

## Two furopyridine complexes of nickel(II) isothiocyanate

Jozef Miklovič,<sup>a</sup> Alžbeta Krutošiková<sup>a</sup> and Peter Baran<sup>b\*</sup><sup>a</sup>Department of Chemistry, Faculty of Natural Sciences, University of St Cyril and Methodius, SK 917 01 Trnava, Slovakia, and <sup>b</sup>Department of Chemistry, University of Puerto Rico, Río Piedras Campus, PO Box 23346, San Juan, PR 00931-3346, USA  
Correspondence e-mail: baranp@adam.uprr.pr

Received 4 March 2004

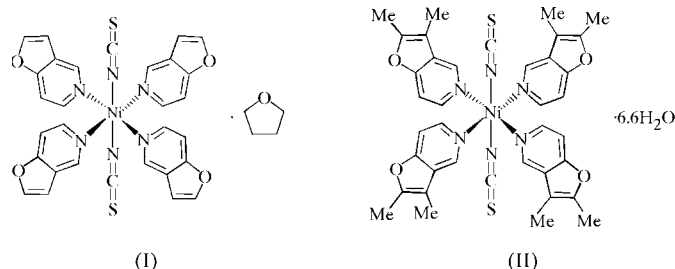
Accepted 31 March 2004

Online 30 April 2004

Pyridine fused with a furan ring (fupy), and its dimethyl derivative, have been used for the first time as ligands to synthesize potentially new Werner clathrates. The extended aromatic system of pyridine-like ligands influences considerably the molecular structure of prepared nickel complexes. The molecular structure of tetrakis(furo[3,2-*c*]pyridine)bis(isothiocyanato)nickel(II) tetrahydrofuran (THF) solvate,  $[\text{Ni}(\text{NCS})_2(\text{C}_7\text{H}_5\text{NO})_4] \cdot \text{C}_4\text{H}_8\text{O}$  or  $[\text{Ni}(\text{NCS})_2(\text{fupy})_4] \cdot \text{THF}$ , (I), reveals a 'four-blade propeller' arrangement of ligands, with the angles between the fupy planes and the basal octahedron plane spanning the range 38.7–55.3°. These angles are much larger (69.9–78.8°) in the centrosymmetric complex tetrakis(2,3-dimethylfuro[3,2-*c*]pyridine)bis(isothiocyanato)nickel(II) 6.6-hydrate,  $[\text{Ni}(\text{NCS})_2(\text{C}_9\text{H}_9\text{NO})_4] \cdot 6.6\text{H}_2\text{O}$  or  $[\text{Ni}(\text{NCS})_2(\text{Me}_2\text{fupy})_4] \cdot 6.6\text{H}_2\text{O}$ , (II), in which crystallographically imposed inversion symmetry is present.

## Comment

Pyridine and its derivatives are common organic ligands in transition metal coordination compounds. Interest in nickel complexes with pyridines increased after 1957, when it was demonstrated (Schaeffer *et al.*, 1957) that some Werner complexes are able to absorb organic compounds in a reversible manner. Recently, the syntheses of furo[3,2-*c*]pyridines and pyrrolo[2',3':4,5]furo[3,2-*c*]pyridines have been reported



(New *et al.*, 1989; Bencková & Krutošiková, 1995; Krutošiková & Dandárová, 1994; Krutošiková & Sleziač, 1996). To the best

of our knowledge, until our recent synthesis of a series of  $[\text{Ni}(\text{NCS})_2(\text{fupy}^*)_4]$  complexes, with fupy\* being differently substituted furopyridines (Miklovič *et al.*, 2003), these compounds had not been used in complexation reactions. This paper describes the molecular and crystal structures of the first two members of this family, namely  $[\text{Ni}(\text{NCS})_2(\text{fupy})_4] \cdot \text{THF}$ , (I) (where fupy is furo[3,2-*c*]pyridine and THF is tetrahydrofuran), and  $[\text{Ni}(\text{NCS})_2(\text{Me}_2\text{fupy})_4] \cdot 6.6\text{H}_2\text{O}$ , (II), (where  $\text{Me}_2\text{fupy}$  is 2,3-dimethylfuro[3,2-*c*]pyridine).

