ligand or as a bridging ligand (Haddleton *et al.*, 1998; Patra *et al.*, 2003). In our laboratory, both chiral and achiral bioxazolines have been used to construct novel coordination compounds. We obtained the two title novel mononuclear transition metal compounds, $[Cu(C_6H_8N_2O_2)_3](ClO_4)_2$, (I), and $[Ni(C_6H_8N_2O_2)_3](ClO_4)_2$, (II). The syntheses and X-ray crystal structures of these two compounds are reported here.



(I) M = Cu
(II) M = Ni

Selected geometric parameters for (I) are listed in Table 1. As shown in Fig. 1, the asymmetric unit of (I) consists of two counter-ions, *viz*. two perchlorate anions, and a discrete $[Cu(C_6H_8N_2O_2)_3]^{2+}$ cation composed of one Cu atom and three 2,2′-bioxazoline molecules. The local coordination geometry around the Cu centre can be described as a distorted octahedron, formed by six N atoms from three 2,2′-bioxazoline molecules. The Cu atom and the four N atoms (N1, N2, N3 and N6) in the equatorial plane are nearly coplanar, and the Cu—N bond distances are similar. The average Cu—N bond distance for atoms N1, N2, N3 and N6 is 2.018 Å, compared with a value of 2.020 Å in $[CuBrL^1]_n$ {L^1 is 2,2′-bis[(4*S*)-4-benzyl-2-oxazoline]; Haddleton *et al.*, 1998}, but slightly longer than the value of 1.972 Å in $[(Cu_2L_3)(ClO_4)_2]$ {L is 2,2′-bis[(4*R*)-benzyl-1,3-oxazoline]; Patra *et al.*, 2001}, in which the Cu atom is tricoordinated. However, the Cu—N bond distances for atoms N4 and N5 in the axial positions are 2.597 (3) and 2.410 (3) Å, respectively, much longer than the other Cu—N distances in (I), which results in a distorted

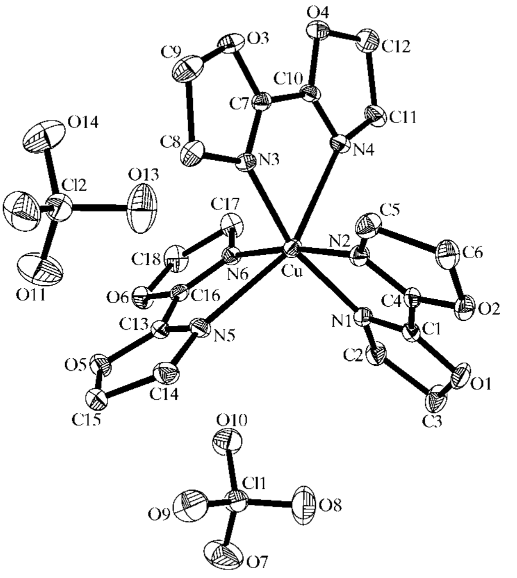


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids drawn at the 30% probability level. H atoms have been omitted for clarity.

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octahedral coordination environment around the Cu^{II} centre. It is noted that there is a much more pronounced Jahn–Teller distortion in (I) than in the related compound $[(CuL_3)(ClO_4)_2]$ {Cu—N bond distances in the range 2.028 (6)–2.364 (6) Å; L is 2,2′-bis[(4*R*)-benzyl-1,3-oxazoline]; Patra *et al.*, 2003}. This is in agreement with the smaller chelate angles of 73.35 (12) (N3—Cu—N4) and 75.57 (12)° (N5—Cu—N6), compared with 79.97 (13)° for N1—Cu—N2. For the three bioxazoline ligands, the C=N double-bond distances are in the range 1.255 (5)–1.273 (5) Å, which is similar to those reported previously (Walther *et al.*, 1999). The two five-membered rings of each bioxazoline molecule are approximately coplanar, with the dihedral angles varying from 4.45 (2) to 5.97 (3)°.

