

Transition metal complexes with pyrazole-based ligands. XIX. Diaqua-bis(3,5-dimethyl-1*H*-pyrazole-1-carboxamidine- κ^2N,N')metal(II) dinitrate, with metal = Co and Ni

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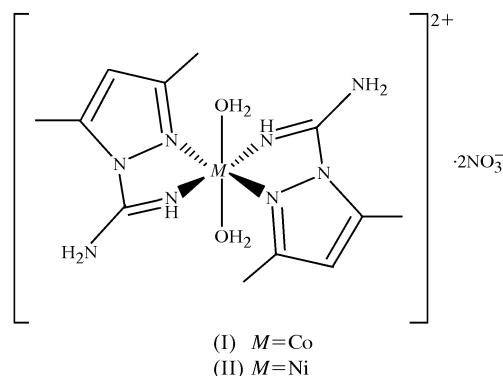
The two title isostructural and isomorphous complexes, $[M(C_6H_{10}N_4)_2(H_2O)_2](NO_3)_2$ (M is Co or Ni), contain the transition metal in a distorted octahedral geometry, coordinated by four N atoms of two neutral bidentate organic ligands in the equatorial plane and two water O atoms molecules in the axial positions. The cation is centrosymmetric, with the transition metal located on an inversion centre. The structures are stabilized by a three-dimensional network of hydrogen bonding.

Comment

Transition metal complexes with pyrazole-derived ligands exhibit interesting coordination chemistry and have attracted the research interest of numerous authors (Trofimenko, 1972, 1986, 1993, and references therein). These compounds find application in antipyretics and antirheumatics, in herbicides and fungicides, and also as metal ion extractants (Ding *et al.*, 1994; Goslar *et al.*, 1988). A more recent area of research activity has focused on the biocoordination chemistry of pyrazole and its macrocyclic derivatives (Bienvenue *et al.*, 1995; Gupta *et al.*, 1996).

We have synthesized and characterized a number of pyrazole-derived ligands and their metal complexes, with the aim of investigating the influence of the pyrazole ring substituents on complex formation (Jaćimović *et al.*, 1999, 2003; Tomić *et al.*, 2000; Mészáros Szécsényi *et al.*, 2001, 2003). We report here the crystal structures of the isomorphous Co and Ni complexes of the ligand 3,5-dimethyl-1*H*-pyrazole-1-carboxamidine nitrate (Khudoyarov *et al.*, 1995). The Co complex, (I), has been prepared for the first time, while the structure of

the Ni analogue, (II), has been determined previously (Podder *et al.*, 1986). However, the geometry and orientation of the water molecules in the previously reported structure were implausible. For example, the O—H bond lengths were 0.64 and 0.90 Å, the H—O—H bond angle was 96°, and the molecule was oriented in such a way that one of the H atoms was only 1.4 Å from the Ni centre. Clearly, such an incorrect model does not permit an accurate description of the hydrogen-bonding interactions, which play a significant role in the stability of this complex and which will be discussed below.



The asymmetric units of (I) and (II) contains half an $[M(C_6H_{10}N_4)_2(H_2O)_2]^{2+}$ cation, located on an inversion centre, and an NO_3^- anion. The Co^{II} and Ni^{II} cations are found in a distorted octahedral environment, coordinated to the ligand in the equatorial plane through pyrazole ring N atoms and the adjacent amidinium group N atoms. The coordination sphere

