

Triorganophosphine–dithiomono-  
metaphosphoryl halidesAnnegrit Rabis,<sup>a</sup> Burkhard Ziemer,<sup>b\*</sup> Dirk Wulff-Molder,<sup>c</sup>  
Manfred Meisel<sup>b</sup> and Sebastian Beck<sup>b</sup><sup>a</sup>Max Planck Institut für Chemische Physik fester Stoffe, Nöthnitzer Straße 40, D-01187 Dresden, Germany, <sup>b</sup>Institut für Chemie, Humboldt Universität zu Berlin, Brook Taylor Straße 2, D-12489 Berlin, Germany, and <sup>c</sup>Hardenbergstraße 15, D-24105 Kiel, Germany  
Correspondence e-mail: burkhard.ziemer@chemie.hu-berlin.deReceived 29 January 2002  
Accepted 1 March 2002  
Online 29 March 2002

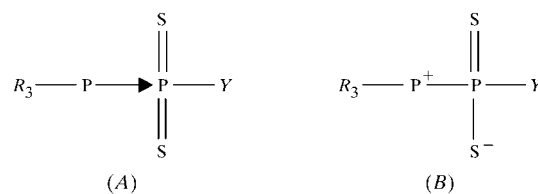
The title compounds, ethyldiphenylphosphine–dithiomonometaphosphoryl chloride,  $\text{EtPh}_2\text{P}\rightarrow\text{PS}_2\text{Cl}$ ,  $\text{C}_{14}\text{H}_{15}\text{ClP}_2\text{S}_2$ , (I), and tris-*n*-propylphosphine–dithiomonometaphosphoryl chloride and bromide,  ${}^n\text{Pr}_3\text{P}\rightarrow\text{PS}_2\text{Cl}$ ,  $\text{C}_9\text{H}_{21}\text{ClP}_2\text{S}_2$ , (II), and  ${}^n\text{Pr}_3\text{P}\rightarrow\text{PS}_2\text{Br}$ ,  $\text{C}_9\text{H}_{21}\text{BrP}_2\text{S}_2$ , (III), respectively, are the first phosphine-stabilized dithiomonometaphosphoryl halides to be structurally characterized. In the tris-*n*-propylphosphine derivatives, the central P→P donor–acceptor bond becomes longer in the order bromo < chloro < fluoro. Substitution of the tris-*n*-propylphosphine group in (II) by the more bulky ethyldiphenylphosphine group also leads to a longer P→P bond. These structural features agree with the observed  ${}^{31}\text{P}$  NMR data. In (II) and (III), the central P–P bond coincides with the crystallographic threefold axis, entailing site-occupational disorder for the  $\text{S}_2\text{Y}$  group.

## Comment

The first inner organylphosphonium dithiomonometaphosphonic salts were obtained by the reaction of perthioarylphosphonic anhydrides,  $(\text{RPS}_2)_2$ , with tris-*n*-butylphosphine (Fluck & Binder, 1967). The authors proposed a betaine structure for these compounds because of two doublets visible in the  ${}^{31}\text{P}$  NMR spectra. The observed doublets represent an *AB* spin system (see Scheme below), which should be typical for a betaine structure. At the same time, the first pyridine-stabilized dithiomonometaphosphoryl chloride,  $\text{py}\rightarrow\text{PS}_2\text{Cl}$ , was isolated (Meisel & Grunze, 1968). This compound was synthesized by nucleophilic degradation of the adamantane cage,  $\text{P}_4\text{S}_{10}$ , by pyridine in the presence of thio-phosphoryl chloride. Initially,  $\text{py}\rightarrow\text{PS}_2\text{Cl}$  was also described as a betaine. Later on, owing to the bonding data (especially the N→P bond distance) obtained from a crystal structure determination (Averbuch-Pouchot & Meisel, 1989), a donor–acceptor bond between the pyridine N atom and the  $\text{PS}_2\text{Cl}$  group was formulated. The relevant N→P bond length of