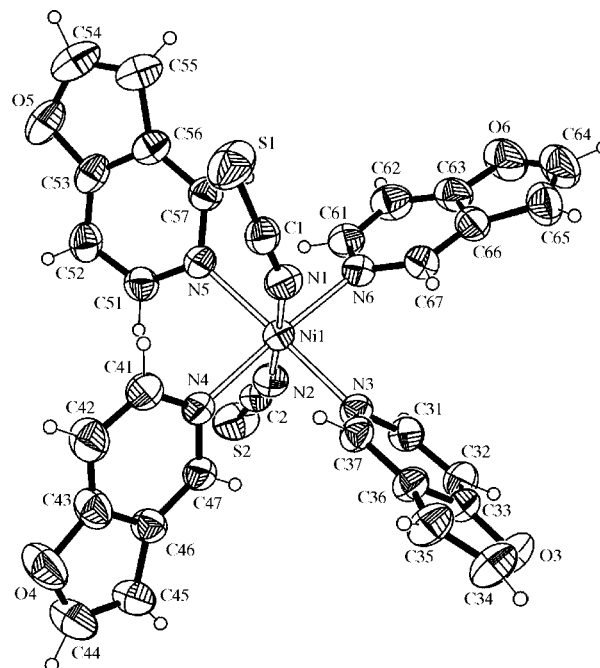


Figure 1

A view of (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The solvate THF molecule is not shown.

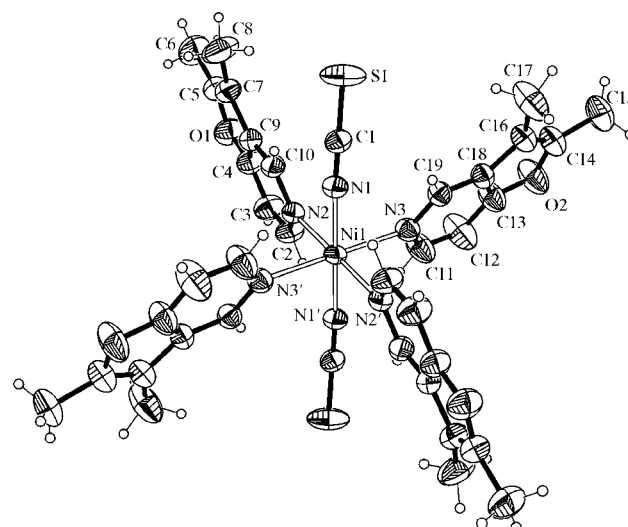


Figure 2

A view of (II), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Lattice water molecules are not shown.

In complexes (I) (Fig. 1) and (II) (Fig. 2), the central Ni atom is in a tetragonally distorted bipyramidal environment. Four N atoms from monodentate furo-pyridine ligands form the tetragonal base, with atom Ni1 sitting in the idealized plane. Two N atoms from isothiocyanate anions occupy the apical positions, at the Ni–N distances [2.0730 (18) and 2.0781 (18) Å for (I), and 2.051 (2) Å for (II)] considerably shorter than the equatorial ones [2.1262 (16)–2.1547 (17) Å for (I), and 2.172 (2) and 2.195 (2) Å for (II)]. Both compounds contain interstitial solvent molecules in the crystal structure and can be considered as Werner clathrates (Lipkowski, 1996). Indeed, their molecular structures possess all the characteristics of Werner host complexes.

A Cambridge Structural Database (CSD; Allen, 2002) search for mononuclear complexes with four monodentate pyridine-type ligands coordinated to Ni<sup>II</sup> revealed 110 structures, all of them containing Ni in a *trans*-octahedral coordination, with a high preference (84 compounds) for species with NCS<sup>−</sup> as the two *trans* anionic ligands. These 84 structures represent 91 hits (more than one symmetry-independent molecule present in multiple cases), from which only 79 were used for comparison with (I) and (II) for the following reasons. Eight hits were omitted (CSD refcodes CULLOK10, CULLUQ10, GAJXOE, GAJXUK and SABHAE10), since their structural parameters were of poor quality and the geometrical data for their [NiN<sub>6</sub>] polyhedra were out of the range of the other 79 species. Another four hits, all describing complexes with 4-vinylpyridine, were omitted from the pool because of anomalous rhombohedral distortion of their [NiN<sub>6</sub>] polyhedra (CSD refcodes DOJXOP, DOJXOP01, VAXVEV and VAXVIZ). In addition to 79 hits with differently substituted pyridines, one Ni<sup>II</sup> complex was found with quinoline as an equatorial ligand (Soldatov & Lipkovski, 1997). This means that the title compounds, (I) and (II), represent only the second and third examples of [Ni(NCS)<sub>2</sub>(L)<sub>4</sub>] complexes, with *L* being a monodentate ligand in which pyridine is part of a condensed ring system.

