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Reaction of tertiary phosphine selenides, R_3PSe (R = Me_2N, Et_2N or C_6H_{11}), with dibromine. The first reported examples of 1 : 1 addition

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The R_3PSeBr_2 compounds (R = Me_2N, Et_2N or C_6H_{11}) have been prepared and characterised by ^{31}P-{H} and infrared spectroscopy. The compounds R_3PSeBr_2 (R = Me_2N or C_6H_{11}) have also been crystallographically characterised. In contrast to the analogous diiodo compounds R_3PSeI_2 (which have a molecular Ψ-tetrahedral charge-transfer structure, $R_3PSeI–I$), the R_3PSeBr_2 compounds adopt Ψ-trigonal bipyramids at the selenium centre (taking account of the stereochemically active lone pairs). The crystal structure of $(Me_2N)_3PSeBr_2$ exhibits very different *d*(Se–Br), 2.602(2) and 2.544(2) Å. This phenomenon is reasoned to be due to the fact that both staggered and eclipsed Se–Br bonds are observed in the structure. The crystal structure of $(C_6H_{11})_3PSeBr_2$ shows two crystallographically independent molecules in the asymmetric unit, *d*(Se–Br) being identical in one molecule, 2.568(3) and 2.566(3) Å, but significantly different in the second molecule, 2.591(3) and 2.556(3) Å. A possible explanation for this is the presence of a close non-bonded Br $\cdots$ Br contact in this second $(C_6H_{11})_3PSeBr_2$ molecule. The compounds R_3PSeBr_2 (R = Me_2N or C_6H_{11}) both exhibit P–Se bonds typical of those expected for single bonds, 2.262(2) and 2.263(2) average, respectively, again in contrast to the analogous diiodo compounds, R_3PSeI_2, in which significant P–Se double bond character was retained. The ^{31}P-{H} NMR and infrared spectroscopic data for R_3PSeBr_2 (R = Me_2N, Et_2N or C_6H_{11}) are discussed with respect to those of the parent tertiary phosphine selenide, R_3PSe.

Introduction

The nature of compounds formed between tertiary phosphine selenides and dihalogens has received only limited study. Spectroscopic studies by Zingaro and Meyers[1,2] concerning the reaction of Ph_3PSe with diiodine or iodine monobromide point to the formation of a stable 1 : 1 adduct of formula Ph_3PSeX_2 ($X_2 = I_2$ or IBr). In contrast, the stoichiometric reaction of diiodine with triphenylphosphine sulfide produced an unexpected compound of formula $2Ph_3PS{\cdot}3I_2$. An X-ray crystallographic study of this molecule,[3] the first reported crystallographic study of a compound formed from the interaction of R_3PS with dihalogens, revealed an interesting dimeric structure where two Ph_3PSI_2 moieties are linked into pairs by a diiodine molecule. The *d*(I–I) for the I_2 is significantly lengthened [2.85(1) Å compared to *d*(I–I) for solid diiodine, 2.71(1) Å], indicating that electron density is being donated to the σ* antibonding orbitals of the diiodine by the two Ph_3PSI_2 moieties. The *d*(I–I) between the terminal iodide atoms on the Ph_3PSI_2 moieties and the diiodine molecule are 3.57(1) Å, constituting long but significant I–I interactions when compared to the van der Waals radius for two iodine atoms (4.3 Å). From this observation, and the fact that lengthening of the *d*(I–I) for the diiodine molecule is observed, it would appear that the donor power of Ph_3PS towards diiodine is not sufficiently strong to form a stable 1 : 1 adduct[3] and that a further Ph_3PS moiety and a diiodine molecule are required to form a stable adduct.

However, very recently Bricklebank and co-workers[4] reported the single crystal structure of the 1 : 1 adduct Ph_3PSI_2, clearly illustrating that triphenylphosphine sulfide is able to form a charge-transfer complex with diiodine. The crystal structure reveals approximately tetrahedral geometry for the phosphorus atom and Ψ-tetrahedral geometry for the sulfur atom; *d*(P–S) for the complex, 1.998(2) Å, is rather short suggesting some retention of phosphorus–sulfur double bond character, an analogous phenomenon being observed by us[5] for the compound Ph_3PSeI_2, in which significant retention of phosphorus–selenium double bond character is observed. In fact the structural features of Ph_3PSI_2 are generally very similar to those exhibited by Ph_3PSeI_2. One notable difference between Ph_3PEI_2 (E = S or Se) is the difference in iodine–iodine bond lengths, *d*(I–I) for Ph_3PSI_2 and Ph_3PSeI_2 being 2.823(1) and 2.881(3) Å respectively. These differences reflect the fact that the selenium atom in Ph_3PSe is a better donor towards diiodine than the sulfur atom in Ph_3PS, as expected. Nevertheless, despite the poorer donor ability of Ph_3PS towards diiodine it is still able to form a 1 : 1 complex, Ph_3PSI_2, which is contrary to the conclusions of previous workers.

