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Two 2,5-bis(2-pyridinyl)-1,3,4-oxadiazole–metal complexes ($M = \text{Cu}$ and Ni)

A. Gueddi,^a B. Mernari,^a M. Giorgi^b and M. Pierrot^{b*}

^aLaboratoire de Chimie de Coordination et Analytique, Faculté des Sciences, Université Chouaib Doukkali, El Jadida, Morocco, and ^bLBS-UMR 6517, Centre Scientifique Saint-Jérôme, 13397 Marseille CEDEX 20, France
Correspondence e-mail: marcel.pierrot@lbs.u-3mrs.fr

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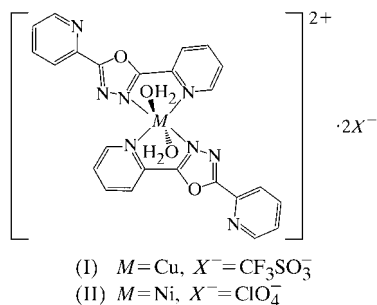
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The reaction of the diazine ligand 3,5-bis(2-pyridinyl)-1,3,4-oxadiazole (pod, $\text{C}_{12}\text{H}_8\text{N}_4\text{O}$), with $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ or $\text{Ni}(\text{ClO}_4)_2$ afforded the title complexes diaquabis[3,5-bis(2-pyridinyl)-1,3,4-oxadiazole- N^2,N^3]copper(II) bis(trifluoromethanesulfonate), $[\text{Cu}(\text{pod})_2(\text{H}_2\text{O})_2](\text{CF}_3\text{SO}_3)_2$, and diaquabis[3,5-bis(2-pyridinyl)-1,3,4-oxadiazole- N^2,N^3]nickel(II) diperchlorate, $[\text{Ni}(\text{pod})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$. Both complexes present a crystallographically centrosymmetric mononuclear cation structure which consists of a six-coordinated Cu^{II} or Ni^{II} ion with two pod molecules acting as bidentate ligands and two axially coordinated water molecules.

Comment

Diazine bridging ligands of six- and five-membered rings provide binuclear complexes with a metal ion/diazine ligand ratio of 2:2 or 2:1, both bringing two metal centres into close proximity and thus providing an intramolecular pathway for spin-exchange interactions (Escuer *et al.*, 1997; Mernari *et al.*, 1993; Vreugdenhill *et al.*, 1987; Ball & Blake, 1969, 1974). However, a metal ion/diazine ligand ratio of 1:2 has also been



obtained (El Gueddi *et al.*, 1996; Wignacourt *et al.*, 1990). In our study of the structure and properties of new polyaza ligands (Mernari *et al.*, 1998), we have investigated the reactions of a copper and nickel salt with the diazine ligand pod, *i.e.* 3,5-bis(2-pyridinyl)-1,3,4-oxadiazole, and obtained mono-

nuclear complexes with a Cu^{II} or Ni^{II} /pod ratio of 1:2 in a *trans* coordination mode. The structures of diaquabis[3,5-bis(2-pyridinyl)-1,3,4-oxadiazole]copper(II) bis(trifluoromethanesulfonate), (I), and diaquabis[3,5-bis(2-pyridinyl)-1,3,4-oxadiazole]nickel(II) diperchlorate, (II), are presented here.