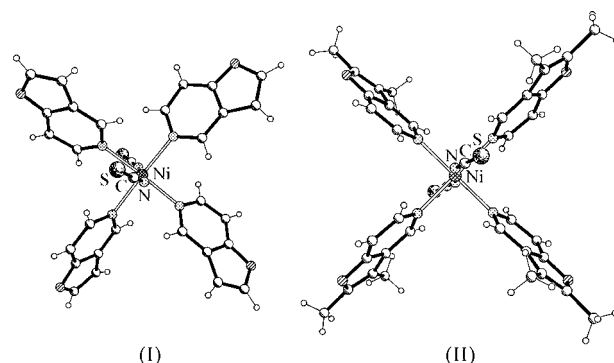
As was elegantly described by Lipkowski (1996), the most common structure for [Ni(NCS)<sub>2</sub>(L)<sub>4</sub>] complexes is a ‘four-blade propeller’ arrangement of ligands around the central Ni atom, which minimizes the energy of the non-bonded interactions within the molecule. Compound (I) adopts the ‘propeller’ structure, while (II) represents an alternative centrosymmetric arrangement of the Me<sub>2</sub>fupy ligands. It is believed (Lipkowski, 1996) that the preference for the alternative arrangement is probably affected by the presence of interstitial molecules; in the case of the title compounds, these are THF in (I) and H<sub>2</sub>O in (II). The differences in molecular conformation between (I) (Fig. 1) and (II) (Fig. 2) are worth discussing in detail and comparing with compounds from the CSD.

The axial–equatorial effect in Ni<sup>II</sup> complexes is known as a version of the ‘*cis* effect’ (Gažo *et al.*, 1982). The ranges for Ni–N<sub>ax</sub> and Ni–N<sub>eq</sub> distances for the above-mentioned 79 hits from the CSD were 2.01–2.10 and 2.11–2.17 Å, respectively. The calculated mean difference between the averaged Ni–N<sub>ax</sub> and Ni–N<sub>eq</sub> distances was 0.07 Å for the database

data, 0.06 Å for (I), and noticeably higher (0.13 Å) for (II), but still within the range of the CSD data (0.03–0.15 Å). A more extreme compression of the tetragonal bipyramid (0.22 Å) was observed for the quinoline complex (Soldatov & Lipkovski, 1997). Because (II) has a centrosymmetric arrangement of ligands, the three angles in the Ni coordination polyhedron are 180°, while they are 176.43 (6), 175.81 (6) and 177.03 (7)° in (I).

The ‘propeller’ arrangement of four equatorial ligands is a preferred environment for the central Ni atom and is observed in (I), while the Me<sub>2</sub>fupy ligands in (II) are not far from being perpendicular to the basal octahedron plane formed by four N donor atoms. However, the propeller arrangement of the fupy ligands in (I) is not very regular, as seen from the conformational angles between the normals of the calculated fupy planes and the octahedron basal plane [38.70 (7), 47.02 (6), 51.98 (5) and 55.28 (4)°]. Much higher conformational angles are observed for the Me<sub>2</sub>fupy ligands in (II) [69.97 (9) and 78.86 (8)°]. The calculated best-fit planes for the ligands, which are mutually *trans*, are almost perpendicular to each other [81.44 (5) and 86.12 (5)°] in (I), while being coplanar in (II). It seems to be a general trend that, when equatorial ligands are coplanar or almost coplanar, their conformational angles are higher. Lower conformational angles (ideally 45°) minimize steric hindrance between equatorial ligands and axial NCS<sup>−</sup> anions. This is why the plane in which lie two NCS<sup>−</sup> anions in (II) is almost diagonal to the [N<sub>4</sub>] square (which forms the base of the Ni octahedron), while in (I), the same plane collides with the Ni1→N5 vector (Fig. 3).