Until recently, no X-ray crystallographic data were available for any tertiary phosphine selenide dihalogen compounds, however in 1996 we[5] investigated the structural nature of the diiodide adducts, R_3PSeI_2 (R = Ph, Me_2N or Et_2N). All such compounds were shown to be charge-transfer, $R_3PSe–I–I$, complexes. The *d*(I–I) was found to be dependent on R, 2.881(2), 2.962(2) (average) and 2.985(2) Å, for Ph_3PSeI_2, $(Me_2N)_3PSeI_2$ and $(Et_2N)_3PSeI_2$, respectively. These observations clearly illustrate that *d*(I–I) is sensitive to the basicity of the parent tertiary phosphine,[4] despite the fact that the R groups are bound to the phosphorus atom and not to the donor selenium atom.[5] There are no reports concerning the reaction of any tertiary phosphine selenide with the lighter halogens.

We are currently engaged in a study of the interaction of organogroup 15 and 16 donor atoms with dihalogens. We have found that the nature of the products formed are dependent on three variables: the organo substituents resident on the Group 15 or 16 donor atom, the donor atom itself, and the dihalogen employed. For example, triphenylarsine–diiodine is a molecular charge transfer compound $Ph_3As–I–I$, whereas triphenylarsine dibromide is trigonal bipyramidal.[6] Our studies on the analogous Group 16 systems, R_2SeX_2, have similarly shown that

Table 1 Analytical and $^{31}P-\{H\}$ NMR and infrared spectroscopic data for the compounds R_3PSe and R_3PSeBr_2 (R = Me_2N, Et_2N or C_6H_{11})

Compound	Colour	% Elemental analysis: Found (Calc.) C	H	N	Br	$\delta(^{31}P-\{H\})^a$	$\tilde{\nu}$(P–Se)/cm^{-1}
$(Me_2N)_3PSe$	White	29.6(29.8)	7.4(7.4)	17.2(17.4)	—	83.2	530
$(Me_2N)_3PSeBr_2$	Yellow	17.7(17.9)	4.2(4.5)	10.1(10.4)	40.4(39.8)	66.1	504
$(Et_2N)_3PSe$	White	43.8(44.1)	9.4(9.2)	12.8(12.9)	—	77.1	553
$(Et_2N)_3PSeBr_2$	Yellow	29.8(29.6)	29.8(29.6)	7.0(7.2)	32.8(32.9)	66.1	517
$(C_6H_{11})_3PSe^b$	White	60.4(60.2)	9.0(9.2)	—	—	59.0	550
$(C_6H_{11})_3PSeBr_2$	Yellow	41.5(41.6)	6.5(6.4)	—	30.4(30.8)	56.7	517

[a] Shifts recorded in $CDCl_3$ solution, relative to concentrated phosphoric acid as standard. [b] Selenium analysis 22.2(22.0)%.

Me_2SeI_2 adopts a molecular three-co-ordinate charge-transfer structure, Me_2Se–I–I, whereas the adducts with the lighter halogens (Cl, Br) adopt a Ψ-trigonal bipyramidal structure.[7] Finally, we have also shown that the solvent of preparation for these compounds is of importance; for example, we treated equimolar quantities of triphenylphosphine and dichlorine in dichloromethane solution and crystallographically characterised[8] the product as the solvated dinuclear ionic species $[Ph_3PCl\cdots Cl\cdots ClPPh_3]Cl\cdot 2CH_2Cl_2$; however, the same reaction performed in diethyl ether solution produces the non-solvated molecular trigonal bipyramidal species, Ph_3PCl_2.[9] We were, therefore, interested structurally to characterise the products formed from the reaction of tertiary phosphine selenides and dibromine, for three reasons: first, there are no reports concerning such reactions,[5] secondly to determine if changes in the R groups on a given tertiary phosphine selenide affect the nature of any product(s) formed upon reaction with dibromine and finally to investigate whether tertiary phosphine selenide–dibromine compounds adopt a structure analogous to that of the corresponding diiodine compounds, *viz.* the charge transfer structure, R_3PSeX–X, or whether a different structure would be revealed.