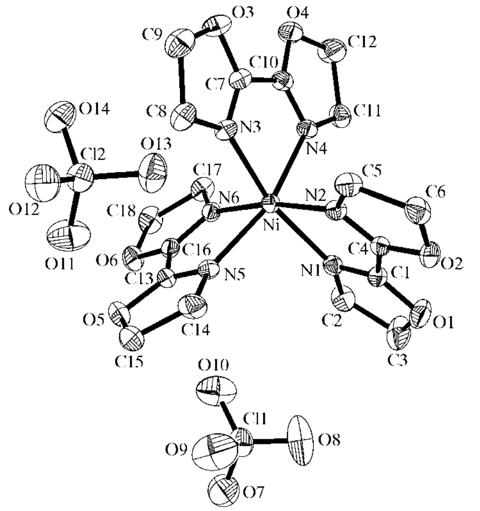

Figure 2
The molecular structure of (II), showing the atom-numbering scheme. Displacement ellipsoids drawn at the 30% probability level. H atoms have been omitted for clarity.

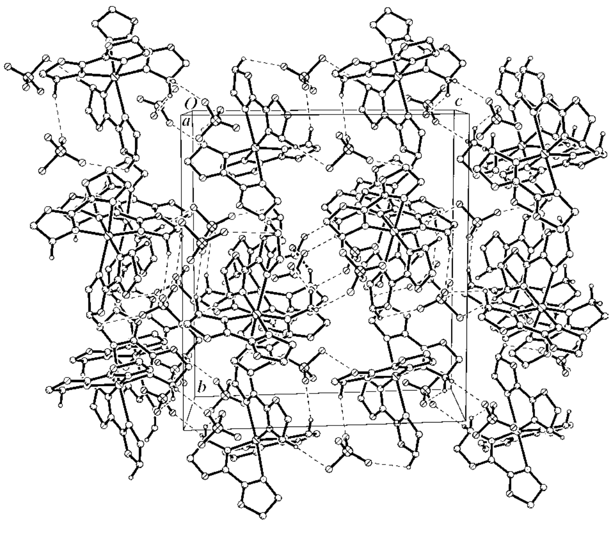

Figure 3
The crystal packing of (I), viewed along the *a* axis, with hydrogen bonds shown as dashed lines.

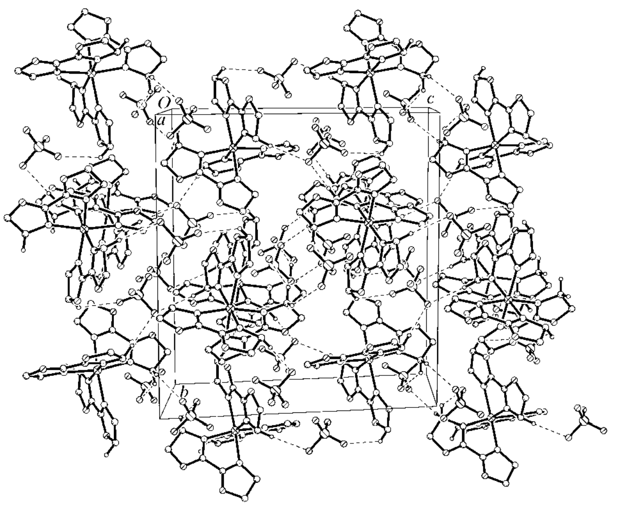

Figure 4
The crystal packing of (II), viewed along the *a* axis, with hydrogen bonds shown as dashed lines.

