

Transition metal complexes with thiosemicarbazide-based ligands. III. [4-(2-Diphenylphosphino- α -ethoxybenzyl- κP)-*S*-methyl-1-(4-oxidopent-3-en-4-ylidene- κO)-thiosemicarbazido- $\kappa^2 N^1, N^4$]nickel(II)

Bojana M. Drašković,^a Goran A. Bogdanović,^{a*}
Vukadin M. Leovac,^b Ilija D. Brčeski^c and Dejan Poletić^d

^aVinča Institute of Nuclear Sciences, Laboratory of Theoretical Physics and Condensed Matter Physics, PO Box 522, 11001 Belgrade, Serbia and Montenegro, ^bDepartment of Chemistry, Faculty of Sciences, University of Novi Sad, Trg Dositeja Obradovića 3, 21000 Novi Sad, Serbia and Montenegro, ^cFaculty of Chemistry, University of Belgrade, Studentski trg 16, 11000 Belgrade, Serbia and Montenegro, and ^dDepartment of General and Inorganic Chemistry, Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11000 Belgrade, Serbia and Montenegro

Correspondence e-mail: goranb@vin.bg.ac.yu

Received 20 March 2006

Accepted 22 May 2006

Online 30 June 2006

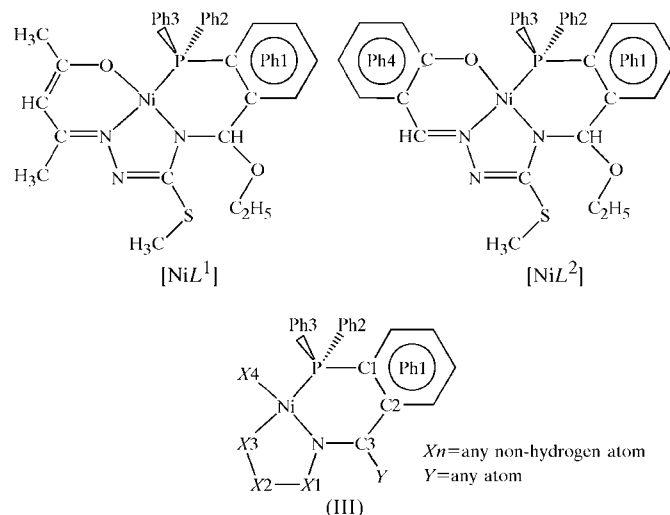
The title compound, $[\text{Ni}(\text{C}_{28}\text{H}_{30}\text{N}_5\text{O}_2\text{PS})]$, crystallizes with two independent molecules in the asymmetric unit. The Ni^{II} atoms are in significantly deformed square-planar environments formed by an ONNP donor set from a thiosemicarbazide-based tetradentate ligand. The Ni^{II} atom and the ONN donor atoms are nearly coplanar, while the P atom deviates from their mean planes by 0.278 (4) and 0.202 (4) Å for the two independent molecules. The P-containing chelate rings are remarkably non-planar, adopting a boat conformation, which is unusual for chelate rings in transition metal complexes with thiosemicarbazide-based tetradentate ligands. The orientation of the ethoxy group bonded to this chelate ring is caused by an intramolecular C—H $\cdots\pi$ interaction with the opposing phenyl ring. There are no hydrogen bonds; instead, numerous intermolecular C—H $\cdots\pi$ interactions dominate in the crystal packing.

Comment

Transition metal complexes with thiosemicarbazide-based ligands have been very extensively investigated because of their interesting structural properties and biological activities (Campbell, 1975; Padhye & Kauffman, 1985; West *et al.*, 1991; Casas *et al.*, 2000; Beraldo & Gambino, 2004). The present work is part of a systematic study of transition metal complexes containing thiosemicarbazide-based ligands, aimed at investigating their structural properties and the influence of

the thiosemicarbazide substituents on the properties of the complexes (Leovac *et al.*, 2000, 2002; Bogdanović *et al.*, 2001).

