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## Two Ternary Ni<sup>II</sup> Complexes: Bisglycinato(1,10-phenanthroline)nickel(II) Trihydrate and Bisglycinato(2,2'-bipyridine)nickel(II) Trihydrate

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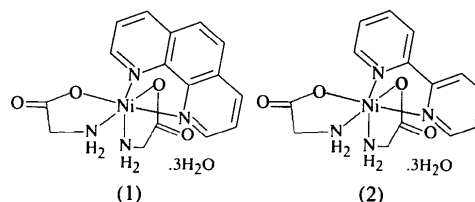
### Abstract

The two title compounds,  $[\text{Ni}(\text{C}_2\text{H}_4\text{NO}_2)_2(\text{C}_{12}\text{H}_8\text{N}_2)] \cdot 3\text{H}_2\text{O}$  and  $[\text{Ni}(\text{C}_2\text{H}_4\text{NO}_2)_2(\text{C}_{10}\text{H}_8\text{N}_2)] \cdot 3\text{H}_2\text{O}$ , are isostructural. Their structures consist of discrete complex molecules, together with water molecules of crystallization. All ligands are bidentate and the coordination polyhedron is a distorted octahedron. Distinct segregation of hydrophilic and hydrophobic regions appears along the *c* axis. In the hydrophilic region a three-dimensional network of hydrogen bonds is formed involving principally the water molecules. Aromatic interactions exist in the hydrophobic region.

### Comment

It is widely known that crystallization kinetics and consequently crystal morphology may be influenced by the presence of small amounts of foreign substances (Addadi, Berkovitch-Yellin, Weissbuch, Van Mil, Shimon, Lahav & Leiserowitz, 1985). In a previous study (Skoulika, Michaelides & Aubry, 1991), we reported the crystallization of the complex  $[\text{Ni}(\beta\text{-ala})_2] \cdot 2\text{H}_2\text{O}$  ( $\beta\text{-ala}$  is  $\beta\text{-alanine}$ ) in the presence of glycine. By stereochemical considerations we showed that it is probably the ternary complex  $[\text{Ni}(\beta\text{-ala})(\text{gly})] \cdot 2\text{H}_2\text{O}$  (gly is glycine) that is selectively adsorbed onto a particular crystal face and inhibits deposition onto that face. As part of a systematic investigation of similar systems, we undertook a study of the crystallization of  $[\text{Ni}(\text{gly})_2] \cdot 2\text{H}_2\text{O}$  in the presence of the aromatic amines

1,10-phenanthroline and 2,2'-bipyridine. In order to elucidate the geometry of the host-guest system, we determined the crystal structures of the two title ternary complexes  $[\text{Ni}(\text{gly})_2(o\text{-phen})] \cdot 3\text{H}_2\text{O}$  (1) (*o*-phen is 1,10-phenanthroline) and  $[\text{Ni}(\text{gly})_2(2,2'\text{-bpy})] \cdot 3\text{H}_2\text{O}$  (2) (2,2'-bpy is 2,2'-bipyridine).



Compounds (1) and (2) are isostructural. Their crystal structures consist of discrete complex molecules, which are very similar in shape and geometry, and water molecules of crystallization (Figs. 1 and 2). The coordination polyhedron around the Ni<sup>II</sup> atom is represented by a distorted octahedron. The equatorial positions [O(1), N(3), N(2) and O(3)] are occupied by the N atom and one O atom of one glycine ligand, the O atom of a second glycine ligand and one N atom belonging to the N–N ligand, while the axial positions [N(1) and N(4)] are occupied by the N atom of the second glycine and the remaining N atom of the N–N ligand. The geometry of the glycine ligands is as expected (Freeman & Guss, 1968). They have ‘bite’ angles of 80.7° for compound (1) and 80.6 and 80.7° for (2). The *o*-phenanthroline moiety is not exactly planar; the dihedral angles between the mean plane through the central six-membered ring and those through the adjacent aromatic rings are 3.7 and 1.8°. It is interesting to note that recently the structure of another isomer,  $[\text{Ni}(\text{gly})_2(\text{bpy})] \cdot 5.5\text{H}_2\text{O}$  (space group *Fddd*), has been published (Žák, Głowiak, Kameníček & Březina, 1990). In this case, compared with the title structures, one glycine O atom of the equatorial plane is replaced by a glycine N atom, while the remaining O atom occupies an axial position.

