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Rationalization of the metal–ligand bonding in organotin(IV) complexes of anionic nitrogen heterocycles containing a thioketo exocyclic group. The case of 1-organyl-1H-tetrazole-5-thiones†

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Abstract—A systematic crystallographic study of organotin(IV) complexes of the 1-phenyl-1H-tetrazole-5-thiolato heterocycle (L), has been undertaken in order to examine the metal–ligand bonding behaviour. The structural evidence accumulated from several X-ray determinations of complexes of the type SnR_3L and SnR_2L_2 performed mainly by us, as well as that of dimethylbis(1-phenyl-1H-tetrazole-5-thiolate)tin(IV), $SnMe_2L_2$, presented in this manuscript (the first reported with a heterocyclic ligand containing the N⋯C⋯S unit and two non-bulky organic groups), has led us to propose a rationalization of the solid-state bonding behaviour of organotin(IV) derivatives toward tetrazolethiolates and closely related ligands. © 1997 Elsevier Science Ltd

Keywords: tin(IV) complexes; organometallics; tetrazole complexes; tetrazole-5-thiones.

The great interest in metal complexes of heterocyclic ligands containing a nitrogen atom (or more) and an adjacent, exocyclic thioketo group, has been largely due to their wide ranging applications in fields such as analytical chemistry, polymers and plastics, medical-biological systems, metal treatment, photography and agriculture [1].

From the structural viewpoint, such complexes are interesting on account of the diversity of coordination modes that stem from the presence of the N⋯C⋯S moiety, i.e. monodentate or bridging through sulfur when the heterocycles act as neutral ligands and *N*- or *S*-monodentate, iso- or aniso-bidentate or also as a bridge between two or three metal atoms, when present in the anionic form [2]. Thus, examples of transition metal complexes with this family of heterocycles, including pyrrolidine-, pyridine-, imidazoline- and triazoline-thiones, *inter alia*, abound in the literature [1–3]. As regards the Main Group elements, however, the situation is rather different, since the number of crystallographically authenticated complexes is far smaller [4]. In the case of tin(IV), the interest in the bonding features with such ligands has been recognized [5–7] given the gamut of coordination geometries that this metal displays [8], and some X-ray diffraction studies have been performed to shed some light on the problem. Thus, in the case of dichlorobis(2-pyridinethiolato)tin(IV) the metal is six-coordinated, with two strong four-membered Sn,S,C,N chelate rings [9], whilst in the complex with four such heterocycles a mixed behaviour is observed, with two monodentate ligands bound to the metal through sulfur, in a *cis* fashion, and two bidentate ligands attached by *cis*-nitrogen and *trans*-sulfur atoms [10]. With regard to organo-derivatives of tin(IV), much of the work has been centred on the structural characterization of the adducts they form with *neutral* ligands, namely imidazolinethione [11–13] and pyridinethione [14], where the metal–

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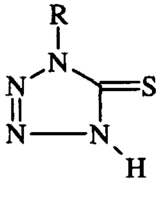
heterocycle bonding was found to occur invariably through sulfur. The crystal structures of some diorganotin complexes of *anionic* pyridine- and 5-nitropyridine-thiolato ligands, with the general formula $SnR_2(S\text{-}Py)_2$, where R = *n*-Bu [15], Ph [16], and cyclo-C_6H_{11} [17], have revealed a most interesting bonding mode, with the metal covalently bound to the exocyclic sulfur, but participating also in intramolecular interactions with the nitrogen atoms (2.636(4)–2.77(1) Å). Such interactions are longer than the normal tin–nitrogen covalent bond (2.15 Å), but considerably shorter than the sum of van der Waals radii (3.75 Å). With 1-organyl-1H-tetrazole-5-thiones, **1**, in their deprotonated form, the synthesis and spectroscopic characterization of some triorganotin(IV) derivatives has been reported [18–20] and the metal–ligand bonding was assumed to take place solely through nitrogen(4).