Among the more than 150 crystal structures of metal complexes with isothiosemicarbazide-based ligands (ITSC), the title compound, $[\text{NiL}^1]$, represents a rare example of a transition metal complex involving a P atom in its coordination environment. Only one other metal complex, [4-(2-diphenylphosphino- α -ethoxybenzyl)-3-methyl-1-salicylideneisothiosemicarbazido]nickel(II), with an ITSC ligand possessing a P atom as one of ligand atoms, has hitherto been reported (Bogdanović *et al.*, 1998).



The asymmetric unit of the $[\text{NiL}^1]$ complex (Fig. 1) contains two crystallographically independent molecules, denoted $[\text{NiL}^1]^a$ and $[\text{NiL}^1]^b$. These molecules are of the same composition but have slightly different conformations. The mutual orientation of the molecules is shown in Fig. 2, from which it can be seen that the angle between the coordination plane of molecules $[\text{NiL}^1]^a$ and $[\text{NiL}^1]^b$ is 56.4 (1)°. The

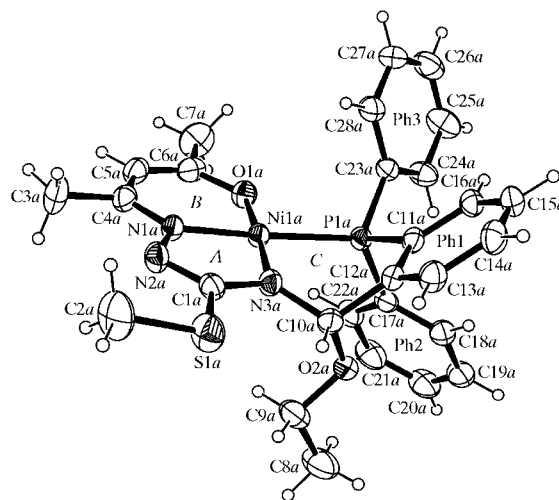


Figure 1

An ORTEP (Burnett & Johnson, 1996) drawing of $[\text{NiL}^1]^a$, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 40% probability level.

square-planar coordination geometry of the Ni atom is significantly deformed. Atoms Ni1, O1, N1 and N3 are nearly coplanar, but atoms P1 deviate from the mean plane by 0.278 (4), 0.202 (4) and 0.280 (3) Å for molecules $[\text{NiL}^1]^a$, $[\text{NiL}^1]^b$ and $[\text{NiL}^2]$, respectively. The L^1 ligands are coordinated to the Ni atom through four atoms (O1, N1, P1 and N3), forming three fused chelate rings (Fig. 1), one being five-membered (ring A; Ni1/N1/N2/C1/N3) and two six-membered [ring B (Ni1/N1/C4–C6/O1) and ring C (Ni1/N3/C10/C12/C11/P1)]. Rings A and B are nearly planar, with delocalized π bonds (Table 1). However, ring C is non-planar, adopting a boat conformation with atoms Ni1, N3, C11 and C12 approximately coplanar. The conformational parameters (Cremer & Pople, 1975) of molecules $[\text{NiL}^1]^a$, $[\text{NiL}^1]^b$ and $[\text{NiL}^2]$ (Table 2) are very similar. This non-planar form of a six-membered chelate ring in metal complexes with ITSC ligands is unusual and could be caused by (i) the addition of EtOH across the azomethine N3=C10 bonds and/or (ii) the presence of P atoms, which tends to decrease the Ni1–P1–C11 angles, as described by Brčeski *et al.* (2003).

The conformation of ring C in similar square-planar metal complexes [structure (III) in the scheme] that possess a triphenylphosphine fragment and two condensed chelate rings were also analyzed. In almost all of the 29 examples found in the Cambridge Structural Database (Version of April 2005; Allen, 2002), the six-membered rings were more or less non-planar, with an average value of 22.3° for the largest C1–P–M–N torsion angle. On the other hand, the most planar part of the rings was the P–C1–C2–C3 fragment, with a mean P–C1–C2–C3 torsion angle of 5.7°. As shown in Fig. 3, a direct relation exists between the values of the C1–P–M–N torsion angle and the displacement of the P atom (Δ_P) from the mean plane of the chelate ring. The rings are the most puckered when the N–C3 and C3–C2 bonds are single