The structure of compound (II) is depicted in Fig. 2. Similar to (I), (II) is also an ionic complex. Each Ni atom of the cation in (II) lies approximately on a threefold axis and is coordinated by six N atoms from three 2,2′-bioxazoline molecules, which form a slightly distorted octahedral geometry. Selected geometric parameters for (II) are listed in Table 3. The Ni—N bond distances, in the range 2.089 (3)–2.127 (3) Å, are comparable with the range of 2.070 (3)–2.085 (5) Å in the related 2,2′-bpy–nickel(II) hexafluorophosphate, in which two hexafluorophosphate ions act as counter-ions (2,2′-bpy is 2,2′-bipyridine; Breu *et al.*, 2000), and with similar corresponding Ni—N chelate angles of 77.95 (12) (N1—Ni—N2), 78.53 (12) (N3—Ni—N4) and 78.53 (12)° (N5—Ni—N6). All 2,2′-bioxazoline molecules in (II) act as bidentate terminal ligands.

There are extensive hydrogen-bonding interactions between the perchlorate anions and the discrete cations in the structures of (I) and (II). The crystal packing in both structures is stabilized by intermolecular C—H⋯O(perchlorate) hydrogen bonds, leading to three-dimensional supramolecular structures (Figs. 3 and 4). The hydrogen-bonding geometries for (I) and (II) are listed in Tables 2 and 4, respectively.

Experimental

All organic solvents and common materials were of reagent grade and used without further purification. 2,2′-Bioxazoline was prepared according to the literature method of Evans *et al.* (1998). Compound (I) was synthesized by adding an acetonitrile solution (20 ml) containing copper(II) perchlorate hexahydrate (0.181 g, 0.5 mmol) dropwise with continuous stirring into a dichloromethane solution (10 ml) of 2,2′-bioxazoline (1.5 mmol, 0.21 g) over a period of 20 min. Slow evaporation of the resulting blue solution at room temperature yielded blue crystals of (I) within 4 d. Compound (II) was prepared in the same way as (I), using nickel(II) perchlorate hexahydrate. Slow evaporation of the resulting green solution at room temperature yielded green crystals of (II) within 7 d. Elemental analysis calculated for compound (I): C 31.65, H 3.52, N 12.31, Cl 10.40%; found: C 31.45, H 3.54, N 12.36, Cl 10.44%; calculated for compound (II): C 31.86, H 3.54, N 12.39, Cl 10.47%; found: C 31.82, H 3.55, N 12.43, Cl 10.50%.

Compound (I)

Crystal data

$[Cu(C_6H_8N_2O_2)_3](ClO_4)_2$
$M_r = 682.87$
Monoclinic, $P2_1/n$
$a = 9.3766 (19)$ Å
$b = 17.734 (4)$ Å
$c = 16.350 (3)$ Å
$\beta = 98.54 (3)^\circ$
$V = 2688.7 (10)$ Å^3
$Z = 4$
$D_x = 1.687$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 350 reflections
$\theta = 1.7–27.5^\circ$
$\mu = 1.09$ mm^{-1}
$T = 293 (2)$ K
Block, blue
0.23 × 0.15 × 0.14 mm

Data collection

Rigaku R-AXIS RAPID IP diffractometer
Oscillation scans
Absorption correction: empirical (*ABSCOR*; Higashi, 1995)
$T_{\min} = 0.732$, $T_{\max} = 0.862$
23 475 measured reflections
6132 independent reflections

2689 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.067$
$\theta_{\max} = 27.5^\circ$
$h = -12 \rightarrow 12$
$k = 0 \rightarrow 22$
$l = -21 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.112$
$S = 0.83$
6132 reflections
370 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0339P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.45$ e Å^{-3}
$\Delta\rho_{\min} = -0.29$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

Cu—N1	2.045 (3)	Cu—N4	2.597 (3)
Cu—N2	2.028 (3)	Cu—N5	2.410 (4)
Cu—N3	1.995 (3)	Cu—N6	2.006 (3)
N1—Cu—N2	79.97 (14)	N2—Cu—N6	171.97 (14)
N1—Cu—N3	163.80 (14)	N3—Cu—N4	73.35 (12)
N1—Cu—N4	95.96 (13)	N3—Cu—N5	93.74 (13)
N1—Cu—N5	100.61 (13)	N3—Cu—N6	96.04 (13)
N1—Cu—N6	94.79 (13)	N4—Cu—N5	154.34 (11)
N2—Cu—N3	90.40 (13)	N4—Cu—N6	83.69 (12)
N2—Cu—N4	102.82 (12)	N5—Cu—N6	75.57 (13)
N2—Cu—N5	99.28 (13)		

