organic compounds

Twinning by merohedry in bis(4-methoxyphenyl)tellurium(IV) diiodide dimethyl sulfoxide hemi-solvate[1]

Joan Farran,[a] Angel Alvarez-Larena,[a]* Joan F. Piniella,[a] Mario V. Capparelli[a] and Karen Friese[b]

[a]Unitat de Cristal·lografia, Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain, and [b]Departament Física Materia Condensada, Facultad de Ciencia y Tecnología, Universidad del País Vasco, Apartado 644, E-48080 Bilbao, Spain
Correspondence e-mail: angel.alvarez@uab.es

Green crystals of the title compound, $C_{14}H_{14}I_2O_2Te\cdot 0.5C_2H_6OS$, space group $P3_2$, show twinning by merohedry (class II). The asymmetric unit contains two organotellurium molecules and one dimethyl sulfoxide (DMSO) molecule. The crystal structure displays secondary $Te\cdots I$ and $Te\cdots O(DMSO)$ bonds that lead to $[(4\text{-}MeOC_6H_4)_2TeI_2]_2\cdot DMSO$ supramolecular units in which the two independent organotellurium molecules are bridged by the DMSO O atom. In addition to these secondary bonds, $I\cdots I$ interactions link translationally equivalent organotellurium molecules to form nearly linear $\cdots I\text{-}Te\text{-}I\cdots I\text{-}Te\text{-}I\cdots$ chains. These chains are crosslinked, forming two-dimensional arrays parallel to (001). The crystal packing consists of a stacking of these sheets, which are related by the 3_2 axis. This study describes an unusual dimeric arrangement of $X\text{-}Te\text{-}X$ groups.

Comment

As part of our studies of organotellurium compounds (Farran *et al.*, 2002*a*,*b*, and references therein), we have synthesized several bis(aryl)tellurium(IV) dihalides, among them bis(4-methoxyphenyl)tellurium diiodide, (I). During crystallization trials of (I), we observed the formation of crystals of various morphologies and colours, depending on the solvents and conditions used. This observation, and the well known facts that organotellurium(IV) iodides frequently display secondary bonding, which gives rise to a wide variety of supramolecular assemblies (Zukerman-Schpector & Haiduc, 2001; Haiduc & Zukerman-Schpector, 2001), that they are often polymorphic [see, for example, McCullough *et al.* (1985), Närhi *et al.* (2004), Srivastava *et al.* (2004) and Beckmann *et al.*

(2005), and references therein], and that they have colours that are related to the occurrence of noncovalent interactions (McCullough *et al.*, 1985; Dewan & Silver, 1977), led us to a systematic study of these specimens.
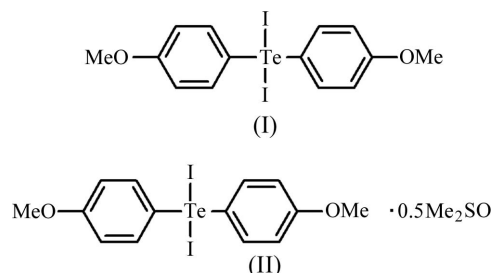
In a previous paper (Farran *et al.*, 1998), we reported the crystal structures of two polymorphs of (I), namely (I*a*) in space group $P\bar{1}$ with $Z = 8$ and (I*b*) in space group $P\bar{1}$ with $Z = 4$, and mentioned several other crystal phases containing (I) and iodine, benzene, acetonitrile and dimethyl sulfoxide (DMSO). Among these crystals, those including DMSO were remarkable in their colour as, unlike the shades of red displayed by the other crystals, they were green with a metallic lustre (Fig. 1). Chemical and spectroscopic analyses revealed that these green crystals correspond to the title DMSO hemisolvate of (I), *viz.* (II). We describe here the crystal structure determination of (II) based on X-ray diffraction data from a merohedral twin. The study revealed that the asymmetric unit contains a supramolecular entity made up of two molecules of (I) bridged by one DMSO molecule (Fig. 2).