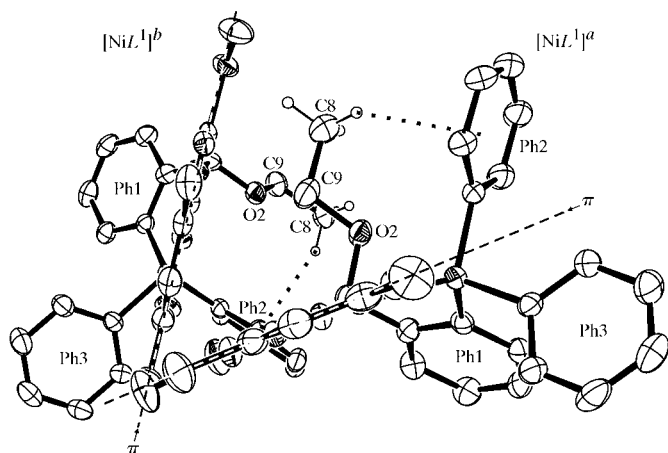


Figure 2

A view of the mutual orientation of the $[\text{NiL}^1]^a$ and $[\text{NiL}^1]^b$ molecules. Displacement ellipsoids are drawn at the 30% probability level. Some H atoms have been omitted for clarity. π is the plane defined by atoms Ni1, N1, N3 and O1. Intramolecular C–H... π interactions are represented by dotted lines.

bonds, which enables additional rotation around them. For this reason, four of the six highest Δ_P values are found for $[\text{NiL}^1]$, described in this work, and the previously published structures of $[\text{NiL}^2]$ (Bogdanović *et al.*, 1998), $[\text{PtL}^3]\cdot\text{CHCl}_3$ and $[\text{Pt}(\text{C}_{44}\text{H}_{32}\text{N}_2\text{O}_2\text{P}_2)]\cdot\text{CCl}_3\text{H}$ (Burger *et al.*, 2003), all of which are shown as circles in Fig. 3.

It was considered worthwhile to analyze the orientation of the ethoxy group (–O2/C9H₂/C8H₃). Although the rotation around the O2–C9 and C9–C8 single bonds is not restricted, the orientation of the ethoxy group is very similar in all of the three compared molecules, *viz.* $[\text{NiL}^1]^a$, $[\text{NiL}^1]^b$ and $[\text{NiL}^2]$. An explanation for this structural behavior can be found in the intramolecular C–H... π interaction between the C8 methyl group and the Ph2 (C17–C22) phenyl ring (Fig. 2), which was not observed in the previously published crystal structure of $[\text{NiL}^2]$ (Bogdanović *et al.*, 1998). The geometrical parameters of this interaction for the $[\text{NiL}^1]^a$, $[\text{NiL}^1]^b$ and $[\text{NiL}^2]$ complexes are listed in Table 3.

There are no intermolecular hydrogen bonds or significant π – π interactions with participation of the phenyl rings from the triphenylphosphine fragment in the crystal structure of the $[\text{NiL}^1]$ complex. However, numerous intermolecular C–H... π interactions are found in the crystal packing. The geometrical parameters listed in Table 3 were calculated for normalized C–H distances (1.08 Å), as is usual for the analysis of C–H... π interactions (Desiraju & Steiner, 1999). Four interactions have an H... Ω distance (where Ω is the centroid of the ring) shorter than 2.70 Å. It is known that chelate rings with π delocalized bonds are able to participate in C–H... π interactions as π -acceptors (Bogdanović *et al.*, 2002), which was here observed in the case of rings A and B in $[\text{NiL}^1]^b$. The $[\text{NiL}^1]^b$ molecule forms as many as seven intermolecular interactions (four as C–H donor and three as