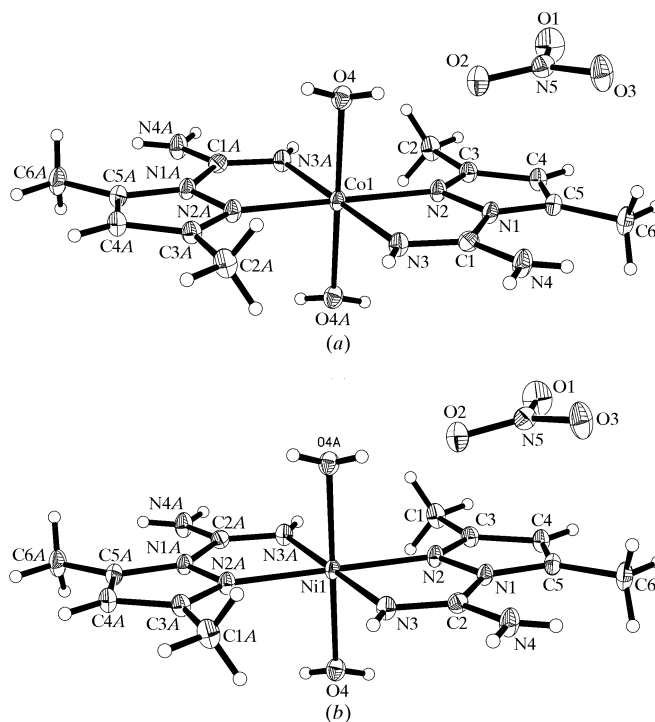


Figure 1
Views of the (a) the Co complex, (I), and (b) the Ni complex, (II), with their atom-numbering schemes. Each asymmetric unit consists of half a cation, with the metal on an inversion centre, and one nitrate anion. Displacement ellipsoids are shown at the 50% probability level.

is completed by two O atoms belonging to water molecules in axial positions (Fig. 1).

In (I), the equatorial bond lengths are Co–N2 = 2.0871 (8) Å and Co–N3 2.0842 (9) Å, and the ligand bite angle is 76.46 (3)°. The axial Co–O4 bond length is 2.1737 (7) Å. The corresponding parameters for (II) are 2.0474 (11) and 2.0552 (12) Å, 77.67 (4)°, and 2.1520 (10) Å. In both cases, the ligand ring system is essentially planar, with the amidinium group tilted relative to the substituted pyrazole ring by 3.7° in (I) and by 2.2° in (II). This is in contrast to the molecular structure of the ligand itself (Khudoyarov *et al.*, 1995), where a significant departure from planarity exists, with the amidinium group twisted at an angle of 34° relative to the plane of the pyrazole ring. In the formation of complexes (I) and (II), the geometry of the ligand is adjusted to accommodate the coordination requirements of the transition metal.

Packing diagrams for the title complexes are shown in Fig. 2. The cations pack in such a way that molecules lying parallel form layers of alternating orientation. Layers of cations are

separated by layers of nitrate anions. This arrangement gives rise to a system of hydrogen bonding involving the N atoms of the amino group and the water O atoms as donors, and the O atoms of the nitrate groups as acceptors. Two O atoms of a given nitrate group form hydrogen bonds to two cations in the layer above (with the amino group of one molecule and water in the other), while the third forms a bifurcated hydrogen bond to two cations in the layer below. The adjacent nitrate group forms the same number and types of hydrogen bonds, but in the opposite orientation, as shown in Fig. 2. Details of the hydrogen-bonding geometries for the two complexes are given in Tables 2 and 4. This three-dimensional pattern of hydrogen bonding imparts stability to the crystal structures of these two complexes.

Experimental

For the preparation of (I), an ethanol solution (5 ml) of Co(OAc)₂·4H₂O (0.06 g, 0.25 mmol) was added to an ethanol solution (5 ml) of the ligand 3,5-dimethylpyrazole-1-carboxamide nitrate (0.1 g, 0.5 mmol) and the mixture was gently heated. After 48 h, orange crystals of (I) were filtered off and washed with ethanol (yield 0.18 g, 65%). Elemental analysis, found (calculated): C 28.89 (29.08), N 28.30 (28.27), H 4.96% (4.89%). For the preparation of (II), an ethanol solution (5 ml) of Ni(OAc)₂·4H₂O (0.06 g, 0.25 mmol) was added to an ethanol solution (5 ml) of the ligand 3,5-dimethylpyrazole-1-carboxamide nitrate (0.1 g, 0.5 mmol) and the mixture was gently heated. After 60 h, purple crystals of (II) were filtered off and washed with ethanol (yield 0.18 g, 65%). Elemental analysis, found (calculated): C 28.93 (29.10), N 28.30 (28.29), H 4.96% (4.89%).

