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Polymorphism in bipodal *O*,*O*′-dimethyl *N*,*N*′-(*m*-phenylenedicarbonyl)-bis(thiocarbamate)

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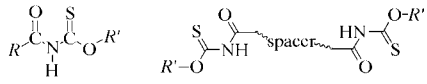
The title compound, $C_{12}H_{12}N_2O_4S_2$, crystallizes in white and yellow polymeric forms as a result of interesting *anti–anti* and *syn–anti* conformational isomerism of the thiocarbonyl and carbonyl moieties relative to one another. This work is the first reported X-ray crystallographic structure determination of isomers of this class of bipodal ligand. The white form, *anti–anti*, (I), crystallizes with the benzene ring lying about a twofold rotation axis, resulting in both of the thiocarbonyl and carbonyl moieties being *anti* relative to each other. The yellow modification crystallizes as *syn–anti*, (II), with one thiocarbonyl moiety *syn* and the other *anti* relative to the respective carbonyl groups. The individual molecules of both (I) and (II) are extensively linked through intermolecular hydrogen bonds. Intermolecular hydrogen bonding in (II) includes a network of bifurcated N—H···O and N—H···S hydrogen bonds, while molecules of (I) include bifurcated C—H···O hydrogen bonds.

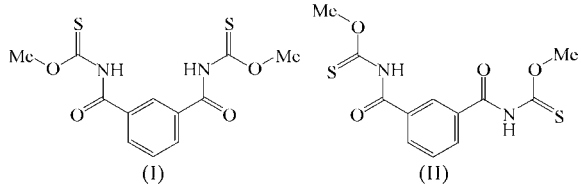
Comment

Substituted acylthioureas with the general motif *R*C(O)NHC(S)N(R')$_2$ have been studied extensively as a result of their coordination chemistry, particularly with the softer transition metal ions (Hoyer *et al.*, 1986; Köhler *et al.*, 1986; König *et al.*, 1983, 1986; Richter *et al.*, 1989; Schröder *et al.*, 2000). We have extensively studied these molecules and their bipodal analogues, (R')$_2$NC(S)NHC(O)*R*C(O)NHC(S)N(R')$_2$, as part of an investigation examining their potential uses in the platinum group metal industry (Bourne *et al.*, 2005; Hallale *et al.*, 2005; Koch, 2001; Koch *et al.*, 1999).

Despite the several reported applications of these acylthiourea derivatives, there are few structural reports concerning the uncoordinated substituted thiourea derivatives (Bourne *et al.*, 2005; Koch, 2001; Koch, Sacht & Bourne, 1995; Koch, Sacht, Grimmbacher & Bourne, 1995; Ramadas *et al.*, 1993; Ugur *et al.*, 2003). Recent work in our laboratory, however, has shown that these molecules show some interesting inter- and intramolecular hydrogen-bonding interactions in the solid state (Bourne *et al.*, 2005). In this context, we have become interested in the synthesis and potential coordination chemistry of the structurally related *O*-alkyl *N*-benzoylthiocarbamates, which, to our knowledge, have received very little attention in the literature.



O-Alkylthiocarbamic acid esters have previously been reported as having potential as 'collectors' in ore flotation (Azizyan & Ryaboi, 1989; Konev & Ryaboi, 1971), and have also been proposed as being the intermediates for the regio- and chemoselective deoxygenation of primary and secondary aliphatic alcohols (Oba & Nishiyama, 1994). To date, the only crystal structures of uncoordinated molecules similar to the title compound that have been reported in the literature are those of *O*-isopropyl *N*-(2-furoyl)thiocarbamate (Morales *et al.*, 2000*b*), *O*-benzyl *N*-(2-furoyl)thiocarbamate (Montiel-Ortega *et al.*, 2004) and a recently reported bipodal thiocarbamic ester, *O*,*O*′-diethyl *N*,*N*′-(*p*-phenylenedicarbonyl)-bis(thiocarbamate) (Blewett *et al.*, 2004).