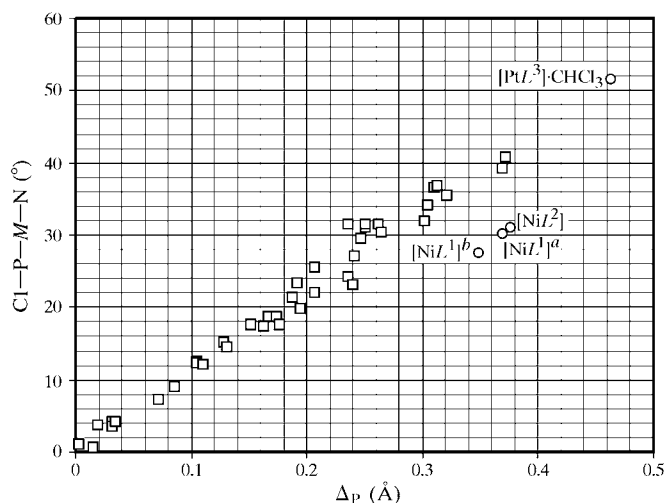


Figure 3

The relation between the values of the C1–P–M–N torsion angle and the displacement of the P atom from the mean plane of the chelate ring. Crystal structures are represented by squares, except those that possess N–C3 and C3–C2 single bonds (represented by circles).

π -acceptor). Generally speaking, it can be concluded that C—H $\cdots\pi$ interactions play a dominant role in the crystal packing.

The existence of C—H $\cdots\pi$ interactions in (III), as well as the mutual position of the three phenyl rings bonded to one P atom, was also analyzed. 25 of the 29 structures lack significant intermolecular hydrogen bonds, but form C—H $\cdots\pi$ interactions with phenyl or chelate rings acting as π -acceptors. Comparing the angle between the mean planes of the phenyl rings bonded to the P atom and taking into account their position relative to the coordination plane, it was found that the conformations of the triphenylphosphine structural part in all 29 crystal structures, including the structures presented in this work, are very similar. Such a mutual position of the phenyl rings avoids short and destabilizing H \cdots H contacts of their H atoms in the *ortho* positions. Nevertheless, it is interesting to note the existence of three short H \cdots C contacts between an H atom in the *ortho* position and a C atom bonded to the P atom from a neighboring phenyl group. These H \cdots C distances range from 2.5 to 2.8 Å, with C—H \cdots C angles of about 110°. A similar orientation of the phenyl rings exists in uncoordinated triphenylphosphine and its derivatives (Daly, 1964; Dunne & Orpen, 1991; Chekhlov, 1993; Bruckmann *et al.*, 1995; Kooijman *et al.*, 1998; Ziemer *et al.*, 2000), suggesting the presented mutual orientation of phenyl rings is the most stable.

Experimental

The title complex was obtained by the reaction between a warm (about 313 K) ethanol solution containing 0.5 mmol each of [Ni(L)-NH₃] \cdot 2H₂O (*L* is the dianion of 2,4-pentanedione *S*-methylisothiosemicarbazone) (Leovac *et al.*, 1993) and 2-(diphenylphosphino)benzaldehyde.

Crystal data

[Ni(C ₂₈ H ₃₀ N ₃ O ₂ PS)]	$V = 2765.9$ (12) Å ³
$M_r = 562.29$	$Z = 4$
Triclinic, $P\bar{1}$	$D_x = 1.350$ Mg m ⁻³
$a = 11.974$ (3) Å	Mo $K\alpha$ radiation
$b = 12.531$ (2) Å	$\mu = 0.86$ mm ⁻¹
$c = 20.827$ (7) Å	$T = 293$ (2) K
$\alpha = 89.81$ (2)°	Prism, black
$\beta = 73.56$ (2)°	$0.36 \times 0.30 \times 0.26$ mm
$\gamma = 68.26$ (2)°	

Table 1

Selected geometric parameters (Å, °).

Ni1a—O1a	1.836 (3)	Ni1b—O1b	1.835 (2)
Ni1a—N3a	1.856 (3)	Ni1b—N1b	1.852 (3)
Ni1a—N1a	1.864 (3)	Ni1b—N3b	1.857 (3)
Ni1a—P1a	2.2001 (10)	Ni1b—P1b	2.1780 (12)
O1a—C6a	1.314 (4)	O1b—C6b	1.303 (4)
N1a—C4a	1.315 (4)	N1b—C4b	1.320 (4)
N1a—N2a	1.408 (4)	N1b—N2b	1.412 (4)
N2a—C1a	1.302 (4)	N2b—C1b	1.307 (4)
N3a—C1a	1.354 (4)	N3b—C1b	1.347 (4)
C4a—C5a	1.394 (5)	C4b—C5b	1.411 (5)
C5a—C6a	1.355 (5)	C5b—C6b	1.353 (6)
O1a—Ni1a—N1a	95.34 (13)	O1b—Ni1b—N1b	95.85 (13)
N3a—Ni1a—N1a	82.79 (13)	N1b—Ni1b—N3b	82.64 (13)
O1a—Ni1a—P1a	88.92 (8)	O1b—Ni1b—P1b	87.09 (9)
N3a—Ni1a—P1a	93.17 (9)	N3b—Ni1b—P1b	94.53 (10)