Results and discussion

Analytical and spectroscopic data for the tertiary phosphine selenides, and their 1 : 1 addition compounds with dibromine, are displayed in Table 1. The tertiary phosphine selenides were easily prepared from the direct reaction of tertiary phosphine with elemental selenium at room temperature (r.t.) in diethyl ether according to literature methods.[10] The reaction time was approximately 1 d to yield quantitatively the air stable R_3PSe compound which was isolated by filtration. After drying under vacuum for *ca.* 1 d, the tertiary phosphine selenides were treated with dibromine in a 1 : 1 stoichiometric ratio under anhydrous conditions according to eqn. (1).

$$R_3PSe + Br_2 \xrightarrow[Et_2O,\ r.t.]{N_2,\ ca.\ 2\ d} R_3PSeBr_2 \qquad (1)$$

$$(R = Me_2N,\ Et_2N \text{ or } C_6H_{11})$$

Table 2 Selected bond lengths (Å) and angles (°) for $(Me_2N)_3PSeBr_2$

Br(1)–Se(1)	2.602(2)	Se(1)–P(1)	2.262(2)
Br(2)–Se(1)	2.544(2)		
P(1)–Se(1)–Br(2)	95.46(8)	N(1)–P(1)–Se(1)	107.4(3)
P(1)–Se(1)–Br(1)	89.83(8)	N(3)–P(1)–Se(1)	108.9(3)
Br(2)–Se(1)–Br(1)	174.60(6)	N(2)–P(1)–Se(1)	113.7(3)

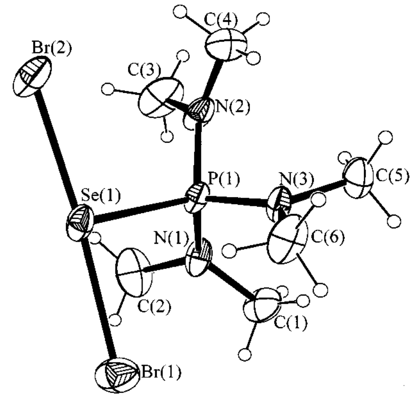

Fig. 1 Crystal structure of $(Me_2N)_3PSeBr_2$.

All of the compounds were isolated in quantitative yield. In direct contrast to the analogous diiodo compounds, R_3PSeI_2 (R = Me_2N, Et_2N or Ph), which were found to be stable towards air and moisture,[5] the dibromo compounds, R_3PSeBr_2, described herein proved to be quite sensitive to moisture, decomposing in less than an hour if exposed to the atmosphere. Consequently anaerobic conditions were adhered to throughout (see Experimental section). This observation alone perhaps suggests a different solid-state structure for R_3PSeBr_2 compounds compared to R_3PSeI_2. In order to investigate this possibility, we decided crystallographically to characterise $(Me_2N)_3PSeBr_2$. Recrystallisation of this yellow powder from diethyl ether–dichloromethane (1 : 1) solution at 50 °C produced a large quantity of yellow-orange crystals on standing at room temperature for *ca.* 3 d. From these a crystal was chosen for analysis by single crystal X-ray diffraction. The structure of $(Me_2N)_3PSeBr_2$ is illustrated in Fig. 1, and selected bond lengths and angles are given in Table 2. This represents the first report of a tertiary phosphine selenide–dibromine compound and clearly establishes that R_3PSeX_2 (X = Br or I) compounds are geometrically dependent on X at the selenium centre. In $(Me_2N)_3PSeBr_2$ the geometry at selenium is T-shaped or approximately trigonal bipyramidal (taking account of the stereochemically active lone pairs on the selenium atom, VSEPR model). In contrast, we previously reported[5] the crystal structure of $(Me_2N)_3PSeI$–I, which exhibited a charge-transfer structure, *i.e.* containing a lengthened but unbroken I–I bond and bent or approximately tetrahedral geometry for the selenium atom (again taking account of the stereochemically active lone pairs on the selenium centre, VSEPR model). It was also noted for $(Me_2N)_3PSeI_2$ that significant phosphorus–selenium double bond character was retained, d(P–Se) = 2.180(7) Å compared to 2.24(1) Å for a typical phosphorus–selenium single bond. In contrast, for $(Me_2N)_3PSeBr_2$, it would appear that any P–Se double bond character formally present in the parent tertiary phosphine selenide is destroyed, since for this compound d(P–Se), 2.262(2) Å, falls within the range expected for a P–Se single bond. Another feature of $(Me_2N)_3PSeBr_2$ worthy of note is the large difference in the two Se–Br distances, 2.602(2) and 2.544(2) Å. A closer inspection of the structure offers a possible explanation. One of the Se–Br bonds almost eclipses an NMe_2 group [N(2)–P(1)–Se(1)–Br(2) −13.3°]; the effect of this is that the N(2)–P(1)–Se(1) and P(1)–Se(1)–Br(2) angles are opened up to 113.7 and 95.5° respectively compared to the angles associated with the staggered Se–Br bond; N(1)–P(1)–