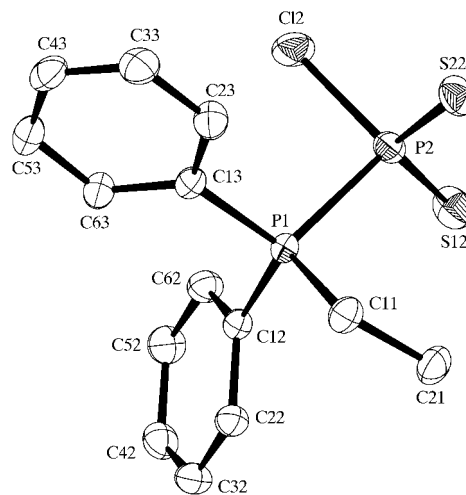
1.849 (6) Å was the longest known at that time. The proposed bonding model corresponds with the thermal behaviour of this type of compound, which has been shown by photoelectron spectroscopic experiments on  $\text{py}\rightarrow\text{PX}_2\text{Y}$  (*X* is O or S and *Y* is F or Cl; Meisel *et al.*, 1989; Bock *et al.*, 1992).

The present work is aimed at investigating the bonding situation of some analogous phosphine adducts, which are the two chlorides, ethyldiphenylphosphine–dithiomonometaphosphoryl chloride, (I), and tris-*n*-propylphosphine–dithiomonometaphosphoryl chloride, (II), and the bromide, tris-*n*-propylphosphine–dithiomonometaphosphoryl bromide, (III). These compounds provide the first structure examples of phosphine-stabilized dithiomonometaphosphoryl derivatives.



- (A) Phosphine-stabilized dithiophosphoryl halide  
 (B) Resonance-stabilized zwitterionic phosphonium halidodithiophosphinate  
 (I)  $\text{R}_3=\text{EtPh}_2$ ,  $\text{Y}=\text{Cl}$       (II)  $\text{R}_3=\text{Pr}_3$ ,  $\text{Y}=\text{Cl}$   
 (III)  $\text{R}_3=\text{Pr}_3$ ,  $\text{Y}=\text{Br}$       (IV)  $\text{R}_3=\text{Pr}_3$ ,  $\text{Y}=\text{F}$

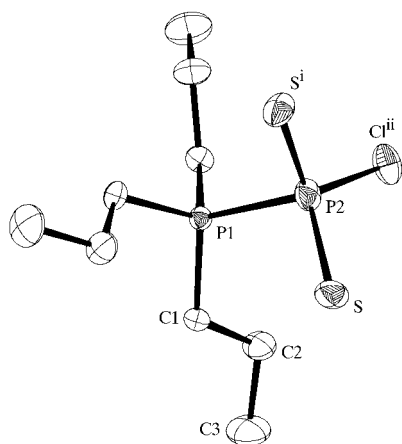
Compound (I) crystallizes in a monoclinic space group, forming a well ordered structure. Compounds (II) and (III) both crystallize in a trigonal space group and are isotypic with one another. Because the P→P bond of the molecules in (II) and (III) lies on a threefold axis, the  $\text{S}_2\text{Y}$  (*Y* is Cl or Br) ligands must be disordered. The same has been observed for the analogous fluoride compound, (IV), although the results for this compound are unpublished, because of another disorder problem restricting the results of additional structure determination (Rabis, 1999). In the tris-*n*-propylphosphine derivatives, the length of the P→P donor–acceptor bond is dependent on the halogen ligand and increases from Br *via* Cl



**Figure 1**  
A view of the molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

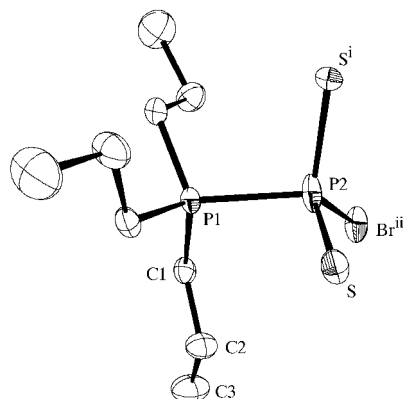
to F, *i.e.* from 2.2035 (16) *via* 2.2253 (10) to 2.251 (4) Å. These experimental results correlate with the  $\pi$ -donating properties of the halides, which increase from Br to F.