Data collection

Enraf–Nonius CAD-4 diffractometer	10824 independent reflections
$\omega/2\theta$ scans	6782 reflections with $I > 2\sigma(I)$
Absorption correction: Gaussian (PLATON; Spek, 2003)	$R_{\text{int}} = 0.025$
$T_{\text{min}} = 0.756$, $T_{\text{max}} = 0.820$	$\theta_{\text{max}} = 26.0^\circ$
11363 measured reflections	3 standard reflections
	frequency: 60 min
	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0452P)^2 + 0.729P]$
$R[F^2 > 2\sigma(F^2)] = 0.044$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.117$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.01$	$\Delta\rho_{\text{max}} = 0.43$ e Å ⁻³
10824 reflections	$\Delta\rho_{\text{min}} = -0.28$ e Å ⁻³
657 parameters	
H-atom parameters constrained	

Table 2

The puckering parameters (Å, °) for the P1—C11—C12—C10—N3—Ni1 sequence.

	Q	q^2	q^3	θ	φ
[NiL ¹] ^a	0.714 (4)	0.714 (4)	-0.005 (3)	90.4 (2)	178.7 (3)
[NiL ¹] ^b	0.696 (4)	0.696 (4)	0.018 (3)	88.5 (2)	-178.7 (3)
[NiL ²]	0.70	0.70	-0.03	92.3	179.4

Table 3

Geometrical parameters (Å, °) for selected C—H $\cdots\pi$ interactions.

Ω is the centroid of an aromatic ring; β is the angle between the line connecting the H atom and Ω and the normal to the ring.

	C—H $\cdots\Omega$	H $\cdots\Omega$	C $\cdots\Omega$	β	C—H $\cdots\Omega$
[NiL ¹] ^a	C8a—H78a $\cdots\Omega_{1a}$	2.91	3.85	4.2	146
	C14a—H14a $\cdots\Omega_{2b}^i$	2.79	3.67	10.1	140
	C21a—H21a $\cdots\Omega_{3a}^{ii}$	2.90	3.69	13.5	130
	C27a—H27a $\cdots\Omega_{3a}^{iii}$	2.65	3.55	19.3	141
	C3b—H73b $\cdots\Omega_{4b}^{iv}$	2.84	3.60	24.0	128
[NiL ¹] ^b	C8b—H78b $\cdots\Omega_{1b}$	2.61	3.64	0.4	159
	C21b—H21b $\cdots\Omega_{4b}^i$	2.68	3.52	7.0	135
	C25b—H25b $\cdots\Omega_{4a}^v$	2.66	3.67	15.3	157
	C26b—H26b $\cdots\Omega_{2a}^v$	2.79	3.61	10.6	133
	[NiL ²]	C8c—H78c $\cdots\Omega_{1c}$	3.06	4.00	26.2
C9c—H79c $\cdots\Omega_{5c}^{vi}$		3.01	3.87	25.3	137
C19c—H19c $\cdots\Omega_{2c}^i$		3.00	3.95	11.5	147
C21c—H21c $\cdots\Omega_{6c}^{vii}$		2.97	3.79	16.9	134

Notes: Ω_{1a} is the centroid of the C17a—C22a ring, Ω_{2a} the C11a—C16a ring, Ω_{3a} ring B, Ω_{4a} ring A, Ω_{1b} the C17b—C22b ring, Ω_{2b} the C11b—C16b ring, Ω_{4b} ring A, Ω_{1c} the C17c—C22c ring, Ω_{2c} the C11c—C16c ring, Ω_{5c} the C23c—C28c ring, and Ω_{6c} the C5c—C31c ring. Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $-x + 1, -y, -z$; (iii) $-x, -y + 1, -z$; (iv) $-x + 1, -y, -z + 1$; (v) $-x, -y + 1, -z + 1$; (vi) $x - 1, y, z$; (vii) $-x, -y, -z + 1$.