The reasons for propeller *versus* centrosymmetric arrangements seem to be well understood (Lipkowski, 1981; Nassimbeni *et al.*, 1986), but to the best of our knowledge, nobody has previously discussed the orientation of NCS<sup>−</sup> ligands with respect to the arrangement of four equatorial ligands, nor the mutual conformation of two NCS<sup>−</sup> ligands. Linear NCS groups are attached to the Ni atoms, forming Ni–N–C angles of 151.07 (16) and 167.61 (18)° in (I) and two angles of 161.2 (2)° in (II). *Trans* NCS ligands are not necessarily coplanar. They form a C–N···N–C dihedral angle of −13.9 (8)° in (I) and 180° in (II), as depicted in Fig. 3. The observed centrosymmetric ‘*trans*-NCS’ conformation in (II) is by far the most preferable arrangement of NCS<sup>−</sup> anions in Ni<sup>II</sup>



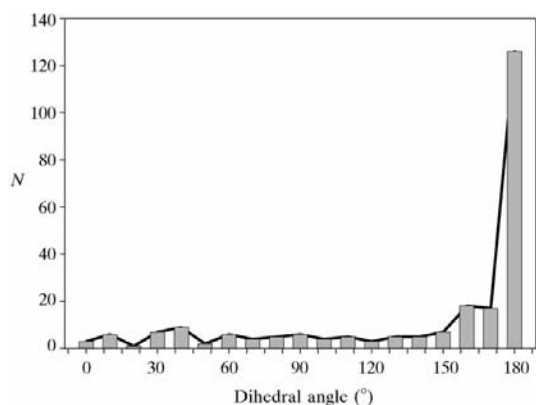
**Figure 3**

A view into the basal octahedral plane of [Ni(NCS)<sub>2</sub>(fupy\*)<sub>4</sub>] for (I) and (II), showing the differences in NCS conformation.

Werner complexes (Fig. 4), while the 'cis' conformation found in (I) is relatively rare. Since it is believed that the propeller arrangement of four equatorial pyridine-type ligands is adopted in order to minimize intramolecular interactions, the apical NCS<sup>-</sup> anions could be liberated to afford any orientation with respect to the basal plane. Indeed, the angle between the plane in which both NCS and Ni lie and an Ni→N<sub>pyridine</sub> vector is typically in the range 42–45°, which not inevitably further minimizes the steric hindrance between equatorial and axial ligands. Such behaviour would be rather expected for centrosymmetric complexes in which the 45° angle (as defined above) was the only means of minimizing intramolecular interactions, but angles close to 0 or 31° were observed for centrosymmetric complexes in the CSD search.

In contrast with the database statistical results, (I) possesses the 'cis' mutual conformation of NCS groups. The latter form angles of 3.2 and 21.3° with the Ni1→N5 vector. This angle is 41.6° in (II), the highest value among the centrosymmetric database complexes. It seems to us that other factors (probably intermolecular host–guest or host–host interactions) might significantly influence the fine-tuning of the molecular structure of Werner clathrates.

In (I), a THF molecule is trapped in the intermolecular cavity between four complex molecules, with closest H...H or O1...H intermolecular contacts of 2.5 Å and longer. In (II), the water molecules which were present were disordered (see *Experimental*). Two mutually almost perpendicular [86.7 (1)°] π–π stacking interactions between coplanar aromatic furan rings, which are held 3.52 (2) and 3.61 (4) Å apart, seem to be the driving packing forces. The energetic contribution to the packing from the aromatic ring interactions and a lack of dominant determining host–guest interactions might explain the centrosymmetric arrangement in (II). Since the involvement of more extended aromatic molecules, such as fupy and Me<sub>2</sub>fupy, as equatorial ligands does not have (beside quinoline) an analogy in the family of [Ni(NCS)<sub>2</sub>(L)<sub>4</sub>] complexes, more structures with extended aromatic monodentate ligands will have to be studied to draw statistically more relevant and precise conclusions about the molecular structure.