The pyridine rings of the bipyridine ligand are planar but twisted with respect to each other by an angle of 9.4° due to chelation strain. The *o*-phen and 2,2'-bpy ligands have bite angles of 78.6 and 77.9°, respectively. Their dimensions compare well with those observed in other metal complexes (Antolini, Marcotrigiano, Menabue, Pellacani, Saladini & Sola, 1985; Poletti, Stojaković, Prelesnik & Manojlović-Muir, 1990). The bond distances between Ni<sup>II</sup> and the ligands are within the ranges of literature values (Poletti, Stojaković, Prelesnik & Manojlović-Muir, 1990; Freeman & Guss, 1978). The equatorial coordination plane, from which the Ni atom deviates towards the axial N(1) atom by 0.033 Å for compound (1) and 0.038 Å for (2), shows a very slight tetrahedral distortion.

The molecules are ordered in the crystal lattice so that distinct segregation of hydrophobic and hydrophilic

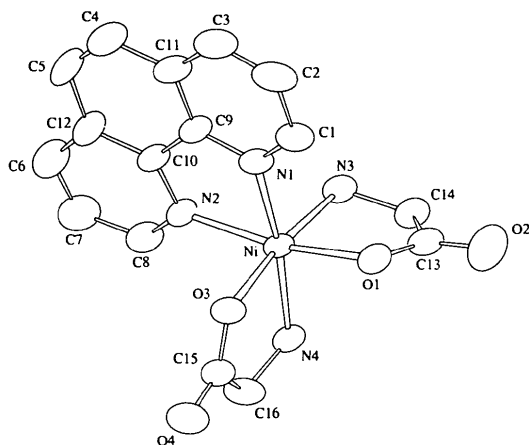


Fig. 1. ORTEP (Johnson, 1965) drawing of molecule (1). Ellipsoids are shown at the 50% probability level.

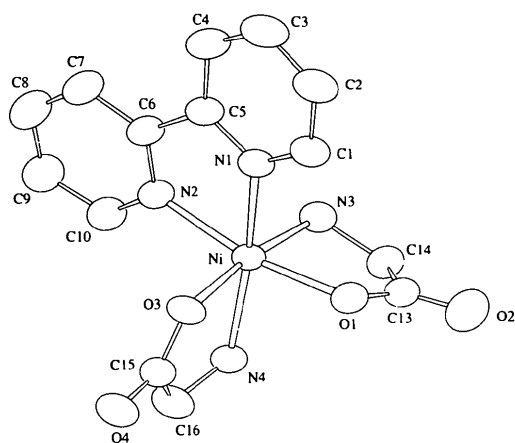


Fig. 2. ORTEP (Johnson, 1965) drawing of molecule (2). Ellipsoids are shown at the 50% probability level.

regions occurs along the *c* axis (Fig. 3). The hydrophilic layers comprise two parallel chains of glycine moieties linked by two hydrogen bonds. The aromatic parts of the molecules related by a center of symmetry interact through stacking interactions. The ordering of the aromatic rings in the structure may be approximated by the sandwich-herringbone structure type (Desiraju, 1989). The angle between the aromatic rings of the molecules related by a 2<sub>1</sub> axis is 89.8° for compound (1) and 83.1° for (2). This mode of packing results in the formation of channels along *c*. The three water molecules which bridge five complex molecules through hydrogen bonds are located within these channels. In this way a polymeric hydrogen-bonded lattice is formed. Generally, the replacement of the bpy ligand by the larger and more planar *o*-phen molecule results in stronger ring-stacking interactions with shorter interatomic separations. In some cases (Antolini, Battaglia, Bonamartini Corradi, Marcotrigiano, Menabue, Pellacani, Saladini & Sola, 1986; Antolini, Marcotrigiano, Menabue & Pel-