All H atoms were found in a difference Fourier map, but they were placed at geometrically calculated positions (C—H = 0.93–0.97 Å) and refined using a riding model. The idealized methyl groups were allowed to rotate about their X—C bonds using the difference electron-density synthesis as a criterion for the final H-atom positions. $U_{\text{iso}}(\text{H})$ values were set equal to 1.2 (or 1.5 for methyl groups) times U_{eq} of the parent atom.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2003).

This work was supported financially by the Ministry of Science and Environmental Protection of the Republic of Serbia (project No. 142028B – ‘Synthesis, physical, structural and biological characteristic of new complex compounds’).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3009). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Beraldo, H. & Gambino, D. (2004). *Mini Rev. Med. Chem.* **4**, 159–165.
- Bogdanović, G. A., Leovac, V. M., Novaković, S. B., Češljević, V. I. & Spasojević-de Biré, A. (2001). *Acta Cryst.* **C57**, 1138–1140.
- Bogdanović, G. A., Spasojević-de Biré, A., Prelesnik, B. V. & Leovac, V. M. (1998). *Acta Cryst.* **C54**, 766–768.
- Bogdanović, G. A., Spasojević-de Biré, A. & Zarić, S. D. (2002). *Eur. J. Inorg. Chem.* pp. 1599–1602.
- Brčeski, I. D., Leovac, V. M., Bogdanović, G. A., Sovilj, S. P. & Revenko, M. (2003). *Inorg. Chem. Commun.* **7**, 253–256.
- Bruckmann, J., Kruger, C. & Lutz, F. (1995). *Z. Naturforsch. Teil B*, **50**, 351–360.
- Burger, S., Therrien, B. & Suss-Fink, G. (2003). *Eur. J. Inorg. Chem.* pp. 3099–3103.
- Burnett, M. N. & Johnson, C. K. (1996). *ORTEPIII*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
- Campbell, M. J. M. (1975). *Coord. Chem. Rev.* **15**, 279–319.
- Casas, J. S., García-Tasende, M. S. & Sordo, J. (2000). *Coord. Chem. Rev.* **209**, 197–261.
- Chekhlov, A. N. (1993). *Kristallografiya (Crystallogr. Rep.)*, **38**, 79–84.
- Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
- Daly, J. J. (1964). *J. Chem. Soc.* pp. 3799–3810.
- Desiraju, G. R. & Steiner, T. (1999). In *The Weak Hydrogen Bond in Structural Chemistry and Biology*. New York: Oxford University Press Inc.
- Dunne, B. J. & Orpen, A. G. (1991). *Acta Cryst.* **C47**, 345–347.
- Enraf-Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf-Nonius, Delft, The Netherlands.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Harms, K. & Wocadlo, S. (1995). *XCAD4*. University of Marburg, Germany.
- Kooijman, H., Spek, A. L., van Bommel, K. J. C., Verboom, W. & Reinhoudt, D. N. (1998). *Acta Cryst.* **C54**, 1695–1698.
- Leovac, V. M., Bogdanović, G. A., Češljević, V. I. & Divjaković, V. (2000). *Acta Cryst.* **C56**, 936–938.
- Leovac, V. M., Češljević, V. I., Gerbeleu, N. V., Simonov, Yu. A., Dvorkin, A. A. & Arion, V. B. (1993). *Transition Met. Chem.* **18**, 309–311.
- Leovac, V. M., Jevtović, V. S. & Bogdanović, G. A. (2002). *Acta Cryst.* **C58**, m514–m516.
- Padhye, S. & Kauffman, G. B. (1985). *Coord. Chem. Rev.* **63**, 127–160.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
- West, D. X., Padhye, S. B. & Sonawane, P. B. (1991). *Struct. Bonding*, **76**, 1–49.
- Ziemer, B., Rabis, A. & Steinberger, H.-U. (2000). *Acta Cryst.* **C56**, e58–e59.