The structures consist of $[\text{M}(\text{pod})_2(\text{H}_2\text{O})_2]^{2+}$ ($M = \text{Cu}$, Ni) centrosymmetric monomeric cations and discrete entities of the counter-ions $[\text{CF}_3\text{SO}_3]^-$ or $[\text{ClO}_4]^-$. The pod molecule plays the role of a bidentate ligand coordinated to the metal ion *via* an oxadiazole and a pyridine N atom. The equatorial coordination of the metal is completed by a second pod molecule related to the former by a symmetry centre which coincides with the metal-atom position. The octahedral coordination of the metal is achieved by two water molecules in axial positions. These structures reveal a *trans* coordination mode which is the same as already found with the pod ligand (Wignacourt *et al.*, 1990). In the equatorial plane, the formation of a chelate ring of five atoms produces relatively acute $\text{N1}-\text{Cu}-\text{N7}$ and $\text{N1}-\text{Ni}-\text{N7}$ angles of $81.12(8)$ and $79.36(3)^\circ$, respectively. The metal–pyridine-N bonds [$2.0579(5)$ Å for Cu and $2.1073(7)$ Å for Ni] are longer than the metal–oxadiazole-N bonds [$1.993(2)$ Å for Cu and $2.0475(7)$ Å for Ni]. These variations of bond lengths are approximately the same as in $[\text{Cu}(\text{pod})_2(\text{H}_2\text{O})](\text{ClO}_4)_2$ (Wignacourt *et al.*, 1990) and in $[\text{Cu}_2(\text{C}_4\text{H}_{10}\text{N}_6)_2(\text{H}_2\text{O})_2](\text{SO}_4)\cdot 4\text{H}_2\text{O}$ (Koningsbruggen *et al.*, 1992). However, in $[\text{Cu}(\text{pod})_2\text{Cl}_2]\cdot \text{H}_2\text{O}$, the Cu–pyridine-N bond of $2.008(2)$ Å is shorter than the Cu–oxadiazole-N bond of $2.484(1)$ Å (Lagrenez *et al.*, 1991). The axial bond lengths Cu–O19 [$2.312(2)$ Å], Ni–O18 [$2.088(3)$ Å] and Ni–O19 [$2.1122(13)$ Å] are similar to those found in the complexes with diazine ligands (Keij *et al.*, 1984; Rosenberg *et al.*, 1986; Koningsbruggen *et al.*, 1992). The metal ion is located essentially in the 5-pyridinyloxadiazole plane, at $-0.025(2)$ Å for Cu and at $-0.022(9)$ Å for Ni. In the case of the Cu complex, the 3-pyridinyl ring is almost coplanar with the 5-pyridinyloxadiazole plane [angle: $6.6(5)^\circ$], but is at $24.0(4)^\circ$ in the case of the Ni complex. Despite the disordered structure of the counter-ions one can say that $[\text{ClO}_4]^-$ or $[\text{CF}_3\text{SO}_3]^-$ ions are probably linked to the water molecules *via* hydrogen bonds; however, a clear description cannot be given. Thus, in the Cu complex, O19 is $2.793(6)$ Å from O26, $2.805(6)$ Å from O21 and $2.847(7)$ Å from O22; in the Ni complex, where the water molecule is disordered and located on two sites, O18 and O19, we found O18 $2.813(6)$ Å, $2.823(5)$ Å and $2.949(5)$ Å from O27, O24 and O40, respectively, while O19 is $2.648(7)$, $2.642(8)$ and $2.716(8)$ Å from the same atomic sites.

Experimental

The pod ligand was prepared according to the literature method of Sharma & Tandon (1984). The metal complexes were obtained by addition of $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ or $\text{Ni}(\text{ClO}_4)_2$ (2 mmol) to a methanolic solution of pod (4 mmol). After filtration of the undissolved reactants the filtrates were left at room temperature. After two weeks, blue crystals appeared and were filtered off and washed with water.

Compound (I)

Crystal data

[Cu(C₁₂H₈N₄O)₂(H₂O)₂](CF₃SO₃)₂
M_r = 846.15
 Monoclinic, *P*2₁/*c*
a = 13.5897 (5) Å
b = 10.0316 (4) Å
c = 22.6240 (10) Å
 β = 147.261 (3)°
V = 1668.0 (3) Å³
Z = 2

D_x = 1.685 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 12 050 reflections
 θ = 1.0–25.8°
 μ = 0.881 mm⁻¹
T = 298 K
 Prism, colourless
 0.20 × 0.15 × 0.10 mm

Data collection

KappaCCD diffractometer
 φ scans
 3270 measured reflections
 3117 independent reflections
 2633 reflections with *I* > 3σ(*I*)

*R*_{int} = 0.035
 θ _{max} = 25.8°
h = -14 → 16
k = -12 → 0
l = -27 → 14

Refinement

R = 0.065
wR = 0.074
S = 1.635
 2633 reflections
 270 parameters

H-atom parameters not refined
 $w = 1/[\sigma^2(F_o^2) + 0.03F_o^2]$
 (Δ/σ)_{max} = 0.045
 $\Delta\rho$ _{max} = 0.59 e Å⁻³
 $\Delta\rho$ _{min} = -0.60 e Å⁻³

Table 1

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

Cu1—O19	2.3125 (6)	N13—C14	1.3347 (13)
Cu1—N7	2.0579 (5)	C5—C6	1.4509 (11)
Cu1—N1	1.9926 (5)	C3—C12	1.4629 (10)
O4—C5	1.3418 (9)	C6—C11	1.3704 (11)
O4—C3	1.3762 (9)	C8—C9	1.3880 (13)
N1—N2	1.3894 (9)	C9—C10	1.3640 (13)
N1—C5	1.2986 (10)	C10—C11	1.3564 (12)
N2—C3	1.2895 (10)	C12—C17	1.3642 (12)
N7—C6	1.3545 (10)	C14—C15	1.3552 (15)
N7—C8	1.3268 (10)	C15—C16	1.355 (2)
N13—C12	1.3338 (11)	C16—C17	1.3830 (13)
O19—Cu1—N7	93.01 (2)	N7—C6—C11	122.91 (7)
N1—Cu1—N7	81.12 (3)	C5—C6—C11	126.39 (7)
C5—O4—C3	102.52 (6)	N7—C8—C9	121.86 (8)
N2—N1—C5	107.66 (6)	C8—C9—C10	119.46 (8)
N1—N2—C3	105.13 (6)	C9—C10—C11	119.43 (9)
C6—N7—C8	117.56 (7)	C6—C11—C10	118.78 (8)
C12—N13—C14	115.20 (8)	N13—C12—C3	115.43 (7)
O4—C5—N1	111.86 (6)	N13—C12—C17	124.60 (7)
O4—C5—C6	125.59 (7)	C3—C12—C17	119.93 (8)
N1—C5—C6	122.55 (7)	N13—C14—C15	124.71 (10)
O4—C3—N2	112.83 (6)	C14—C15—C16	118.67 (9)
O4—C3—C12	119.45 (7)	C15—C16—C17	119.14 (9)
N2—C3—C12	127.70 (7)	C12—C17—C16	117.66 (9)
N7—C6—C5	110.69 (6)		