Table 3 Selected bond lengths (Å) and angles (°) for $(C_6H_{11})_3PSeBr_2$

Br(1)–Se(1)	2.568(3)	Br(4)–Se(2)	2.556(3)
Br(2)–Se(1)	2.566(3)	Se(1)–P(2)	2.271(6)
Br(3)–Se(2)	2.591(3)	Se(2)–P(1)	2.254(6)
P(2)–Se(1)–Br(2)	94.5(1)	P(1)–Se(2)–Br(4)	95.3(1)
P(2)–Se(1)–Br(1)	95.6(1)	P(1)–Se(2)–Br(3)	94.8(1)
Br(2)–Se(1)–Br(1)	169.1(1)	Br(4)–Se(2)–Br(3)	169.2(1)

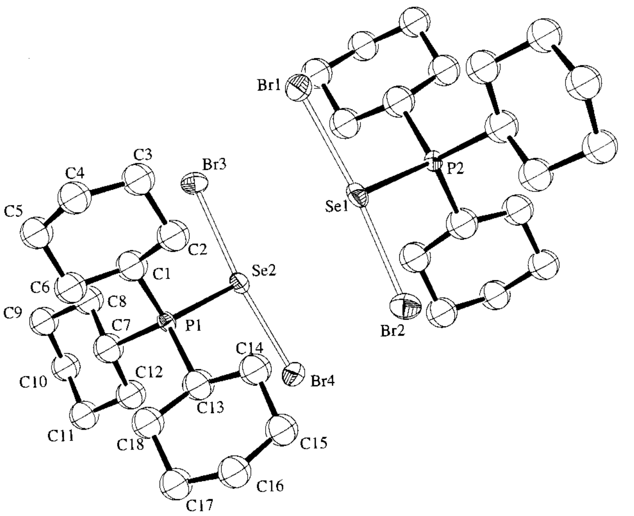

Fig. 2 Crystal structure of $(C_6H_{11})_3PSeBr_2$ (two independent molecules are present in the asymmetric unit, hydrogen atoms are omitted for clarity).

Se(1)–Br(1) 46.6, N(1)–P(1)–Se(1) 10.7.4, P(1)–Se(1)–Br(1) 89.8°. Consequently a significant shortening of the sterically congested Se(1)–Br(2) bond is observed, 2.544(2) Å, compared to the staggered Se(1)–Br(1) bond, 2.602(2) Å.

In order to compare the structural features of $(MeN)_3PSeBr_2$ with those of another R_3PSeBr_2 compound, we decided crystallographically to characterise $(C_6H_{11})_3PSeBr_2$. Single crystals of this material were grown in an identical way to that described for $(Me_2N)_3PSeBr_2$. The crystal structure of $(C_6H_{11})_3PSeBr_2$ is illustrated in Fig. 2. Selected bond lengths and angles are displayed in Table 3. In common with $(Me_2N)_3PSeBr_2$, $(C_6H_{11})_3PSeBr_2$ also adopts a T-shape or Ψ-trigonal bipyramidal geometry for the selenium atoms (two crystallographically independent molecules are present in the asymmetric unit). The phosphorus–selenium distances again fall within the range expected for single bonds, 2.271(6) and 2.254(6) Å, with no evidence for any retention of double bond character. The selenium–bromine bond distances for $(C_6H_{11})_3PSeBr_2$ show less variation compared to those exhibited by $(Me_2N)_3PSeBr_2$. In one molecule of $(C_6H_{11})_3PSeBr_2$, *d*(Se–Br) are identical, 2.568(3) and 2.566(3) Å, however a significant difference is observed in the second molecule [*d*(Se–Br) = 2.591(3) and 2.556(3) Å]. Again a closer look at the crystal structure provides a possible explanation.