Bond distances and angles in the molecule of (I) in the title hemisolvate (Table 1) are similar to those observed in polymorphs (I*a*) and (I*b*). In the supramolecular unit, each Te atom has an extended environment that can be described as a distorted octahedron based on the two Te—C and the two Te—I bonds, together with the secondary interactions $Te\cdots I$ and $Te\cdots O$ (Fig. 2). The $Te\cdots I$ distances are similar to those
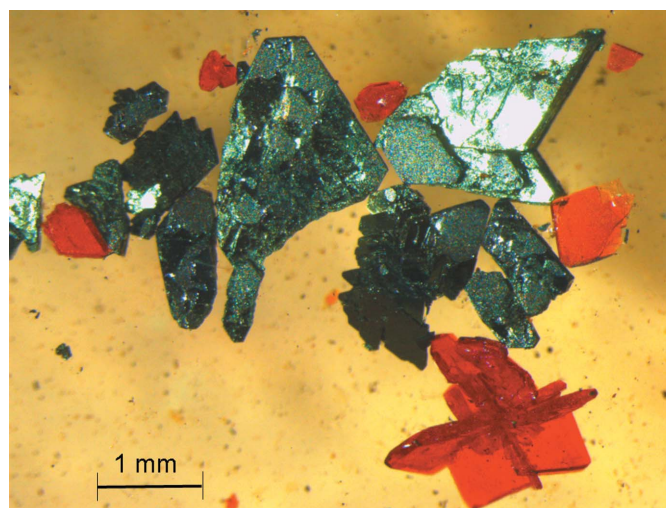
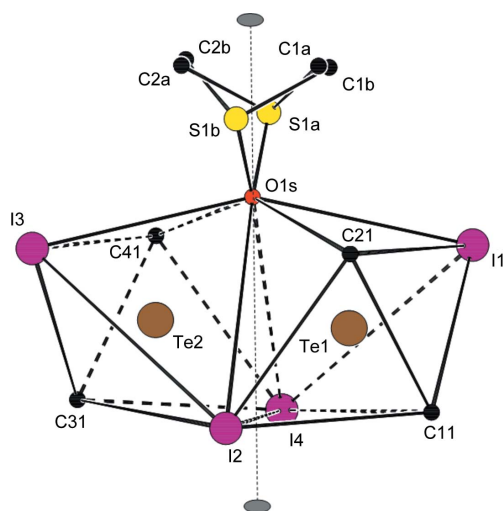**Figure 1**
Crystals of (I*b*) and (II) as obtained by evaporation from DMSO [crystals of (I*b*) are red and crystals of (II) are green, as can be seen in the electronic version of the paper].

---

[1] In memory of our colleague and friend Professor Libardo Torres Castellanos (1938–2006), who pioneered the study of organotellurium compounds in Colombia.

organic compounds
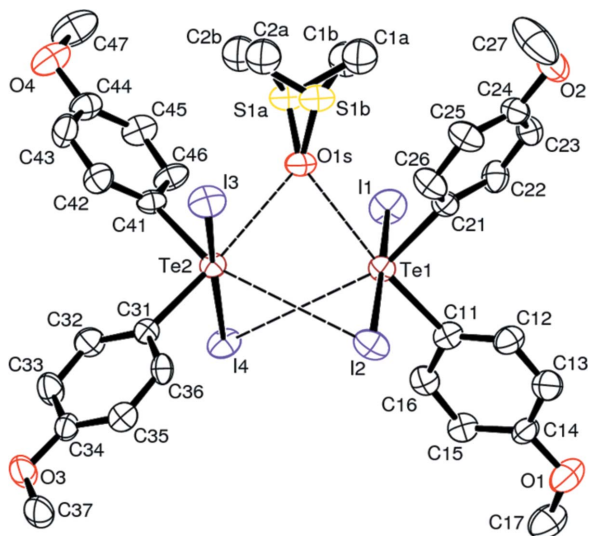
Figure 2
The supramolecular assembly of (II). Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity. Both disorder components of the DMSO molecule are shown.

Figure 3
The dioctahedral core around the Te atoms. Both disorder components of the DMSO molecule and the pseudo-twofold axis have also been included.

observed in polymorphs (Ia) and (Ib) (Table 2), while the Te$\cdots$O distances are comparable with those found in similar DMSO solvates (*e.g.* Mørkved *et al.*, 1997). The two TeC$_2$I$_3$O octahedra share the face defined by atoms I2, I4 and O1s (Fig. 3). Two regular octahedra joined by a common face display $\overline{6}2m$ point symmetry but, in this case, the different nature of the atoms at the vertices reduces the symmetry to 2. Indeed, in the crystal structure a pseudo-twofold axis through atom O1s can be considered. This local symmetry axis also relates the methyl groups of DMSO and the two disordered positions of the S atom (site-occupancy factors = 0.56:0.44) (Fig. 3), while the aryl groups break down the pseudosymmetry.