Compound (I)

Crystal data

[Co(C₆H₁₀N₄)₂(H₂O)₂](NO₃)₂
M_r = 495.32
 Monoclinic, *P*2₁/*n*
a = 9.1067 (11) Å
b = 10.9344 (13) Å
c = 10.4425 (13) Å
 β = 107.602 (2)°
V = 991.1 (2) Å³
Z = 2

D_x = 1.660 Mg m⁻³
 Mo K α radiation
 Cell parameters from 7486 reflections
 θ = 5.2–61.7°
 μ = 0.93 mm⁻¹
T = 120 K
 Rectangular prism, orange
 0.24 × 0.10 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
T_{min} = 0.840, *T_{max}* = 0.911
 13 055 measured reflections

2975 independent reflections
 2920 reflections with *I* > 2 σ (*I*)
R_{int} = 0.02
 θ_{max} = 30.9°
h = -12 → 13
k = -15 → 15
l = -15 → 14

Refinement

Refinement on *F*²
R(*F*) = 0.027
wR(*F*²) = 0.062
S = 0.98
 2920 reflections
 190 parameters
 All H-atom parameters refined
 Weighting scheme: method, part 1, Chebyshev polynomial (Watkin, 1994; Prince, 1982),
 $[\text{weight}] = 1/[A_0T_0(x) + A_1T_1(x) + \dots + A_{n-1}T_{n-1}(x)],$

where *A_i* are the Chebyshev coefficients 1.62, 2.12 and 0.556, and $x = F_{calc}/F_{max}$.
 Method = robust weighting (Prince, 1982),
 $W = [\text{weight}] \times [1 - (\Delta F/6\sigma F)^2]$
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 0.44 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -0.38 \text{ e \AA}^{-3}$

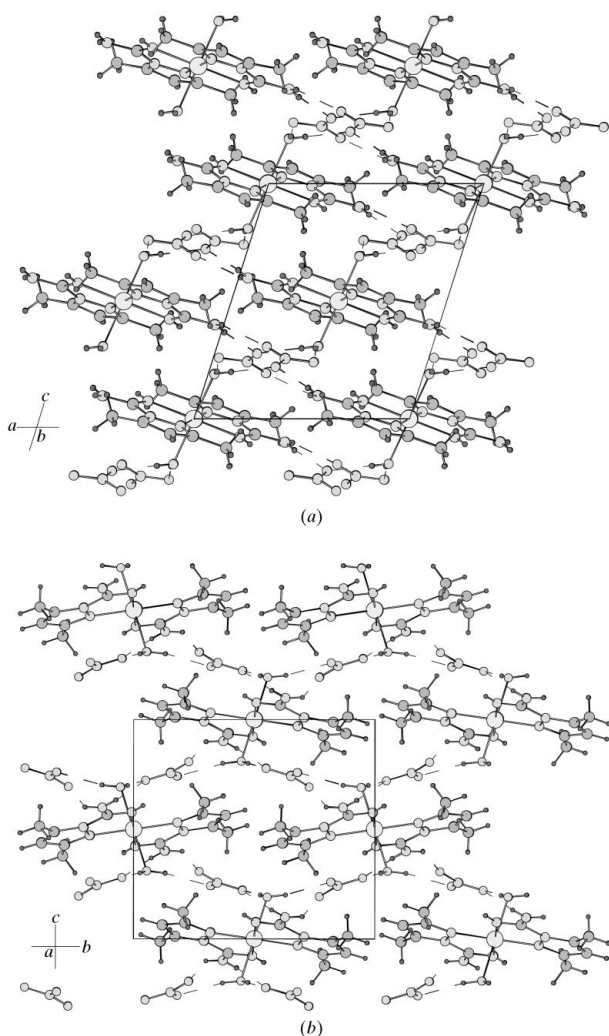


Figure 2
 Views of the packing and hydrogen-bonding schemes for (a) complex (I) and (b) complex (II).

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

Co1—N2	2.0871 (8)	N5—O1	1.2408 (11)
Co1—N3	2.0842 (9)	N5—O2	1.2582 (11)
Co1—O4	2.1737 (7)	N5—O3	1.2546 (11)
N1—N2	1.3778 (10)	N4—C1	1.3361 (12)
N1—C1	1.4176 (12)	C2—C3	1.4918 (13)
N1—C5	1.3731 (12)	C3—C4	1.4104 (12)
N2—C3	1.3256 (12)	C4—C5	1.3717 (13)
N3—C1	1.2890 (12)	C5—C6	1.4860 (13)
N2—Co1—N3	76.46 (3)	N3—Co1—O4	87.79 (3)
N2—Co1—O4	91.79 (3)		

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N4—H9...O1 ⁱ	0.84 (2)	2.249 (18)	2.8572 (13)	129.7 (16)
N4—H10...O2 ⁱⁱ	0.811 (18)	2.114 (18)	2.9136 (13)	168.8 (18)
O4—H11...O2	0.772 (19)	2.081 (19)	2.8539 (12)	179.5 (14)
O4—H12...O3 ⁱⁱⁱ	0.85 (2)	2.14 (2)	2.9799 (12)	169.6 (18)

Symmetry codes: (i) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (ii) $3 - x, 1 - y, 2 - z$; (iii) $\frac{5}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$.