The asymmetric unit of $(C_6H_{11})_3PSeBr_2$ is composed of two molecules related by a non-crystallographic inversion centre, each molecule being bisected by an approximate mirror plane through the phosphorus and selenium atoms as well as one of the cyclohexyl rings. Despite the similarity between the two molecules, their crystal packing differs considerably, with one molecule exhibiting a relatively short Br · · · Br non-bonded contact [Br(4) · · · Br(4′) 3.615(3) Å; where ′ denotes $-x$, $1 - y$, $1 - z$; van der Waals radius for two bromine atoms = 3.9 Å]. This phenomenon, which is not observed in the other molecule of $(C_6H_{11})_3PSeBr_2$ (which exhibits identical Se–Br bonds), may be responsible for the asymmetric Se–Br bonds illustrated in this molecule of $(C_6H_{11})_3PSeBr_2$.

Although no compound of formula R_3PSeBr_2 has previously been reported, a few related R_2SeBr_2 compounds have been studied by single crystal X-ray diffraction.[7,11,12] The Se–Br bond lengths for these compounds are similar to or a little shorter than those in the R_3PSeBr_2 compounds described herein [*e.g.* *d*(Se–Br) for Me_2SeBr_2 = 2.546(4) and 2.551(4) Å].[7] The change in structure of R_3PSeX_2 compounds (X = Br or I) from a molecular charge-transfer structure, $R_3PSeI–I$, to a Ψ-trigonal bipyramidal structure, R_3PSeBr_2, upon changing the halogen complements studies concerning organogroup 15 and 16 dihalogen adducts previously reported. For example, Me_2SeI_2 is a charge-transfer compound, $Me_2SeI–I$, whereas Me_2SeBr_2 is Ψ-trigonal bipyramidal.[7] Similarly Ph_3AsI_2 adopts the charge-transfer structure but Ph_3AsBr_2 is trigonal bipyramidal.[6]

The loss of double bond character for the R_3PSe compounds upon reaction with dibromine is clearly illustrated from their infrared spectra, a shift to lower energy of 25–30 cm^{-1} being observed for the compounds R_3PSe after reaction with dibromine, Table 1. The ^{31}P-{H} NMR results indicate that δ values for R_3PSe are shifted upfield upon reaction with dibromine, although the effect is slight for $(C_6H_{11})_3PSe$ and $(C_6H_{11})_3PSeBr_2$ (δ 59.0 and 56.7, respectively).

Conclusion

The synthesis and characterisation of R_3PSeBr_2 (R = Me_2N, Et_2N or C_6H_{11}) is reported for the first time. The solid state structure of these materials is revealed to be T-shaped or Ψ-trigonal bipyramidal which is in contrast to that of the analogous R_3PSeI_2, previously reported,[5] which are charge-transfer species, $R_3PSeI–I$, and contain bent or Ψ-tetrahedral selenium atoms (both geometries take account of the stereochemically active lone pairs present at the selenium centre). The geometrical dependence of the selenium atom in R_3PSeX_2 upon X (X = Br or I) is therefore clearly established. It has previously been shown that reaction of R_3PSe with I_2 results in the charge-transfer adduct $R_3PSeI–I$ in which the parent tertiary phosphine selenide retains significant phosphorus–selenium double bond character (the P–Se bond distances being intermediate between typical single P–Se and double P=Se bond lengths). This phenomenon is not observed for R_3PSeBr_2, the P–Se bond lengths falling in the range expected for a typical P–Se single bond. The ^{31}P-{H} NMR and infrared data for the compounds are also described, the first such data on a compound of formula R_3PSeBr_2, the latter illustrating the downfield shift of *ν*(P–Se) upon co-ordination of dibromine, as expected. The ^{31}P-{H} NMR resonances illustrate a downfield shift for R_3PSeBr_2 compared to the parent R_3PSe for a given R group.