In the (Ia) and (Ib) crystal structures, each Te atom forms two secondary Te$\cdots$I bonds and has a distorted TeC$_2$I$_4$ octa-
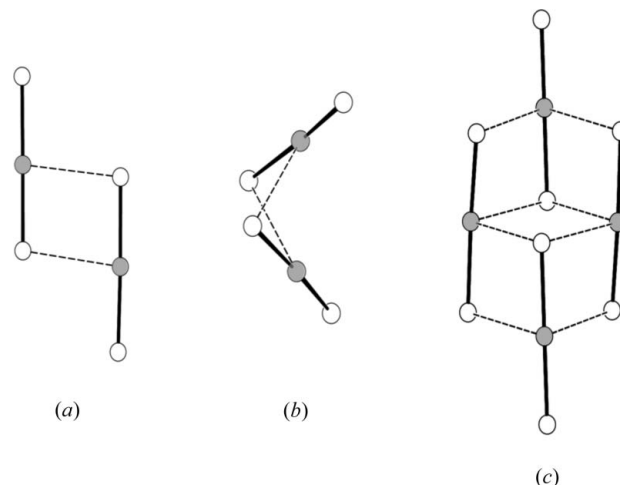
Figure 4
Dimeric and tetrameric supramolecular assemblies of $X-$Te$-X$ in TeX_2R_2 (see *Comment*).

hedral environment. This arrangement results in centrosymmetric tetramers with step-like Te$_4$I$_8$ cores (Fig. 4c). This seems to be the basic structural unit that dominates the crystal packing of (I) in the absence of other donor atoms capable of forming Te$\cdots X$ secondary bonds (*e.g.* X = O). In the title hemisolvate, one of the Te$\cdots$I interactions is replaced by a Te$\cdots$O interaction. As a result of this arrangement, the linear I$-$Te$-$I groups are not nearly parallel as in the step-like Te$_4$I$_8$, but form an angle of 61.09 (3)° (Fig. 4b). Zukerman-Schpector *et al.* (2002) discussed the possible dimeric, tetrameric and polymeric assemblies formed by diorganotellurium(IV) dihalides through Te$\cdots$halogen interactions, and the nonparallel dimeric arrangement observed in the present structure is included in their scheme. The structure of (p-PhOC$_6$H$_4$)$_2$TeCl$_2$, previously studied by us (de Matheus *et al.*, 1991), was wrongly given as an example of a nonparallel dimer, whereas in reality it is a parallel dimer (Fig. 4a). The structure of (II), however, does constitute an example of this nonparallel dimeric arrangement. Two other cases of nonparallel $X-$Te$-X$ groups are bis(dichlorophenyltelluro)-methane (Batchelor *et al.*, 1987) and bis(dibromomesityl-telluro)methane (Dakternieks *et al.*, 2000). In these structures, the $X-$Te$-X$ groups are covalently bridged by a methylene group in a similar way to (II), where they are bridged by the DMSO O atom. Moreover, in these two structures, a crystallographic twofold axis (through the methylene C atom) relates the two groups.

In the present crystal structure, I$\cdots$I interactions link translationally equivalent molecules of (I) to form nearly linear $\cdots$I$-$Te$-$I$\cdots$I$-$Te$-$I$\cdots$ chains (Table 2). Each supramolecular unit, 2(I)·DMSO, is involved in two such chains (in the asymmetric unit, one parallel to the crystallographic a axis and the other to the $a+b$ direction). As a result of the crosslinking of these chains, a two-dimensional array parallel to (001) is formed (Fig. 5a). The crystal structure consists of a stacking of these sheets, which are related by the 3$_2$ axis (Fig. 5b). Nearly linear $\cdots$I$-$Te$-$I$\cdots$I$-$Te$-$I$\cdots$ chains have been reported previously (Chao & McCullough,

(a)