**Figure 4**

A chart showing the population (*N*) of crystallographically characterized [NiA<sub>4</sub>(NCS)<sub>2</sub>] Werner complexes (where *A* is any *N*-monodentate ligand) versus the dihedral angle between *trans* NCS<sup>-</sup> anions.

## Experimental

The organic ligands were prepared according to the literature procedures of Eloy & Deryckere (1971) (fupy) and Bobošík *et al.* (1995) (Me<sub>2</sub>fupy). To NiCl<sub>2</sub>·6H<sub>2</sub>O (0.04 mol) in ethanol (60 ml) was added finely divided KSCN powder (0.08 mol). The KCl which precipitated was filtered off and fupy (0.16 mol) or Me<sub>2</sub>fupy (0.16 mol) in ethanol (60 ml) was added to the pure solution. At room temperature, small crystals were formed within 2–3 d. Crystals suitable for X-ray diffraction study were obtained after the slow diffusion of diethyl ether into a tetrahydrofuran solution of (I) or a wet dichloromethane solution of (II).

## Compound (I)

### Crystal data

[Ni(NCS)<sub>2</sub>(C<sub>7</sub>H<sub>5</sub>NO)<sub>4</sub>].C<sub>4</sub>H<sub>8</sub>O  
*M<sub>r</sub>* = 723.45  
 Triclinic, *P* $\bar{1}$   
*a* = 9.4916 (10) Å  
*b* = 10.7191 (11) Å  
*c* = 17.8360 (19) Å  
 $\alpha$  = 99.580 (2)°  
 $\beta$  = 92.278 (2)°  
 $\gamma$  = 108.726 (2)°  
*V* = 1686.2 (3) Å<sup>3</sup>  
*Z* = 2  
*D<sub>x</sub>* = 1.425 Mg m<sup>-3</sup>

Mo *K*α radiation  
 Cell parameters from 983 reflections  
 $\theta$  = 2.5–27.7°  
 $\mu$  = 0.75 mm<sup>-1</sup>  
*T* = 300 (2) K  
 Prism, blue  
 0.50 × 0.36 × 0.30 mm

### Data collection

Bruker SMART 1K CCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (*XPREP*; Sheldrick, 1990)  
*T<sub>min</sub>* = 0.829, *T<sub>max</sub>* = 0.936  
 10 159 measured reflections

7414 independent reflections  
 6280 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.018  
 $\theta_{max}$  = 28.0°  
*h* = -12 → 11  
*k* = -13 → 11  
*l* = -22 → 23

**Table 1**

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

Ni1–N2	2.0730 (18)	Ni1–N4	2.1547 (17)
Ni1–N1	2.0781 (18)	S1–C1	1.627 (2)
Ni1–N3	2.1262 (16)	S2–C2	1.635 (2)
Ni1–N5	2.1336 (16)	N1–C1	1.154 (3)
Ni1–N6	2.1354 (17)	N2–C2	1.151 (3)
<hr/>			
N2–Ni1–N1	177.03 (7)	N2–Ni1–N4	89.17 (7)
N2–Ni1–N3	93.18 (7)	N1–Ni1–N4	91.04 (7)
N1–Ni1–N3	89.79 (6)	N3–Ni1–N4	86.74 (6)
N2–Ni1–N5	89.99 (7)	N5–Ni1–N4	90.57 (6)
N1–Ni1–N5	87.05 (7)	N6–Ni1–N4	176.43 (6)
N3–Ni1–N5	175.81 (6)	C1–N1–Ni1	151.07 (16)
N2–Ni1–N6	88.26 (7)	C2–N2–Ni1	167.61 (18)
N1–Ni1–N6	91.66 (7)	N1–C1–S1	177.8 (2)
N3–Ni1–N6	90.92 (6)	N2–C2–S2	179.8 (2)
N5–Ni1–N6	91.91 (6)		

**Table 2**

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

Ni1–N1	2.051 (2)	S1–C1	1.620 (3)
Ni1–N3	2.172 (2)	N1–C1	1.156 (3)
Ni1–N2	2.195 (2)		
<hr/>			
N1–Ni1–N3	89.52 (9)	C1–N1–Ni1	161.2 (2)
N1–Ni1–N2	89.76 (9)	N1–C1–S1	178.0 (3)
N3–Ni1–N2	90.12 (9)		