Compound (II)

Crystal data

[Ni(C₁₂H₈N₄O)₂(H₂O)₂](ClO₄)₂
M_r = 742.09
 Monoclinic, *P*2₁/*c*
a = 13.6569 (9) Å
b = 10.9630 (7) Å
c = 18.921 (1) Å
 β = 147.752 (3)°
V = 1511.61 (28) Å³
Z = 2

D_x = 1.63 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 8346 reflections
 θ = 1.0–26.0°
 μ = 0.894 mm⁻¹
T = 298 K
 Prism, colourless
 0.20 × 0.15 × 0.10 mm

Data collection

KappaCCD diffractometer
 φ scans
 3008 measured reflections
 2851 independent reflections
 2576 reflections with *I* > 3σ(*I*)

*R*_{int} = 0.055
 θ _{max} = 26.0°
h = -16 → 17
k = -13 → 0
l = -23 → 16

Refinement

R = 0.086
wR = 0.073
S = 2.154
 2576 reflections
 236 parameters

H-atom parameters not refined
 $w = 1/[\sigma^2(F_o^2) + 0.03F_o^2]$
 (Δ/σ)_{max} = 0.045
 $\Delta\rho$ _{max} = 0.63 e Å⁻³
 $\Delta\rho$ _{min} = -0.46 e Å⁻³

Table 2

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

Ni1—O18	2.088 (2)	N13—C14	1.3292 (13)
Ni1—O19	2.1122 (13)	C8—C9	1.3975 (13)
Ni1—N7	2.1073 (7)	C3—C12	1.4611 (12)
Ni1—N1	2.0475 (7)	C12—C17	1.3665 (10)
O4—C3	1.3755 (10)	C5—C6	1.4591 (12)
O4—C5	1.3396 (10)	C10—C11	1.3732 (14)
N7—C8	1.3244 (11)	C10—C9	1.3631 (14)
N7—C6	1.3567 (10)	C6—C11	1.3721 (12)
N1—N2	1.3958 (10)	C16—C15	1.354 (2)
N1—C5	1.2965 (10)	C16—C17	1.3795 (13)
N2—C3	1.2912 (11)	C15—C14	1.343 (2)
N13—C12	1.3246 (12)		
O18—Ni1—N1	93.21 (8)	N13—C12—C17	123.71 (8)
O18—Ni1—N7	85.60 (7)	C3—C12—C17	119.78 (8)
O19—Ni1—N1	87.69 (4)	O4—C5—N1	112.58 (8)
O19—Ni1—N7	93.46 (4)	O4—C5—C6	124.89 (8)
N7—Ni1—N1	79.36 (3)	N1—C5—C6	122.52 (8)
C3—O4—C5	102.15 (7)	C11—C10—C9	119.80 (9)
C8—N7—C6	117.52 (8)	N7—C6—C5	111.24 (7)
N2—N1—C5	107.19 (7)	N7—C6—C11	123.70 (9)
N1—N2—C3	104.96 (7)	C5—C6—C11	125.05 (8)
C12—N13—C14	116.87 (10)	C10—C11—C6	117.75 (9)
N7—C8—C9	121.89 (9)	C15—C16—C17	119.56 (10)
O4—C3—N2	113.11 (8)	C8—C9—C10	119.34 (9)
O4—C3—C12	119.21 (8)	C16—C15—C14	118.91 (10)
N2—C3—C12	127.64 (9)	N13—C14—C15	123.69 (10)
N13—C12—C3	116.50 (9)	C12—C17—C16	117.25 (7)

In both structures, the counter-ion is fully disordered. For the Cu compound, the O atoms of the perchlorate ion are located on 15 sites, with an occupancy ranging from 0.5 to 0.1. For the Ni compound, the O and F atoms of the trifluoromethanesulfonate are located on eight and nine positions, respectively, with an occupancy ranging from 0.52 to 0.18 for the fluoride sites and from 0.6 to 0.14 for the oxygen sites. Moreover, the water molecule linked to the copper ion occupies two positions, O18 and O19, with occupancies of 0.3 and 0.7, respectively. In this case, the H atoms of the water molecule could not be found in the Fourier maps. Disordered atoms (O of the perchlorate; F and O of the trifluoromethanesulfonate) were refined isotropically. O atoms O18 and O19 of the disordered water molecule (Ni complex) were also refined isotropically.

For both compounds, data collection: *KappaCCD Software* (Nonius, 1997); data reduction: *DENZO* and *SCALEPAK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *maXus* (Mackay *et al.*, 1999); software used to prepare material for publication: *maXus*.

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