(b)
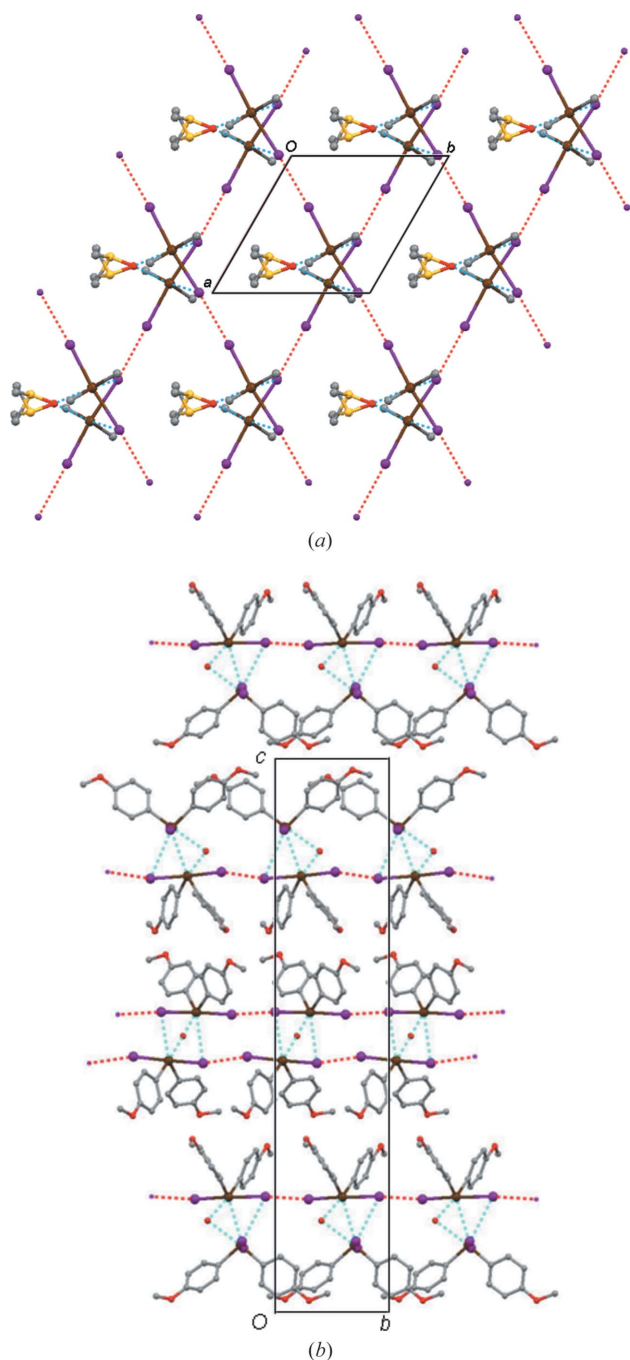
Figure 5
Two perpendicular views of the crystal packing, with dotted lines showing the contacts between supramolecular units (I···I) and those inside supramolecular units (Te···I and Te···O). For clarity, H atoms have been omitted. In (a) only the Te-bonded C atoms of the anisyl groups are shown and in (b) only the DMSO O atom is shown.

1962; Knobler *et al.*, 1970). In the first case, all chains are parallel and no sheets are formed. In the second case, perpendicularly crosslinked chains define sheets similar to those described here.

We have discussed the role of secondary bonds in supramolecular self-assembly and packing of crystal forms of (I). Furthermore, two other points are worthy of note, *viz.* their

influence on covalent bond distances and on colour. The former is a well known characteristic of diorganotellurium(IV) dihalides (McCullough *et al.*, 1985) and can also be observed in the hemisolvate (II), and in the polymorphs (I*a*) and (I*b*): the higher the number of secondary bonds to iodine, the longer the Te—I distance. Thus, in (II), two sets of Te—I distances are found, one for I atoms involved in two secondary bonds and another for I atoms forming one secondary bond only (Table 2), while in (I*a*) and (I*b*), three sets were observed, for I atoms with two, one or zero secondary bonds. With regard to the colour of organotellurium(IV) iodides, the influence of secondary bonds has been discussed previously (McCullough *et al.*, 1985; Dewan & Silver, 1977). Secondary Te···I bonds produce a range of orange-to-red colours, while I···I interactions give rise to darker colours (purple, violet or even black). In contrast, cases of green compounds have proved more difficult to explain (McCullough *et al.*, 1985). In the present structure, the unusual supramolecular arrangement in (II), with the presence of a Te···Te contact (Table 2) and the Te···DMSO coordination, might be an explanation for the green colour.

Experimental

Compound (I) was prepared as described previously by Farran *et al.* (1998). Green crystals of the title hemisolvate, (II), were obtained by slow evaporation from a DMSO solution of (I) at room temperature or at 277 K. After removal from solution and drying, the crystals decomposed slowly (in a few days) in air to give a red unsolvated crystalline powder. The crystal studied was protected with perfluoropolyether oil (FOMBLIN from Aldrich) during the measurement.