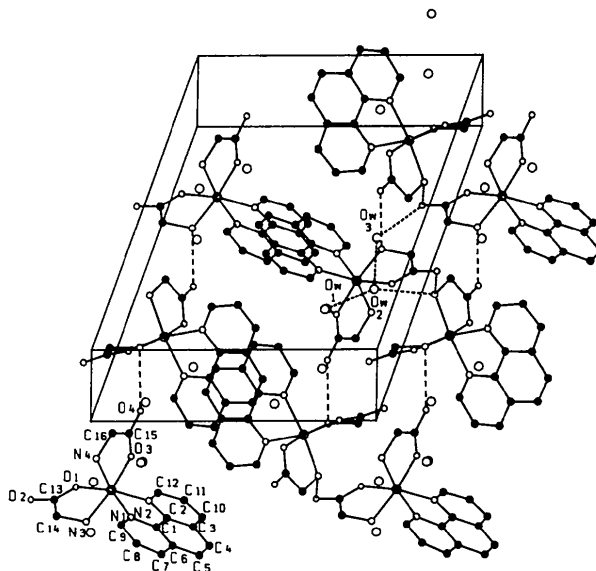


Fig. 3. View of the crystal structure of (1). Part of the hydrogen-bond network around the solvent molecules is depicted. The intermolecular hydrogen bonds are also shown. H atoms are omitted for clarity.

lacani, 1983; Antolini, Marcotrigiano, Menabue, Pellacani, Saladini & Sola, 1985) this may result in different molecular structures for the two complexes.

Preliminary crystallization experiments with [Ni(gly)<sub>2</sub>].2H<sub>2</sub>O in the presence of *o*-phen and bpy showed that these additives reduce the crystallization rate considerably without affecting the crystal morphology, *i.e.* they behave as non-selective inhibitors. An obvious reason for this is that the stereochemistry around the Ni atom of the ternary complex is quite different from that of [Ni(gly)<sub>2</sub>].2H<sub>2</sub>O (Freeman & Guss, 1968) and consequently the ternary complex cannot be selectively adsorbed on any crystal face of the [Ni(gly)<sub>2</sub>].2H<sub>2</sub>O crystals. This is supported by the fact that some changes in crystal morphology are observed by using additives such as serine, threonine, *etc.* Further details will be published later.

## Experimental

Compounds (1) and (2) were synthesized as described in the literature (Brezina, Sindelar, Kameníček & Lasovsky, 1988). Single crystals suitable for X-ray diffraction were obtained by slow evaporation of the solution and were not washed.

### Compound (1)

#### Crystal data

[Ni(C<sub>2</sub>H<sub>4</sub>NO<sub>2</sub>)<sub>2</sub>(C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>)]·  
3H<sub>2</sub>O  
*M<sub>r</sub>* = 441.1  
Monoclinic  
*P*2<sub>1</sub>/*c*

Cu *K*α radiation  
λ = 1.5418 Å  
Cell parameters from 25  
reflections  
θ = 16–23°

$a = 13.467 (1) \text{ \AA}$   
 $b = 9.304 (1) \text{ \AA}$   
 $c = 15.752 (2) \text{ \AA}$   
 $\beta = 109.11 (1)^\circ$   
 $V = 1864.9 \text{ \AA}^3$   
 $Z = 4$   
 $D_x = 1.57 \text{ Mg m}^{-3}$

$\mu = 1.957 \text{ mm}^{-1}$   
 $T = 293 \text{ K}$   
 Prismatic  
 $0.3 \times 0.2 \times 0.2 \text{ mm}$   
 Purple

2925 reflections  
 307 parameters  
 Only coordinates of H atoms  
 refined

Atomic scattering factors  
 from *International Tables*  
 for *X-ray Crystallography*  
 (1974, Vol. IV)

#### Data collection

Enraf–Nonius CAD-4  
 diffractometer  
 $\omega$ - $2\theta$  scans  
 Absorption correction:  
 none  
 3418 measured reflections  
 3249 independent reflections  
 2874 observed reflections  
 $[I > 3\sigma(I)]$

$R_{\text{int}} = 0.018$   
 $\theta_{\text{max}} = 70^\circ$   
 $h = -16 \rightarrow 16$   
 $k = 0 \rightarrow 11$   
 $l = 0 \rightarrow 19$   
 3 standard reflections  
 frequency: 120 min  
 intensity decay: not  
 significant