We report here the molecular structures of a white, (I), and a yellow, (II), polymorph of *O*,*O*′-dimethyl *N*,*N*′-(*m*-phenylenedicarbonyl)dithiocarbamate, which differ only by the relative orientation of the thiocarbonyl moiety with respect to the aminocarbonyl groups. In (I), the orientations of both thiocarbamate O-ester groups are *anti* with respect to the aminocarbonyl moiety (Fig. 1), while in (II), one orientation is *anti* and the other is *syn* (Fig. 2).

In (I), both the thiocarbonyl and carbonyl moieties within the asymmetric unit of (I) are *anti* relative to one another, the complete molecule being generated by a twofold rotation axis passing through atoms C5 and C7 of the benzene ring (Fig. 1).

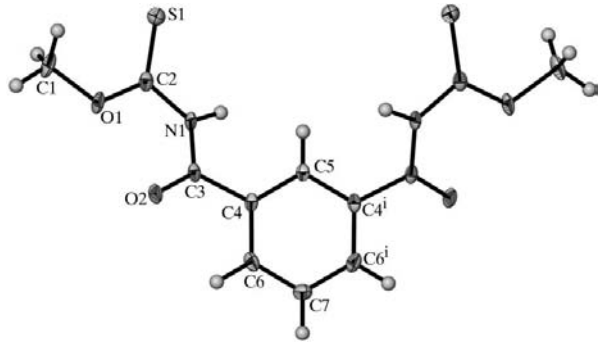


Figure 1
The molecular structure of (I), showing the atomic numbering scheme and 50% probability displacement ellipsoids. A twofold rotation axis passes through atoms C5 and C7. [Symmetry code: (i) $-x, y, \frac{1}{2} - z$.]

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The asymmetric unit of (II) (Fig. 2) consists of a complete molecule and, in contrast to (I), does not contain internal symmetry. The relative orientations of the thiocarbonyl and carbonyl moieties, S1 and O2, are *syn* with respect to each other, while atoms O3 and S2 are *anti* relative to one another. The approximate *anti* orientation of the S and O atoms within the C(S)NHC(O) moieties of (I), and of atoms O3 and S2 in (II), is frequently observed in the closely related bipodal *N*′,*N*′,*N*′′′,*N*′′′-tetraalkyl-*N*,*N*′′-aroylbis(thioureas) (Koch *et al.*, 2001; Ugur *et al.*, 2003). This *anti* orientation of the S and O atoms is also frequently observed in the monopodal *N*-aroyl-*N*′-alkyl- and *N*-aroyl-*N*′,*N*′-dialkylthioureas (Koch, Sacht, Grimmbacher & Bourne, 1995; Morales *et al.*, 1997, 2000*a*; Shanmuga Sundara Raj *et al.*, 1999). The comparable uncommon *syn* orientation of the thiocarbonyl and carbonyl moieties (S1 and O2) observed in (II) was also observed in the structurally related *O*,*O*′-dimethyl *N*,*N*′-(*p*-phenylenedicarbonyl)bis(thiocarbamate) (Blewett *et al.*, 2004).

The *anti–anti* and *syn–anti* conformations of (I) and (II) have a significant effect on their molecular packing. The *anti–anti* conformation in (I) results in intermolecular N1—H1···O2 hydrogen bonds as well as bifurcated C5—H5···O2 hydrogen bonds between adjacent molecules, causing molecules of (I) to pack in chains parallel to the *c* axis. Further distinctive intermolecular C6—H6···S1 hydrogen-bond interactions cause these chains of molecules to extend as sheets parallel to (100) (Fig. 3 and Table 2).