Crystal data

$C_{14}H_{14}I_2O_2Te\cdot0.5C_2H_6OS$	$Z = 6$
$M_r = 634.75$	Mo $K\alpha$ radiation
Trigonal, $P3_2$	$\mu = 4.69$ mm^{-1}
$a = 9.4309$ (4) Å	$T = 296$ K
$c = 38.4799$ (17) Å	$0.38 \times 0.30 \times 0.13$ mm
$V = 2963.9$ (2) Å^3	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	20824 measured reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)	9060 independent reflections
$T_{min} = 0.156$, $T_{max} = 0.545$	7935 reflections with $I > 3\sigma(I)$
	$R_{int} = 0.021$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.031$	$\Delta\rho_{max} = 0.56$ e Å^{-3}
$wR(F^2) = 0.033$	$\Delta\rho_{min} = -0.32$ e Å^{-3}
$S = 1.34$	Absolute structure: refinement as an inversion twin
9060 reflections	Flack parameter: 0.01 (2)
378 parameters	
H-atom parameters constrained	

Refinement was carried out using the program *JANA2000* (Petříček *et al.*, 2000). After successive cycles, the refinement converged to an overall agreement factor of approximately 0.2. In addition, a large number of bond distances and angles showed unreasonable values. As the trigonal metric allows twinning by merohedry of class II (Giacovazzo, 2002), we tried a refinement

organic compounds

Table 1
Selected geometric parameters (Å, °).

Te1—I1	2.8809 (10)	Te2—I3	2.8645 (6)
Te1—I2	2.9780 (10)	Te2—I4	2.9933 (6)
Te1—C11	2.127 (8)	Te2—C31	2.097 (8)
Te1—C21	2.134 (8)	Te2—C41	2.113 (9)
I1—Te1—I2	173.89 (3)	I3—Te2—I4	173.91 (3)
I1—Te1—C11	88.8 (2)	I3—Te2—C31	89.98 (14)
I1—Te1—C21	93.6 (3)	I3—Te2—C41	94.40 (15)
I2—Te1—C11	88.0 (2)	I4—Te2—C31	87.22 (14)
I2—Te1—C21	92.0 (3)	I4—Te2—C41	91.38 (15)
C11—Te1—C21	99.3 (3)	C31—Te2—C41	99.2 (3)

Table 2
Contact distances (Å) and contact angles (°).

Te1···I4	3.8404 (9)	Te2···I2	3.8875 (9)
Te1···O1s	2.920 (6)	Te2···O1s	2.947 (9)
I1···I2[i]	3.6307 (11)	I3···I4[iii]	3.5887 (6)
Te1···Te2	3.8980 (6)		
I1—Te1···I4	90.30 (2)	I3—Te2···I2	91.04 (2)
I2—Te1···I4	85.33 (2)	I4—Te2···I2	84.282 (17)
I1—Te1···O1s	85.02 (19)	I3—Te2···O1s	84.55 (12)
I2—Te1···O1s	98.6 (2)	I4—Te2···O1s	98.45 (12)
C11—Te1···I4	102.4 (2)	C31—Te2···I2	102.2 (2)
C21—Te1···I4	158.05 (19)	C41—Te2···I2	157.9 (2)
C11—Te1···O1s	172.3 (3)	C31—Te2···O1s	174.00 (18)
C21—Te1···O1s	76.6 (2)	C41—Te2···O1s	78.8 (3)
I4···Te1···O1s	82.23 (13)	I2···Te2···O1s	80.42 (15)
Te1···O1s···Te2	83.3 (2)		
Te1—I1···I2[i]	167.15 (4)	Te2—I3···I4[iii]	173.39 (3)
Te1—I2···I1[ii]	167.81 (3)	Te2—I4···I3[iv]	175.62 (3)

Symmetry codes: (i) $x + 1, y, z$; (ii) $x - 1, y, z$; (iii) $x - 1, y - 1, z$; (iv) $x + 1, y + 1, z$.

model assuming a twofold rotation around the *a* axis as the twinning operation. The introduction of the corresponding twin law (100, $\overline{1}\overline{1}0$, $00\overline{1}$) and the subsequent refinement of the volume fraction of the second individual led to a rapid decrease in the overall agreement factor and resulted in reasonable bond distances and angles.