#### Refinement

Refinement on  $F$   
 $R = 0.058$   
 $wR = 0.071$   
 $S = 1.216$   
 2874 reflections  
 327 parameters  
 Only coordinates of H atoms  
 refined

$w = 1/[\sigma^2(F) + 0.006505F^2]$   
 $(\Delta/\sigma)_{\text{max}} = 0.7$   
 $\Delta\rho_{\text{max}} = 0.77 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.94 \text{ e \AA}^{-3}$   
 Atomic scattering factors  
 from *International Tables*  
 for *X-ray Crystallography*  
 (1974, Vol. IV)

#### Compound (2)

##### Crystal data

$[\text{Ni}(\text{C}_2\text{H}_4\text{NO}_2)_2(\text{C}_{10}\text{H}_8\text{N}_2)] \cdot$   
 $3\text{H}_2\text{O}$   
 $M_r = 417.1$   
 Monoclinic  
 $P2_1/c$   
 $a = 12.827 (1) \text{ \AA}$   
 $b = 9.416 (1) \text{ \AA}$   
 $c = 15.716 (1) \text{ \AA}$   
 $\beta = 109.33 (1)^\circ$   
 $V = 1791.2 \text{ \AA}^3$   
 $Z = 4$   
 $D_x = 1.55 \text{ Mg m}^{-3}$

Cu  $K\alpha$  radiation  
 $\lambda = 1.5418 \text{ \AA}$   
 Cell parameters from 25  
 reflections  
 $\theta = 16\text{--}32^\circ$   
 $\mu = 1.996 \text{ mm}^{-1}$   
 $T = 293 \text{ K}$   
 Prismatic  
 $0.2 \times 0.2 \times 0.1 \text{ mm}$   
 Purple

#### Data collection

Enraf–Nonius CAD-4  
 diffractometer  
 $\omega$ - $2\theta$  scans  
 Absorption correction:  
 none  
 3346 measured reflections  
 3232 independent reflections  
 2925 observed reflections  
 $[I > 3\sigma(I)]$

$R_{\text{int}} = 0.012$   
 $\theta_{\text{max}} = 70^\circ$   
 $h = -15 \rightarrow 15$   
 $k = 0 \rightarrow 11$   
 $l = 0 \rightarrow 19$   
 3 standard reflections  
 frequency: 120 min  
 intensity decay: not  
 significant

#### Refinement

Refinement on  $F$   
 $R = 0.056$   
 $wR = 0.068$   
 $S = 1.886$

$w = 1/[\sigma^2(F) + 0.00185F^2]$   
 $(\Delta/\sigma)_{\text{max}} = 0.6$   
 $\Delta\rho_{\text{max}} = 0.66 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.93 \text{ e \AA}^{-3}$