In yellow polymorph (II), the *syn–anti* conformation results in these molecules packing with a network of bifurcated intermolecular N1—H1···O3, C5—H5···O3, N2—H2···O2 and N2—H2···S1 hydrogen bonds to adjacent molecules. As a result, each molecule of (II) interacts with two adjacent molecules *via* a series of hydrogen-bond interactions, producing one-dimensional molecular chains parallel to [010] (Fig. 4 and Table 4). Crystallization and polymorphism are complex phenomena and an appreciation of polymorphism is fundamental to an understanding of the crystallization process itself (Desiraju, 1997). It has been suggested that our understanding of polymorphism is, however, still far from complete and the occurrence of polymorphism cannot be safely predicted (Kirchner *et al.*, 2004). In many cases in the literature, the pattern of hydrogen bonds formed within a molecule studied is said to constitute the basis for polymorphism within those molecules (Kirchner *et al.*, 2004). It is possible that the hydrogen bonding observed in (I) and (II) contributes to the occurrence of the polymorphism observed. However, the overall packing of the molecules of (I) and (II) is undoubtedly dictated by a collection of subtleties, only some of which are the hydrogen-bond interactions reported.

The C2—N1 bonds in both (I) and (II), as well as C11—N2 in (II), are all shorter than the corresponding bonds in the bipodal compound 3,3,3′,3′-tetraethyl-1,1′-terephthaloylbis(thiourea) [1.4173 (16) Å; Ugur *et al.*, 2003] and in 3,3,3′,3′-tetraethyl-1,1′-isophthaloylbis(thiourea) [1.428 (4) Å; Koch *et al.*, 2001]. This fact indicates a greater degree of double-bond character in the C—N bonds in question in (I) and (II). Correspondingly, the C3—N1 bond length of (I) and C10—N2 of (II) are somewhat longer than the corresponding C—N bond length for 3,3,3′,3′-tetraethyl-1,1′-terephthaloylbis(thiourea) [1.3606 (17) Å]. The C3—N1 bond in (II) is significantly

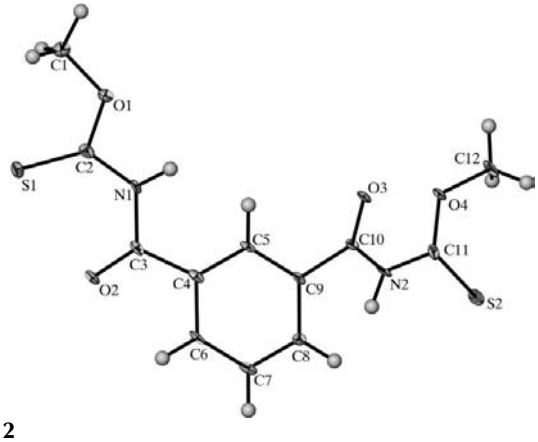

Figure 2
The molecular structure (II), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

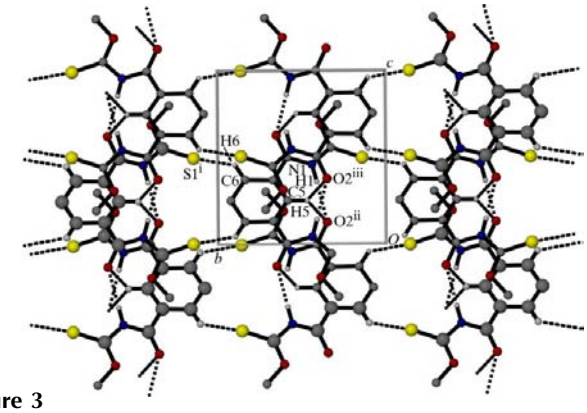

Figure 3
A view of the structure of (I), showing the intermolecular C6—H6···S1^{i}, C5—H5···O2^{ii}, C5—H5···O2^{iii} and N1—H1···O2^{ii} hydrogen-bond interactions. All H atoms, apart from those participating in hydrogen bonding, have been omitted for clarity. [Symmetry codes: (i) x, $y+1$, z; (ii) x, $-y+1$, $z-\frac{1}{2}$; (iii) $-x$, $-y+1$, $-z+1$.]