Table 2
Hydrogen-bonding geometry (Å, °) for (I).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C17—H17*A*···O7$^{\rm i}$	0.97	2.49	3.346 (3)	145
C15—H15*A*···O9	0.97	2.55	3.134 (6)	119
C2—H2*B*···O10	0.97	2.57	3.516 (6)	163
C8—H8*A*···O13	0.97	2.47	3.215 (5)	133
C8—H8*B*···O14$^{\rm ii}$	0.97	2.56	3.338 (4)	137

Symmetry codes: (i) $1 - x, -y, 1 - z$; (ii) $1 - x, -y, -z$.

Table 3
Selected geometric parameters (Å, °) for (II).

Ni—N1	2.123 (3)	Ni—N4	2.127 (3)
Ni—N2	2.114 (3)	Ni—N5	2.112 (3)
Ni—N3	2.089 (3)	Ni—N6	2.105 (3)
N1—Ni—N2	77.95 (12)	N2—Ni—N6	170.86 (12)
N1—Ni—N3	165.71 (12)	N3—Ni—N4	78.53 (12)
N1—Ni—N4	95.22 (12)	N3—Ni—N5	92.86 (12)
N1—Ni—N5	96.21 (12)	N3—Ni—N6	97.01 (12)
N1—Ni—N6	95.60 (12)	N4—Ni—N5	163.19 (12)
N2—Ni—N3	90.22 (12)	N4—Ni—N6	88.14 (12)
N2—Ni—N4	98.81 (11)	N5—Ni—N6	78.53 (12)
N2—Ni—N5	95.60 (12)		

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H5*B*···O7$^{\rm i}$	0.97	2.48	3.451 (6)	179
C17—H17*A*···O7$^{\rm ii}$	0.97	2.50	3.468 (6)	176
C15—H15*A*···O9	0.97	2.54	3.277 (7)	133
C8—H8*A*···O13	0.97	2.57	3.345 (5)	137
C8—H8*B*···O14$^{\rm iii}$	0.97	2.55	3.347 (6)	139

Symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $1 - x, -y, 1 - z$; (iii) $1 - x, -y, -z$.

Compound (II)

Crystal data

$[Ni(C_6H_8N_2O_2)_3](ClO_4)_2$
$M_r = 678.04$
Monoclinic, $P2_1/n$
$a = 9.3911 (19)$ Å
$b = 17.683 (4)$ Å
$c = 16.743 (3)$ Å
$\beta = 101.14 (3)^\circ$
$V = 2728.0 (9)$ Å^3
$Z = 4$

$D_x = 1.651$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 345 reflections
$\theta = 1.7–27.5^\circ$
$\mu = 0.99$ mm^{-1}
$T = 293 (2)$ K
Block, green
0.21 × 0.17 × 0.11 mm

Data collection

Rigaku R-AXIS RAPID IP diffractometer
Oscillation scans
Absorption correction: empirical (*ABSCOR*; Higashi, 1995)
$T_{\min} = 0.804$, $T_{\max} = 0.896$
21 381 measured reflections

5940 independent reflections
2979 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.061$
$\theta_{\max} = 27.5^\circ$
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 22$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.104$
$S = 0.93$
5940 reflections
370 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0298P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.62$ e Å^{-3}
$\Delta\rho_{\min} = -0.34$ e Å^{-3}

For both compounds, all H atoms were located in difference Fourier maps and were then regenerated in ideal positions and refined using a riding model, with C—H distances of 0.95–0.97 Å and with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$.

For both compounds, data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXL97*; software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1208). Services for accessing these data are described at the back of the journal.

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