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

Compound (1)	$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$			$B_{\text{eq}}$
	$x$	$y$	$z$	
Ni	0.17629 (4)	0.20136 (6)	0.28404 (3)	2.18 (2)
O(1)	0.0594 (2)	0.3288 (3)	0.3035 (2)	2.72 (6)
O(2)	-0.0832 (3)	0.3198 (3)	0.3440 (3)	4.95 (9)
O(3)	0.2170 (2)	0.3521 (3)	0.2045 (2)	2.74 (6)
O(4)	0.1964 (3)	0.4137 (3)	0.0635 (2)	4.07 (7)
N(1)	0.2878 (3)	0.2876 (3)	0.3976 (2)	2.76 (7)
N(2)	0.3116 (2)	0.0767 (3)	0.2908 (2)	2.58 (6)
N(3)	0.1168 (2)	0.0577 (3)	0.3568 (2)	2.63 (6)
N(4)	0.0781 (2)	0.1356 (3)	0.1590 (2)	2.65 (7)
C(1)	0.2725 (4)	0.3920 (4)	0.4491 (2)	3.26 (9)
C(2)	0.3547 (4)	0.4397 (5)	0.5263 (3)	4.3 (1)
C(3)	0.4494 (4)	0.3793 (5)	0.5482 (3)	4.3 (1)
C(4)	0.5685 (4)	0.2037 (5)	0.5097 (3)	4.5 (1)
C(5)	0.5830 (3)	0.1023 (6)	0.4535 (3)	4.5 (1)
C(6)	0.5070 (4)	-0.0508 (5)	0.3161 (3)	4.4 (1)
C(7)	0.4199 (4)	-0.0937 (5)	0.2480 (3)	4.3 (1)
C(8)	0.3236 (3)	-0.0286 (4)	0.2384 (3)	3.4 (1)
C(9)	0.3840 (3)	0.2289 (4)	0.4177 (2)	2.65 (8)
C(10)	0.3991 (3)	0.1183 (4)	0.3595 (2)	2.75 (8)
C(11)	0.4688 (3)	0.2708 (5)	0.4935 (3)	3.55 (9)
C(12)	0.4981 (3)	0.0563 (5)	0.3751 (3)	3.45 (9)
C(13)	-0.0060 (3)	0.2628 (4)	0.3307 (2)	2.72 (8)
C(14)	0.0086 (3)	0.1015 (4)	0.3474 (2)	2.79 (8)
C(15)	0.1787 (3)	0.3355 (4)	0.1204 (2)	2.71 (8)
C(16)	0.1076 (4)	0.2061 (4)	0.0884 (3)	3.7 (1)
O(W1)	0.2810 (3)	0.6161 (4)	0.2884 (2)	5.5 (1)
O(W2)	0.1490 (3)	0.7285 (4)	0.3817 (3)	5.5 (1)
O(W3)	0.2095 (4)	0.7844 (4)	0.5703 (4)	7.4 (1)
Compound (2)				
Ni	0.17622 (4)	0.20955 (5)	0.29365 (3)	2.70 (1)
O(1)	0.0494 (2)	0.3346 (2)	0.3090 (1)	3.14 (5)
O(2)	-0.0953 (2)	0.3272 (3)	0.3563 (2)	4.86 (7)
O(3)	0.2191 (2)	0.3541 (3)	0.2115 (1)	3.33 (5)
O(4)	0.1989 (2)	0.4076 (3)	0.0693 (2)	4.11 (6)
N(1)	0.2913 (2)	0.3025 (3)	0.4069 (2)	3.10 (6)
N(2)	0.3199 (2)	0.0876 (3)	0.3085 (2)	3.15 (6)
N(3)	0.1128 (2)	0.0679 (3)	0.3665 (2)	3.25 (6)
N(4)	0.0719 (2)	0.1391 (3)	0.1680 (2)	3.11 (6)
C(1)	0.2688 (3)	0.4095 (4)	0.4543 (2)	3.25 (7)
C(2)	0.3453 (3)	0.4605 (4)	0.5324 (3)	4.25 (9)
C(3)	0.4474 (4)	0.3977 (5)	0.5631 (2)	4.8 (1)
C(4)	0.4717 (3)	0.2890 (5)	0.5137 (2)	4.39 (9)
C(5)	0.3921 (3)	0.2444 (4)	0.4347 (2)	3.59 (7)
C(6)	0.4103 (3)	0.1303 (4)	0.3759 (2)	3.29 (7)
C(7)	0.5127 (3)	0.0704 (5)	0.3880 (3)	4.35 (9)
C(8)	0.5226 (3)	-0.0357 (5)	0.3302 (3)	4.9 (1)
C(9)	0.4288 (3)	-0.0829 (4)	0.2638 (3)	4.38 (9)
C(10)	0.3292 (3)	-0.0179 (4)	0.2552 (2)	3.76 (7)
C(13)	-0.0170 (3)	0.2683 (4)	0.3386 (2)	3.02 (7)
C(14)	-0.0013 (3)	0.1097 (3)	0.3542 (2)	3.34 (7)
C(15)	0.1785 (3)	0.3326 (4)	0.1271 (2)	3.13 (6)
C(16)	0.1024 (3)	0.2071 (4)	0.0958 (2)	4.09 (8)
O(W1)	0.2945 (2)	0.6156 (3)	0.2869 (2)	4.93 (7)
O(W2)	0.1654 (3)	0.7479 (4)	0.3809 (2)	5.65 (8)
O(W3)	0.2365 (3)	0.7988 (3)	0.5716 (3)	5.90 (9)

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

	(1)	(2)
Ni—O(1)	2.073 (3)	2.086 (2)
Ni—O(3)	2.071 (3)	2.072 (2)
Ni—N(1)	2.084 (3)	2.091 (2)