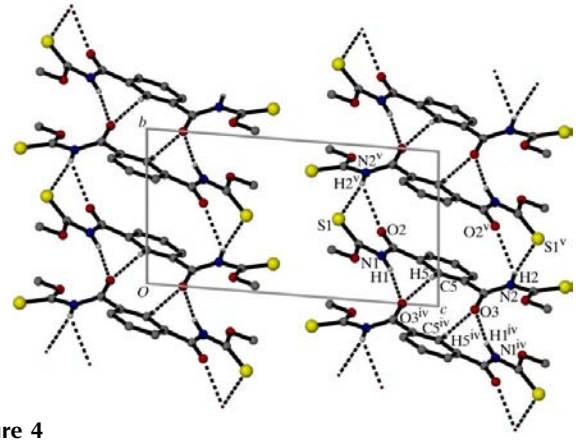

Figure 4
A view of the structure of (II), showing the intermolecular N1—H1···O3^{iv}, N2—H2···S1^{v}, N2—H2···O2^{v} and C5—H5···O3^{iv} hydrogen-bond interactions. All H atoms, apart from those participating in hydrogen bonding, have been omitted for clarity. [Symmetry codes: (iv) $-x$, $-y$, $-z+2$; (v) $-x+1$, $-y+1$, $-z+2$.]

longer than the comparable C—N bonds in both 3,3,3′,3′-tetraethyl-1,1′-terephthaloylbis(thiourea) [1.3606 (17) Å] and 3,3,3′,3′-tetraethyl-1,1′-isophthaloylbis(thiourea) [1.381 (4) Å].

The conformations of the $C(O)NHC(S)OCH_3$ branches of (I) are remarkably planar, with atom O1 deviating from the C4/C3/N1/C2/O1/C1 least-squares plane by only 0.070 (2) Å. Atoms O2 and S1 lie out of this plane by only −0.118 (3) and −0.291 (3) Å, respectively, in contrast to the situation observed for 3,3,3′,3′-tetraethyl-1,1′-terephthaloylbis(thiourea) and 3,3,3′,3′-tetraethyl-1,1′-isophthaloylbis(thiourea). The *anti* coplanarity of S1 and O2 in (I) is further illustrated by the torsion angles listed in Table 1. In (I), the C4/C3/N1/C2/O1/C1 plane intersects the plane of the phenylene ring at an angle of 25.50 (9)°.

Both $C(O)NHC(S)OCH_3$ branches of (II) are also remarkably planar. For the *syn* branch of (II), atom C4 deviates from the C4/C3/N1/C2/O1/C1 least-squares plane by only 0.060 (2) Å, while atoms O2 and S1 deviate from this plane by −0.085 (7) and 0.185 (8) Å, respectively. The *syn* coplanarity of atoms S1 and O2 in (II) is further illustrated by the torsion angles listed in Table 3. The C4/C3/N1/C2/O1/C1 plane intersects the plane of the phenylene ring at an angle of 16.5 (3)°. Similarly, atoms C10, O3 and S2 deviate from the C9/C10/N2/C11/O4/C12 least-squares plane of the *anti* $C(O)NHC(S)OCH_3$ branch of (II) by only 0.147 (3), 0.458 (5) and 0.230 (6) Å, respectively. The *anti* coplanarity of atoms S2 and O3 in (II) is further illustrated by the torsion angles listed in Table 3.

The asymmetry of the C5—C4—C3 and C6—C4—C3 bond angles (Table 1) in (I) may be the result of a repulsion in the N1—H1···H5—C5 system and an attraction in the C6—H6···O2 system. Similar observations pertain to (II), with an asymmetry in the C5—C4—C3 and C6—C4—C3 angles (Table 3) due to a possible repulsion in the N1—H1···H5—C5 system and an attraction between the C6—H6···O2 system. For the *anti* branch in (II), qualitatively similar interactions may be inferred from the asymmetry between the C5—C9—C10 and C8—C9—C10 angles (Table 3), possibly as a result of repulsive interactions in the N2—H2···H8—C8 system and attractive interactions in the C5—H5···O3 system. Similar observations have been made for *O*-isopropyl *N*-(2-furoyl)-thiocarbamate (Morales *et al.*, 2000*b*) and bipodal *O*,*O*′-dimethyl *N*,*N*′-(*p*-phenylenedicarbonyl)bis(thiocarbamate) (Blewett *et al.*, 2004).