The  $^{31}\text{P}$  NMR spectra of (I)–(III) reflect the bonding situation in the magnitudes of the indirect spin–spin coupling constant,  $^1J_{\text{PP}}$ . Usually, it is assumed that the shorter the bond length, the larger the  $J$  value. Our experiments show that the absolute magnitudes of  $^1J_{\text{PP}}$  decrease from  $\text{Br}^-$  to  $\text{F}^-$ . In the case of phosphorus compounds, the coupling constant  $^1J_{\text{PP}}$  depends primarily on the valency of the P atoms involved and is related to the absence or presence of lone pairs. Thus, for  $\text{Me}_2\text{P}-\text{PMe}_2$ ,  $^1J_{\text{PP}}$  is  $-180$  Hz, whereas for the corresponding disulfide, a value of 19 Hz has been found (Harris, 1983). This, in connection with the X-ray results, gives rise to the supposition that, in the present case,  $^1J_{\text{PP}}$  has a positive sign.



**Figure 2**

A view of the molecular structure of (II). Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity. Only one disordered component is shown, and the symmetry codes generate the three crystallographically equivalent positions for the atoms of the  $\text{S}_2\text{Y}$  group [symmetry codes: (i)  $1 - y, x - y, z$ ; (ii)  $1 - x + y, 1 - x, z$ ].



**Figure 3**

A view of the molecular structure of (III). Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity. Only one disordered component is shown, and the symmetry codes generate the three crystallographically equivalent positions for the atoms of the  $\text{S}_2\text{Y}$  group [symmetry codes: (i)  $1 - y, x - y, z$ ; (ii)  $1 - x + y, 1 - x, z$ ].

A comparison of the structural data of the two chloride compounds, (I) and (II), shows that the P→P bond is shorter in the tris-*n*-propylphosphine adduct, (II) [2.2253 (10) Å], than in the ethyldiphenylphosphine adduct, (I) [2.2522 (5) Å]. This can be explained by the higher steric demand of the ethyldiphenylphosphine group compared with the tris-*n*-propylphosphine group, which is also in agreement with the corresponding Tolman cone angles of 140 and 132°, respectively (Tolman, 1977).

## Experimental

Using a method analogous to that of Fluck *et al.* (1973), a solution of tris-*n*-organylphosphine (9.5 mmol) was added dropwise to a suspension of  $\text{py} \rightarrow \text{PS}_2\text{Y}$  (9.5 mmol) (Y is Br, Cl or F) in benzene with stirring. The product was filtered off after 1 h and washed with benzene. Yields: 81% for (I), 67% for (II), 78% for (III), 96% for Y = F, *i.e.* (IV). The  $^{31}\text{P}$  NMR solution spectra of both chlorides and of the bromide showed the two doublets characteristic for AB spin systems, as follows: for (I): 9.2 p.p.m. (*d*), 71.9 p.p.m. (*d*),  $^1J_{\text{PP}} = 59.3$  Hz; for (II): 18.8 p.p.m. (*d*), 69.7 p.p.m. (*d*),  $^1J_{\text{PP}} = 41.5$  Hz; for (III): 17.8 p.p.m. (*d*), 45.7 p.p.m. (*d*),  $^1J_{\text{PP}} = 42.0$  Hz. In the  $^{31}\text{P}$  NMR solution spectrum of  $\text{Pr}_3\text{P} \rightarrow \text{PS}_2\text{F}$ , (IV), there are two doublets of doublets because of the additional coupling to the  $^{19}\text{F}$  nucleus: 11.8 p.p.m. with  $^2J_{\text{PF}} = 117.8$  Hz, and 102.2 p.p.m. with  $^1J_{\text{PF}} = 1111.2$  Hz and  $^1J_{\text{PP}} = 11.4$  Hz. Crystals of all four compounds suitable for X-ray analysis were obtained by recrystallization from solutions in benzene/acetonitrile (10:1).