Ni—N(2)	2.134 (3)	2.118 (3)
Ni—N(3)	2.085 (3)	2.089 (3)
Ni—N(4)	2.073 (3)	2.093 (2)
O(1)—Ni—O(3)	93.8 (1)	94.58 (9)
O(1)—Ni—N(1)	91.2 (1)	91.3 (1)
O(1)—Ni—N(2)	169.0 (1)	167.63 (9)
O(1)—Ni—N(3)	80.7 (1)	80.6 (1)
O(1)—Ni—N(4)	91.7 (1)	90.5 (1)
O(3)—Ni—N(1)	90.0 (1)	89.9 (1)
O(3)—Ni—N(2)	90.4 (1)	91.4 (1)
O(3)—Ni—N(3)	173.2 (1)	172.95 (9)
O(3)—Ni—N(4)	80.7 (1)	80.7 (1)
N(1)—Ni—N(2)	78.6 (1)	77.9 (1)
N(1)—Ni—N(3)	94.2 (1)	95.4 (1)
N(1)—Ni—N(4)	170.4 (1)	170.5 (1)
N(2)—Ni—N(3)	95.8 (1)	94.3 (1)
N(2)—Ni—N(4)	98.9 (1)	101.2 (1)
N(3)—Ni—N(4)	95.3 (1)	94.1 (1)

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

D—H...A	D...A		D—H...A	
	(1)	(2)	(1)	(2)
O(W1)—H'(W1)...O(3)	2.789	2.765	178.8	177.0
O(W2)—H'(W2)...O(W1)	2.851	2.845	165.5	164.5
N(4')—H'(N4)...O(W2)	3.037	3.059	176.5	166.0
N(3 <sup>iv</sup> )—H'(N3)...O(W2)	3.100	3.080	145.3	160.8
O(W2)—H'(W2)...O(W3)	2.861	2.869	158.7	141.7
O(W3)—H'(W3)...O(4 <sup>iii</sup> )	2.814	2.804	160.0	167.3
O(W3)—H'(W3)...O(2 <sup>iv</sup> )	2.677	2.707	153.8	169.3
N(4)—H'(N4)...O(2')	2.939	2.989	149.4	162.3
N(3)—H'(N3)...O(4 <sup>iii</sup> )	3.088	3.017	163.4	159.0

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

*E* maps revealed all non-H atoms and the H atoms appeared on difference maps. Anisotropic displacement parameters were used for non-H atoms and isotropic displacement parameters for H atoms. Data reduction was carried out using the SDP software package (Enraf-Nonius, 1979). The structures were solved by direct methods using SHELXS86 (Sheldrick, 1985) and refined by least squares using SHELX76 (Sheldrick, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HR1020). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## [3,9-Dimethyl-4,8-diaza-3,8-undecadiene-2,10-dione dioximato(1-)](thiocyanato)-copper(II) and [3,6,6,9-Tetramethyl-4,8-diaza-3,8-undecadiene-2,10-dione dioximato(1-)](isothiocyanato)copper(II)

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## Abstract

The coordination geometries about the Cu<sup>II</sup> ions in both [3,9-dimethyl-4,8-diaza-3,8-undecadiene-2,10-dione dioximato(1-)](thiocyanato)copper(II), [Cu(C<sub>11</sub>H<sub>19</sub>N<sub>4</sub>O<sub>2</sub>)(SCN)] (1), and [3,6,6,9-tetramethyl-4,8-diaza-3,8-undecadiene-2,10-dione dioximato(1-)](isothiocyanato)copper(II), [Cu(C<sub>13</sub>H<sub>23</sub>N<sub>4</sub>O<sub>2</sub>)(NCS)] (2), are distorted square pyramidal with the four diazadioxime N atoms in equatorial positions and the monodentate ligand axial. This monodentate axial ligand is an S-bonded thiocyanato group in complex (1) and an N-bonded isothiocyanato group in (2). The intramolecular O...O hydrogen-bond lengths are 2.530 (4) and 2.490 (2) Å in complexes (1) and (2), respectively.

## Comment

Metal–thiocyanato complexes have been investigated extensively in order to solve the interesting problem