Experimental

All syntheses were carried out under a dry argon atmosphere using standard Schlenk and vacuum-line techniques. Compounds (I) and (II) were synthesized using a modification of a procedure initially reported for the preparation of substituted thioureas (Douglas & Dains, 1934). The reagents isophthaloyl dichloride and KSCN were used as supplied without further purification. Acetone (calcium carbonate) and methanol (Mg, I_2) were rendered anhydrous and distilled prior to use. Isophthaloyl dichloride (2.5 mmol) in acetone (25 ml) was added to KSCN (5 mmol) in acetone (25 ml) under an inert atmosphere. The mixture was heated under reflux for 1 h and then cooled to room temperature, after which ethanol (5 mmol) in acetone (25 ml) was added dropwise with stirring and the mixture further warmed to 333 K for 2 h. Water (50 ml) was added, followed by extraction of the product into chloroform. Removal of the solvent *in vacuo* yielded the crude pale-yellow amorphous target product. The product was further purified by crystallization from a 1:1 mixture of chloroform and ethanol, yielding simultaneously both white and yellow crystals from the same sample batch suitable for single-crystal diffraction analysis [overall yield 81.3% (based on isophthaloyl dichloride)]. ^{1}H NMR ($CDCl_3$): δ 10.30 (*br*, *s*, 2H), 8.62 (*s*, 1H, Ph), 8.13 (*d*, 1H, Ph), 8.11 (*d*, 1H, Ph), 7.56 (*tr*, 1H, Ph), 3.96 (*s*, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 190.6 (CS), 170.1 (CO), 134.1 (Ph), 134.0 (*ipso*-Ph), 130.4 (Ph), 127.3 (Ph), 68.4 (CH_3). FT–IR (KBr disks), for (I): 3265 (*s*), 1686 (*s*), 1529 (*s*), 1282 (*s*) cm^{-1}; for (II): 3299 (*s*), 1688 (*s*), 1520 (*s*), 1272 (*s*) cm^{-1}.

Polymorph (I)

Crystal data

$C_{12}H_{12}N_2O_4S_2$	D_x = 1.512 Mg m^{-3}
M_r = 312.36	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 1347 reflections
a = 19.336 (3) Å	θ = 2.1–26.0°
b = 8.2864 (13) Å	μ = 0.40 mm^{-1}
c = 8.6590 (14) Å	T = 100 (2) K
β = 98.435 (3)°	Needle, white
V = 1372.4 (4) Å^3	0.24 × 0.11 × 0.09 mm
Z = 4	

Data collection

Bruker SMART APEX CCD diffractometer	1347 independent reflections
	1183 reflections with $I > 2\sigma(I)$
ω scans	R_{int} = 0.027
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2002)	θ_{max} = 26.0°
	$h = -23 \rightarrow 22$
T_{min} = 0.948, T_{max} = 0.964	$k = -9 \rightarrow 10$
3729 measured reflections	$l = -10 \rightarrow 10$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0659P)^2 + 1.4244P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.045	
$wR(F^2)$ = 0.119	
S = 1.06	$(\Delta/\sigma)_{max} < 0.001$
1507 reflections	$\Delta\rho_{max}$ = 0.50 e Å^{-3}
93 parameters	$\Delta\rho_{min}$ = −0.25 e Å^{-3}
H-atom parameters constrained	

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

S1—C2	1.637 (2)	N1—C3	1.380 (3)
O1—C2	1.318 (2)	N1—C2	1.391 (3)
O2—C3	1.220 (2)		
C6—C4—C3	117.15 (17)	C5—C4—C3	122.78 (19)
C3—N1—C2—S1	164.72 (16)	C2—N1—C3—O2	5.8 (3)