Compound (II)

Crystal data

[Ni(C₆H₁₀N₄)₂(H₂O)₂](NO₃)₂
M_r = 495.10
 Monoclinic, *P*₂₁/*n*
a = 9.077 (3) Å
b = 10.866 (4) Å
c = 10.456 (3) Å
 β = 107.251 (15)°
V = 985.0 (6) Å³
Z = 2

D_x = 1.669 Mg m⁻³
 Mo Kα radiation
 Cell parameters from 6757 reflections
 θ = 5.2–62.2°
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 Rectangular prism, purple
 0.20 × 0.20 × 0.12 mm

Data collection

Bruker SMART CCD area-detector diffractometer
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 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
*T*_{min} = 0.803, *T*_{max} = 0.881
 13 257 measured reflections

2990 independent reflections
 2617 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.02
 θ_{max} = 31.0°
h = -12 → 12
k = -15 → 15
l = -14 → 14

Refinement

Refinement on *F*²
R(*F*) = 0.026
wR(*F*²) = 0.062
S = 0.98
 2617 reflections
 190 parameters
 All H-atom parameters refined
 Weighting scheme, method, part 1, Chebychev polynomial (Watkin, 1994; Prince, 1982),
 [weight] = 1/[*A*₀*T*₀(*x*) + *A*₁*T*₁(*x*) + ... + *A*_{*n*-1}*T*_{*n*-1}(*x*)],

where *A_i* are the Chebychev coefficients 1.85, 2.44 and 0.676, and *x* = *F*_{calc}/*F*_{max}.
 Method = robust weighting (Prince, 1982),
W = [weight] × [1 - (Δ*F*/6σ*F*)²]²
 (Δσ)_{max} = 0.001
 Δρ_{max} = 0.47 e Å⁻³
 Δρ_{min} = -0.47 e Å⁻³

H atoms were located in difference Fourier maps and refined isotropically. Refined distance ranges are as follows: C—H = 0.91 (2)–0.99 (2) Å, N—H = 0.74 (2)–0.84 (2) Å and O—H = 0.76 (2)–0.85 (2) Å.

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

Ni1—N2	2.0474 (11)	N4—C2	1.3402 (14)
Ni1—N3	2.0552 (12)	N5—O1	1.2402 (13)
Ni1—O4	2.1520 (10)	N5—O2	1.2589 (13)
N1—N2	1.3776 (12)	N5—O3	1.2548 (13)
N1—C2	1.4186 (14)	C1—C3	1.4919 (16)
N1—C5	1.3753 (14)	C3—C4	1.4106 (14)
N2—C3	1.3275 (14)	C4—C5	1.3701 (16)
N3—C2	1.2833 (14)	C5—C6	1.4863 (15)
N2—Ni1—N3	77.67 (4)	N3—Ni1—O4	88.43 (4)
N2—Ni1—O4	91.05 (4)		

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N4—H9...O1 ⁱ	0.83 (2)	2.256 (19)	2.8604 (18)	130.0 (17)
N4—H10...O2 ⁱⁱ	0.818 (19)	2.113 (19)	2.9171 (18)	167.5 (18)
O4—H12...O2	0.76 (2)	2.09 (2)	2.8537 (16)	179 (2)
O4—H11...O3 ⁱⁱⁱ	0.82 (2)	2.17 (2)	2.9849 (17)	169.9 (18)

Symmetry codes: (i) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (ii) $3 - x, 1 - y, 2 - z$; (iii) $\frac{5}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$.

For both compounds, data collection: SMART (Bruker, 1999); cell refinement: SAINT (Bruker, 1999); data reduction: SAINT; program(s) used to solve structure: SIR92 (Altomare *et al.*, 1994); program(s) used to refine structure: CRYSTALS (Betteridge *et al.*, 2003); molecular graphics: ATOMS (Dowty, 2000); software used to prepare material for publication: CRYSTALS.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1571). Services for accessing these data are described at the back of the journal.

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