The noncentrosymmetric space group furthermore allows for the formation of racemic twins. If the corresponding additional twinning elements are taken into account, a four-component twin is obtained, where two twin symmetry operations have determinant 1 and the other two have determinant −1. A refinement using this four-component twin model showed that the volume fractions of the components corresponding to twin symmetry operations with determinant −1 are not significantly different from 0. Therefore, the parameter x^- [the sum of the volume fractions corresponding to twin laws of determinant −1; this factor is the equivalent of the Flack parameter for multiply twinned crystals (Flack & Bernardinelli, 1999)] is 0 and the crystalline sample contains exclusively the structure in space group $P3_2$.

H atoms were placed in geometrically idealized positions and treated as riding, with C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for CH groups, and with C—H = 0.96 Å and $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl groups.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS86* (Sheldrick, 2008); program(s) used to refine structure: *JANA2000* (Petříček *et al.*, 2000); molecular graphics: *ORTEP-3* (Farrugia, 1997), *PLUTON* in *PLATON* (Spek, 2003) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *JANA2000*.

References

Batchelor, R. J., Einstein, F. W. B., Jones, C. H. W. & Sharma, R. D. (1987). *Organometallics*, **6**, 2164–2168.

Beckmann, J., Dakternieks, D., Duthie, A., Mitchell, C. & Schürmann, M. (2005). *Aust. J. Chem.* **58**, 119–127.

Bruker (2003). *SADABS* (Version 2.05), *SAINT* (Version 6.22), and *SMART* (Version 5.630). Bruker AXS Inc., Madison, Wisconsin, USA.

Chao, G. Y. & McCullough, J. D. (1962). *Acta Cryst.* **15**, 887–893.

Dakternieks, D., O'Connell, J. & Tiekink, E. R. T. (2000). *Z. Kristallogr. New Cryst. Struct.* **215**, 87–88.

Dewan, J. C. & Silver, J. (1977). *J. Organomet. Chem.* **125**, 125–139.

Farran, J., Alvarez-Larena, A., Capparelli, M. V., Piniella, J. F., Germain, G. & Torres-Castellanos, L. (1998). *Acta Cryst.* C**54**, 995–1000.

Farran, J., Torres-Castellanos, L., Alvarez-Larena, A., Piniella, J. F. & Capparelli, M. V. (2002a). *Z. Kristallogr. New Cryst. Struct.* **217**, 427–429.

Farran, J., Torres-Castellanos, L., Alvarez-Larena, A., Piniella, J. F. & Capparelli, M. V. (2002b). *J. Organomet. Chem.* **654**, 91–99.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Flack, H. D. & Bernardinelli, G. (1999). *Acta Cryst.* A**55**, 908–915.

Giacovazzo, C. (2002). Editor. *Fundamentals of Crystallography*, 2nd ed., pp. 229–236. Oxford University Press.

Haiduc, I. & Zukerman-Schpector, J. (2001). *Phosphorus Sulfur Silicon Relat. Elem.* **171**, 171–185.

Knobler, C., McCullough, J. D. & Hope, H. (1970). *Inorg. Chem.* **9**, 797–804.

Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.

Matheus, M. de, Torres, L., Piniella, J. F., Briansó, J. L. & Miravitlles, C. (1991). *Acta Cryst.* C**47**, 703–705.

McCullough, J. D., Knobler, C. & Ziolo, R. F. (1985). *Inorg. Chem.* **24**, 1814–1818.

Mørkved, E. H., Faccin, G., Manfrotto, D., Kjøsen, H., Becker, J. Y., Shapiro, L., Ellern, A., Bernstein, J. & Khodorkovsky, V. (1997). *J. Mater. Chem.* **7**, 1697–1700.

Närhi, S. M., Oilunkaniemi, R., Laitinen, R. S. & Ahlgrén, M. (2004). *Inorg. Chem.* **43**, 3742–3750.

Petříček, V., Dušek, M. & Palatinus, L. (2000). *JANA2000*. Institute of Physics, Prague, Czech Republic.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

Srivastava, P. C., Bajpai, S., Bajpai, S., Ram, C., Kumar, R., Jasinski, J. P. & Butcher, R. J. (2004). *J. Organomet. Chem.* **689**, 194–202.

Zukerman-Schpector, J. & Haiduc, I. (2001). *Phosphorus Sulfur Silicon Relat. Elem.* **171**, 73–112.

Zukerman-Schpector, J., Haiduc, I., Camillo, R. L., Comasseto, J. V., Cunha, R. L. O. R. & Jorge, A. (2002). *Can. J. Chem.* **80**, 1530–1537.