Experimental

The compounds R_3PSe were easily prepared from the direct reaction of commercially obtained R_3P (R = Me_2N, Et_2N or C_6H_{11}) (Aldrich) and elemental selenium. Reaction time was approximately 1 d. The dibromine adducts, R_3PSeBr_2, are moisture sensitive, consequently strictly anaerobic and anhydrous conditions were employed for their synthesis. Any subsequent manipulations were carried out inside a Vacuum Atmospheres HE-493 glove-box. Diethyl ether (BDH) was dried by standing over sodium wire for *ca.* 1 d, refluxed over CaH_2 in an inert atmosphere and distilled directly into the reaction vessel. Anhydrous CH_2Cl_2 was obtained commercially and used as received, as was dibromine.

The R_3PSeBr_2 compounds described were synthesized in the same way, that of $(C_6H_{11})_3PSeBr_2$ being typical. Tricyclohexylphosphine selenide (2.00 g, 5.57 mmol) was suspended in Et_2O (*ca.* 75 cm^3) and subsequently dibromine (0.89 g, 0.29 cm^3, 5.57 mmol) was added. After *ca.* 2 d the resultant yellow solid was isolated using standard Schlenk techniques. The solids were

Table 4 Crystal data and details of refinement for R_3PSeBr_2 (R = Me_2N or C_6H_{11})

Formula	$(Me_2N)_3PSeBr_2$ $C_6H_{18}Br_2N_3PSe$	$(C_6H_{11})_3PSeBr_2$ $C_{36}H_{66}Br_4P_2Se_2$
M	401.98	1038.39
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)
a/Å	8.151(1)	12.432(5)
b/Å	13.585(2)	18.716(7)
c/Å	12.619(3)	17.788(6)
β/°	97.90(2)	96.86(3)
U/Å^3	1384.1(4)	4109(3)
T/K	293(2)	146(2)
Z	4	4
D_c/g cm^{-3}	1.929	1.678
$F(000)$	776	2080
μ/cm^{-1}	85.71	57.91
Maximum, minimum transmission	0.63, 0.93	0.72, 0.98
Crystal size/mm	0.3 × 0.1 × 0.1	0.35 × 0.3 × 0.25
Maximum 2θ/°	49.92	50.0
Total data measured	2596	5959
No. unique reflections	2424	5307
No. observed reflections	1500	1869
$[I > 2.00\sigma(I)]$	[R(int) 0.073]	[R(int) 0.081]
No. parameters	122	217
Largest difference peak and hole/e Å^3	1.027 and −1.012	0.678 and −0.657
Final R indices $[I > 2\sigma(I)]$	0.0659, 0.1685	0.0842, 0.1154
(all data)	0.1208, 0.1947	0.2611, 0.1641

then transferred to predried argon-filled ampoules which were flame sealed.

Elemental analyses were performed by the analytical laboratory of this department. The ^{31}P-{H} NMR spectra were recorded as $CDCl_3$ solutions on a Bruker AC200 high resolution multiprobe spectrometer relative to concentrated phosphoric acid as standard, infrared spectra on a Nicolet 5PC Fourier transform spectrometer.

Crystallography

Crystals of $(Me_2N)_3PSeBr_2$ were mounted in Lindemann tubes under an atmosphere of dry argon. Crystals of $(C_6H_{11})_3PSeBr_2$ were submerged in an inert oil under anaerobic conditions and a suitable one was chosen by examination under the microscope. The crystal, with its protective coating of oil, was then mounted on a glass fibre and transferred to the diffractometer and cooled to 146(2) K in the cold gas stream derived from liquid nitrogen. All measurements were performed on a MAC3 CAD4 diffractometer employing graphite-monochromated Mo-Kα radiation (λ = 0.71069 Å) and ω–2θ scans. Both structures were solved by direct methods. Unit-cell dimensions were derived from the setting angles of 25 accurately centred reflections. Lorentz-polarisation corrections were applied. Details of the X-ray measurements and subsequent structure determinations are presented in Table 4. Hydrogen atoms were confined to chemically reasonable positions. Neutral atom scattering factors were taken from ref. 13, anomalous dispersion effects from ref. 14. The structure determinations were performed using SHELXS 86[15a] and the refinement based on F^2 by using SHELXL 93[15b] crystallographic software packages.

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