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.036$   
 $wR(F^2) = 0.109$   
 $S = 1.05$   
 7414 reflections  
 448 parameters  
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0644P)^2 + 0.5868P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.56 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.54 \text{ e } \text{Å}^{-3}$

## Compound (II)

### Crystal data

$[\text{Ni}(\text{NCS})_2(\text{C}_9\text{H}_9\text{NO})_4] \cdot 6.6\text{H}_2\text{O}$   
 $M_r = 882.46$   
 Triclinic,  $P\bar{1}$   
 $a = 9.1663 (10) \text{ Å}$   
 $b = 10.5562 (11) \text{ Å}$   
 $c = 12.1745 (13) \text{ Å}$   
 $\alpha = 79.863 (2)^\circ$   
 $\beta = 79.030 (2)^\circ$   
 $\gamma = 74.521 (2)^\circ$   
 $V = 1104.7 (2) \text{ Å}^3$

$Z = 1$   
 $D_x = 1.326 \text{ Mg m}^{-3}$   
 Mo  $K\alpha$  radiation  
 Cell parameters from 801 reflections  
 $\theta = 3.4\text{--}27.9^\circ$   
 $\mu = 0.59 \text{ mm}^{-1}$   
 $T = 299 (2) \text{ K}$   
 Prism, blue  
 $0.18 \times 0.18 \times 0.13 \text{ mm}$

### Data collection

Bruker SMART 1K CCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (XPREP; Sheldrick, 1990)  
 $T_{\min} = 0.793$ ,  $T_{\max} = 0.984$   
 4782 measured reflections

4782 independent reflections  
 3571 reflections with  $I > 2\sigma(I)$   
 $\theta_{\max} = 29.0^\circ$   
 $h = -11 \rightarrow 12$   
 $k = -13 \rightarrow 14$   
 $l = 0 \rightarrow 16$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.052$   
 $wR(F^2) = 0.152$   
 $S = 1.06$   
 4782 reflections  
 236 parameters  
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0690P)^2 + 0.6061P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.54 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -1.52 \text{ e } \text{Å}^{-3}$

All H atoms were positioned geometrically and treated as riding, with C—H distances in the range 0.93–0.97 Å and with  $U_{\text{iso}}(\text{H}) = 1.2$  or  $1.5U_{\text{eq}}(\text{C})$ . In (I), the tetrahydrofuran molecule in the asymmetric unit is equally disordered over two interpenetrating orientations. This was allowed for in the refinement by use of appropriate DFIX restraints on the C—C and C—O distances. There is a solvent-containing volume (*ca* 250 Å<sup>3</sup>) in the lattice of (II) centred at  $(0, \frac{1}{2}, \frac{1}{2})$ . The electron-density peaks corresponding to disordered partial-occupancy water molecules were not well defined. The SQUEEZE option in PLATON (Spek, 2003) identified a density of approximately 66 electrons, corresponding to a disordered solvent of 6.6 water molecules per unit cell. The presence of water as the only solvent in the lattice was confirmed by IR measurement. Refinement was then concluded with a 'dry' data set.

For both compounds, data collection: SMART (Bruker, 1997); cell refinement: SMART; data reduction: SAINT (Bruker, 1997); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997). For compound (I), program(s) used to refine structure: SHELXL97 (Sheldrick, 1997). For compound (II), program(s) used to refine structure: SHELXL97 (Sheldrick, 1997) and PLATON (Spek, 2003). For both compounds, molecular graphics: SHELXTL (Bruker, 1999); software used to prepare material for publication: SHELXTL.

This work was partially supported by funds from the Department of Chemistry, Faculty of Natural Sciences, University of St Cyril and Methodius, and by the Slovak Grant Agency, VEGA, of the Slovak Ministry of Education (grant No. 1/0069/03). Dr Raphael G. Raptis (UPR) is gratefully acknowledged for providing access to the X-ray diffractometer.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1744). Services for accessing these data are described at the back of the journal.

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