## Compound (I)

### Crystal data

$\text{C}_{14}\text{H}_{15}\text{ClP}_2\text{S}_2$   
 $M_r = 344.77$   
 Monoclinic,  $P2_1/n$   
 $a = 13.204$  (1) Å  
 $b = 9.694$  (1) Å  
 $c = 13.655$  (1) Å  
 $\beta = 117.11$  (1)°  
 $V = 1555.8$  (3) Å<sup>3</sup>  
 $Z = 4$

$D_x = 1.472$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 5000 reflections  
 $\theta = 6.9$ – $28.3^\circ$   
 $\mu = 0.70$  mm<sup>-1</sup>  
 $T = 190$  (2) K  
 Prismatic, colourless  
 $0.57 \times 0.38 \times 0.19$  mm

### Data collection

Stoe IPDS diffractometer  
 $\varphi$  scans  
 Absorption correction: refined from  $\Delta F^2$  (ABSCOR; Stoe & Cie, 1996)  
 $T_{\text{min}} = 0.659$ ,  $T_{\text{max}} = 0.875$   
 18 747 measured reflections

3738 independent reflections  
 3485 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.043$   
 $\theta_{\text{max}} = 28.1^\circ$   
 $h = -17 \rightarrow 15$   
 $k = -12 \rightarrow 12$   
 $l = -17 \rightarrow 17$

**Table 1**

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

P1–C12	1.7958 (13)	P2–S12	1.9399 (5)
P1–C13	1.8023 (12)	P2–S22	1.9454 (5)
P1–C11	1.8090 (13)	P2–Cl2	2.0724 (5)
P1–P2	2.2522 (5)		
C12–P1–C13	109.64 (6)	S12–P2–S22	122.76 (2)
C12–P1–C11	110.54 (6)	S12–P2–Cl2	110.64 (2)
C13–P1–C11	109.31 (6)	S22–P2–Cl2	109.07 (2)
C12–P1–P2	110.95 (4)	S12–P2–P1	108.87 (2)
C13–P1–P2	109.08 (4)	S22–P2–P1	105.08 (2)
C11–P1–P2	107.27 (5)	Cl2–P2–P1	97.25 (2)

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.028$   
 $wR(F^2) = 0.081$   
 $S = 1.07$   
 3738 reflections  
 172 parameters  
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0507P)^2 + 0.4476P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.002$   
 $\Delta\rho_{\max} = 0.41 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.37 \text{ e } \text{\AA}^{-3}$

## Compound (II)

## Crystal data

$\text{C}_9\text{H}_{21}\text{ClP}_2\text{S}_2$   
 $M_r = 290.77$   
 Trigonal,  $P\bar{3}c1$   
 $a = 11.413 (3) \text{ \AA}$   
 $b = 11.413 (4) \text{ \AA}$   
 $c = 13.566 (3) \text{ \AA}$   
 $V = 1530.3 (8) \text{ \AA}^3$   
 $Z = 4$   
 $D_x = 1.262 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation  
 Cell parameters from 5000 reflections  
 $\theta = 2.5\text{--}25.0^\circ$   
 $\mu = 0.70 \text{ mm}^{-1}$   
 $T = 180 (2) \text{ K}$   
 Block, colourless  
 $0.68 \times 0.40 \times 0.28 \text{ mm}$

## Data collection

Stoe IPDS diffractometer  
 $\varphi$  scans  
 Absorption correction: numerical  
 [XRED (Stoe & Cie, 1996) and XSHAPE (Stoe & Cie, 1996), based on HABITUS (Herrendorf, 1993)]  
 $T_{\min} = 0.777$ ,  $T_{\max} = 0.848$