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

D—H···A	D—H	H···A	D···A	D—H···A
C6—H6···S1^{i}	0.95	2.76	3.525 (2)	138
C5—H5···O2^{ii}	0.95	2.58	3.068 (2)	113
C5—H5···O2^{iii}	0.95	2.58	3.068 (2)	113
N1—H1···O2^{ii}	0.88	2.08	2.948 (2)	169

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

Polymorph (II)

Crystal data

$C_{12}H_{12}N_2O_4S_2$
M_r = 312.36
Triclinic, $P\overline{1}$
a = 6.3603 (13) Å
b = 7.7016 (15) Å
c = 14.255 (3) Å
α = 92.496 (3)°
β = 97.952 (3)°
γ = 103.496 (3)°
V = 670.4 (2) Å^3
Z = 2
D_x = 1.547 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2617 reflections
θ = 2.7–26.0°
μ = 0.41 mm^{-1}
T = 100 (2) K
Needle, yellow
0.24 × 0.11 × 0.09 mm

Data collection

Bruker SMART APEX CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2002)
T_{min} = 0.947, T_{max} = 0.964
6812 measured reflections
2617 independent reflections
2308 reflections with $I > 2\sigma(I)$
R_{int} = 0.034
θ_{max} = 26.0°
$h = -7 \rightarrow 7$
$k = -9 \rightarrow 9$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.069
$wR(F^2)$ = 0.150
S = 1.26
2617 reflections
183 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0573P)^2 + 1.1105P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.53 e Å^{-3}
$\Delta\rho_{min}$ = −0.41 e Å^{-3}

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

S1—C2	1.634 (4)	O3—C10	1.226 (4)
S2—C11	1.639 (4)	N1—C2	1.377 (5)
O1—C2	1.343 (4)	N1—C3	1.401 (4)
O4—C11	1.327 (4)	N2—C10	1.372 (4)
O2—C3	1.212 (4)	N2—C11	1.381 (4)
C5—C4—C3	125.4 (3)	C5—C9—C10	117.9 (3)
C6—C4—C3	115.6 (3)	C8—C9—C10	122.2 (3)
C3—N1—C2—S1	0.3 (6)	C2—N1—C3—O2	−8.4 (6)
C10—N2—C11—S2	162.2 (3)	C11—N2—C10—O3	−2.7 (6)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O3^{iv}	0.88	2.04	2.913 (4)	169
N2—H2···S1^{v}	0.88	2.57	3.421 (3)	163
N2—H2···O2^{v}	0.88	2.55	2.949 (4)	108
C5—H5···O3^{iv}	0.95	2.32	3.140 (4)	145

Symmetry codes: (iv) $-x, -y, -z+2$; (v) $-x+1, -y+1, -z+2$.

All H atoms were placed in geometrically calculated positions, with C—H distances of 0.98 (for methyl) and 0.95 Å (for phenyl), and were refined using a riding model, with U_{iso}(H) values of $1.2U_{eq}$(parent) (for phenyl and N-bound H atoms) or $1.5U_{eq}$(parent) (for methyl H atoms).

For both compounds, data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; structure solution: *SHELXS97* (Sheldrick, 1997); structure refinement: *SHELXL97* (Sheldrick, 1997); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *X-SEED*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: RB1007). Services for accessing these data are described at the back of the journal.