10 448 measured reflections  
 1001 independent reflections  
 987 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.056$   
 $\theta_{\max} = 26^\circ$   
 $h = -13 \rightarrow 14$   
 $k = -14 \rightarrow 13$   
 $l = -16 \rightarrow 16$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.022$   
 $wR(F^2) = 0.054$   
 $S = 1.10$   
 1000 reflections  
 48 parameters  
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0313P)^2 + 0.2298P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.002$   
 $\Delta\rho_{\max} = 0.30 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.18 \text{ e } \text{\AA}^{-3}$

Table 2

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (II).

Cl1—P1	1.805 (2)	P2—S1	1.964 (6)
P1—P2	2.2253 (10)	P2—Cl1	2.026 (12)
Cl1—P1—Cl1 <sup>i</sup>	108.84 (5)	S1—P2—Cl1 <sup>i</sup>	114.8 (8)
Cl1—P1—P2	110.10 (5)	Cl1—P2—Cl1 <sup>i</sup>	116.1 (3)
S1—P2—S1 <sup>i</sup>	112.2 (2)	S1—P2—P1	106.6 (2)
S1 <sup>i</sup> —P2—Cl1	113.9 (8)	Cl1—P2—P1	101.6 (4)

Symmetry code: (i)  $1 - y, x - y, z$ .

## Compound (III)

## Crystal data

$\text{C}_9\text{H}_{21}\text{BrP}_2\text{S}_2$   
 $M_r = 335.23$   
 Trigonal,  $P\bar{3}c1$   
 $a = 11.522 (3) \text{ \AA}$   
 $b = 11.522 (3) \text{ \AA}$   
 $c = 13.450 (4) \text{ \AA}$   
 $V = 1546.3 (7) \text{ \AA}^3$   
 $Z = 4$   
 $D_x = 1.440 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation  
 Cell parameters from 1524 reflections  
 $\theta = 2.5\text{--}25.0^\circ$   
 $\mu = 3.10 \text{ mm}^{-1}$   
 $T = 180 (2) \text{ K}$   
 Trigonal prism, colourless  
 $0.16 \times 0.15 \times 0.12 \text{ mm}$

Table 3

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (III).

Cl1—P1	1.801 (2)	P1—P2	2.2035 (16)
Br1—P2	2.128 (6)	P2—S1	1.954 (8)
Cl <sup>i</sup> —P1—Cl1	109.38 (8)	S1 <sup>i</sup> —P2—Br1	113.9 (12)
Cl1—P1—P2	109.57 (8)	Br1 <sup>i</sup> —P2—Br1	114.5 (4)
S1 <sup>i</sup> —P2—S1	113.1 (6)	S1—P2—P1	105.5 (7)
S1—P2—Br1 <sup>i</sup>	113.8 (12)	Br1—P2—P1	103.8 (5)

Symmetry code: (i)  $1 - y, x - y, z$ .

## Data collection

Stoe IPDS diffractometer  
 $\varphi$  scans  
 Absorption correction: numerical  
 (XRED; Stoe & Cie, 1996)  
 $T_{\min} = 0.637$ ,  $T_{\max} = 0.707$   
 9325 measured reflections  
 1024 independent reflections

722 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.109$   
 $\theta_{\max} = 26.2^\circ$   
 $h = -14 \rightarrow 13$   
 $k = -14 \rightarrow 14$   
 $l = -16 \rightarrow 16$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.033$   
 $wR(F^2) = 0.061$   
 $S = 0.89$   
 1024 reflections  
 47 parameters

H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0275P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.004$   
 $\Delta\rho_{\max} = 0.36 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.45 \text{ e } \text{\AA}^{-3}$

All checked crystals of (II) were merohedrally twinned to [001]. In the crystal analysed here, the ratio of the two twin domains was 0.522 (2):0.478 (2). Disorder was observed in structures (II) and (III), so that two S atoms and one Cl atom in (II), and two S atoms and one Br atom in (III) partially occupy sites which are equivalent by threefold symmetry. However, the distances between the S-atom and halide sites are less than 0.20  $\text{\AA}$  in each structure. Therefore, the site separation is much lower than the atomic resolution achievable with the current data sets. Hence, the P—S and P—Cl distances were restrained to target values taken from the well ordered structure, (I) (Table 1), and the P—Br distance was restrained to 2.14 (2)  $\text{\AA}$  (Vogt *et al.*, 1993) throughout all the least-squares cycles. The  $U_{ij}$  values for the disordered atoms of (II) and (III) were constrained to be equal. For (I), a  $\Delta F^2$ -based absorption correction was applied, using *ABSCOR* (Stoe & Cie, 1996), a modification of *DIFABS* (Walker & Stuart, 1983). In contrast with *DIFABS*, *ABSCOR* loads  $F^2$  values instead of  $F$ . For (II), a numerical absorption correction using a Gaussian algorithm was applied, using *XRED* (Stoe & Cie, 1996). Before the actual absorption correction, the program *XSHAPE* (Stoe & Cie, 1996) was applied to optimize the predetermined crystal shape. 1462 medium-strong symmetry-equivalent reflections, of which 150 were unique, were used for the optimization. *XSHAPE* is based on the program *HABITUS* (Herrendorf, 1993). For (III), all crystal faces were indexed by microscope on the diffractometer, and thereafter a Gaussian integration numerical absorption correction was applied. All H atoms were placed in geometrically idealized positions, with C—H = 0.95–0.99  $\text{\AA}$ , and constrained to ride on their parent atoms, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . Additionally, the methyl H atoms were allowed to rotate about the C—C bonds.

For all three compounds, data collection: *IPDS* (Stoe & Cie, 1996); cell refinement: *IPDS*; data reduction: *IPDS*. For compounds (I) and (III), program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997). For compound (II), program(s) used to solve structure:

*SHELXS86* (Sheldrick, 1990). For all three compounds, program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1996); software used to prepare material for publication: *SHELXL97*.

This work was supported by the Humboldt Universität zu Berlin.

---

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1136). Services for accessing these data are described at the back of the journal.

---

## References

- Averbuch-Pouchot, M.-T. & Meisel, M. (1989). *Acta Cryst.* **C45**, 1937–1939.
- Bock, H., Kremer, M., Solouki, B., Binnewies, M. & Meisel, M. (1992). *J. Chem. Soc. Chem. Commun.* pp. 9–11.
- Brandenburg, K. (1996). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
- Fluck, E. & Binder, H. (1967). *Z. Anorg. Allg. Chem.* **354**, 113–129.
- Fluck, E., Retuert, P. J. & Binder, H. (1973). *Z. Anorg. Allg. Chem.* **397**, 225–236.
- Harris, R. K. (1983). *Nuclear Magnetic Resonance Spectroscopy*, p. 219. London: Pitman.
- Herrendorf, W. (1993). PhD dissertation, University of Karlsruhe, Germany.
- Meisel, M., Bock, H., Solouki, B. & Kremer, M. (1989). *Angew. Chem.* **101**, 1378–1381.
- Meisel, M. & Grunze, H. (1968). *Z. Anorg. Allg. Chem.* **360**, 277–283.
- Rabis, A. (1999). PhD dissertation, Humboldt University of Berlin, Germany.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.
- Stoe & Cie (1996). *ABSCOR* (Version 2.75), *IPDS* (Version 2.75), *XRED* (Version 1.08) and *XSHAPE* (Version 1.02). Stoe & Cie, Darmstadt, Germany.
- Tolman, C. A. (1977). *Chem. Rev.* **77**, 313–348.
- Vogt, H., Trojanov, S. I. & Rybakov, V. B. (1993). *Z. Naturforsch. Teil B*, **48**, 258–262.
- Walker, N. & Stuart, D. (1983). *Acta Cryst.* **A39**, 158–166.