References

Azizyan, L. V. & Ryaboi, V. I. (1989). *Obogashch. Rud* (*Leningrad*), **2**, 21.
Barbour, L. J. (2001). *J. Supramol. Chem.* **1**, 189–191.
Blewett, G., Esterhuysen, C., Bredenkamp, M. W. & Koch, K. R. (2004). *Acta Cryst.* C**60**, o862–o864.
Bourne, S. A., Hallale, O. & Koch, K. R. (2005). *Cryst. Growth Des.* **5**, 307–312.
Bruker (2001). *SMART*. Version 5.625. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2002). *SAINT*. Version 6.36a. Bruker AXS Inc., Madison, Wisconsin, USA.
Desiraju, G. R. (1997). *Science*, **278**, 404–405.
Douglas, I. B. & Dains, F. B. (1934). *J. Am. Chem. Soc.* **56**, 719–721.
Hallale, O., Bourne, S. & Koch, K. R. (2005). *CrystEngComm*, **7**, 161–166.
Hoyer, E., Köhler, R., Kirmse, R., Richter, R., Sieler, J. & Beyer, L. (1986). *Z. Anorg. Allg. Chem.* **537**, 133.
Kirchner, M. T., Reddy, L. S., Desiraju, G. R., Jetti, R. K. R. & Boese, R. (2004). *Cryst. Growth Des.* **4**, 701–709.
Koch, K. R. (2001). *Coord. Chem. Rev.* **216–217**, 473–488.
Koch, K. R., Bourne, S. A., Coetzee, A. & Miller, J. (1999). *J. Chem. Soc. Dalton Trans.* pp. 3157–3161.
Koch, K. R., Hallale, O., Bourne, S. A., Miller, J. & Bacsa, J. (2001). *J. Mol. Struct.* **561**, 185–196.
Koch, K. R., Sacht, C. & Bourne, S. (1995). *Inorg. Chim. Acta*, **232**, 109–115.
Koch, K. R., Sacht, C., Grimmbacher, T. & Bourne, S. (1995). *S. Afr. J. Chem.* **48**, 71–77.
Köhler, R., Kirmse, R., Richter, R., Sieler, J. & Hoyer, E. (1986). *Z. Anorg. Allg. Chem.* **537**, 133.
Konev, V. A. & Ryaboi, V. I. (1971). *Obogashch. Rud* (*Leningrad*), **16**, 10.
König, K. H., Pletsch, H. J. & Schuster, M. (1986). *Z. Anal. Chem.* **325**, 621–624.
König, K. H., Schuster, M., Schneeweis, G. & Steinbrech, B. (1983). *Z. Anal. Chem.* **319**, 66.
Montiel-Ortega, L. A., Rojas-Lima, S., Otazo-Sanchez, E. & Villagómez-Ibarra, A. R. (2004). *J. Chem. Crystallogr.* **34**, 89–93.
Morales, A. D., de Armas, H. N., Blaton, N. M., Peeters, O. M., De Ranter, C. J., Márquez, H. & Hernández, R. P. (2000*a*). *Acta Cryst.* C**56**, 503–504.
Morales, A. D., de Armas, H. N., Blaton, N. M., Peeters, O. M., De Ranter, C. J., Márquez, H. & Hernández, R. P. (2000*b*). *Acta Cryst.* C**56**, 1042–1043.
Morales, A. D., Garcia-Granda, S., Esteva, Y. R., Stevens, A. P. & Crespo, G. A. A. (1997). *Acta Cryst.* C**53**, IUC9700019.
Oba, M. & Nishiyama, K. (1994). *Synthesis*, pp. 624–627.
Ramadas, K., Srinivasan, N. & Janarthanan, N. (1993). *Tetrahedron Lett.* **34**, 6447–6450.
Richter, R., Sieler, J., Köhler, R., Hoyer, E., Beyer, L. & Hansen, L. K. (1989). *Z. Anorg. Allg. Chem.* **578**, 191–197.
Schröder, U., Beyer, L. & Sieler, J. (2000). *Inorg. Chem. Commun.* **3**, 630–633.
Shanmuga Sundara Raj, S., Puviarasan, K., Velmurugan, D., Jayanthi, G. & Fun, H.-K. (1999). *Acta Cryst.* C**55**, 1318–1320.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Sheldrick, G. M. (2002). *SADABS*. Version 2.05. University of Göttingen, Germany.
Ugur, D., Flörke, U., Külcü, N. & Arslan, H. (2003). *Acta Cryst.* E**59**, o1345–o1346.