However, Molloy *et al.* [21] and ourselves [22] crystallographically demonstrated for di- and tri-organotin(IV) derivatives, respectively, that the metal–ligand primary bonding actually occurs through sulfur. In the latter case, $SnBz_3L$ (L = 1-phenyl-1H-tetrazole-5-thiolate), a polymeric structure built through *inter*molecular, dative Sn—N(3) bonds, is found, the metal being five-coordinated, while for the diorgano species, $Sn(n\text{-}Bu)_2L_2$, an essentially four-coordinated structure occurs; in both cases, only weaker, secondary *intra*molecular Sn—N(4) interactions are observed. These examples clearly illustrate the great structural variety in organotin(IV) complexes of heterocycles of this class, as well as the sparsity of the information. We have therefore initiated a systematic study of compounds with a single type of anionic ligand, 1-phenyl-1H-tetrazole-5-thiolate, and various organotin(IV) moieties, i.e. $SnBz_3L$ [22], $SnMe_3L$ [23], $SnPh_3L$ [24], $Sn(n\text{-}Bu)_2L_2$ [22], as an attempt to rationalize the metal–ligand bonding behaviour in this series of complexes. The crystal and molecular structure of the compound dimethylbis(1-phenyl-1H-tetrazole-5-thiolate)tin(IV), $SnMe_2L_2$, the first of the type with two non-bulky organic ligands, as well as the conclusions of the foregoing bonding analysis, are presented in this manuscript. A discussion of the structural features of some analogous complexes of related ligands, as viewed in the light of our results, is offered as well.



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RESULTS AND DISCUSSION

The synthetic method, as well as the spectroscopic and elemental analysis characterization of the complex dimethylbis(1-phenyl-1H-tetrazole-5-thiolate) tin(IV), **2**, have been previously reported by us [22]. The crystal structure of the compound, obtained by X-ray diffraction, is shown in Fig. 1. Selected bond lengths and angles have been collected in Table 1.

In contrast with the partially substituted $SnMe_2LCl$ derivative reported by Molloy and co-workers [21], the present compound shows the complete substitution of the two chlorine atoms by thiotetrazolato rings. The metal establishes covalent bonds with the two heterocyclic sulfur atoms, apart from the two methyl carbons, and interacts intramolecularly with the unsubstituted nitrogen atoms of the ring thioamide moiety [N(4) and N(4a)]. The molecule has a plane of symmetry perpendicular to the *y* axis (symmetry code: X, Y, Z → X, 0.5 − Y, Z). The Sn—C bond distances (2.105(8) and 2.120(10) Å) fall within the range previously observed for other methyltin(IV) compounds [11b,11c,13b,14,23], around 2.1 Å. The Sn—S bond length (2.481(2) Å) is very close to the sum of the corresponding covalent radii (2.42 Å) [25], and is similar to the distances found in other Sn^{IV} complexes of the present tetrazole with metal-sulfur primary bonds, *viz.* 2.474(3)–2.614(5) Å, which display different metal coordination geometries and different organic groups bound to tin (Table 2) [21–24]. Interestingly, such a distance also compares favourably with those observed in organotin complexes of neutral 1-methyl-imidazolinethione ($C_4H_6N_2S$) with the general formula $SnR_2X_2 \cdot C_4H_6N_2S$ (R = Me, *n*-Bu; X = Cl, Br [11]), anionic (deprotonated) pyridinethiol [9,15,16] and pyrimidinethiol [26], as well as with those of 'authentic' thiolato (absence of C—S double bond character) organotin-compounds, e.g. 1,1-dithiolates [27], heterocyclic dithiastannolanes, $R_2SnSCH_2CH_2S$ [28], trithiastannocanes, $R_2Sn(SCH_2CH_2)_2S$ [29], azadithiastonnocanes, $R_2Sn(SCH_2CH_2)_2NR$ [30], etc. By contrast, the present Sn—S bond length is appreciably shorter than those in the adducts dichloro dimethylbis[2(1H)-pyridinethione-S]tin(IV) [14], 2.279(2) Å, and dibromodiethylbis[3H-imidazole-2-thione-S]tin(IV) [12], 2.771(2) Å.

The intramolecular Sn···N distance in our structure [2.947(4) Å] is longer than the sum of covalent radii (2.15 Å), but is considerably shorter than the sum of van der Waals (3.75 Å) [25]. This bond length is of approximately the same magnitude as that in the di-*n*-butyl analog of the present tetrazole [22] [2.975(5) Å], and longer than those exhibited by the two four-membered (Sn,S,C,N) chelate rings in the closely related diphenlbis(2-pyridinethiolato)tin(IV) [16], 2.667 (mean), di-*n*-butylbis(5-nitro-2-pyridinethiolato)tin(IV) [15], 2.77(1) Å, and dicyclohexylbis(2-pyridinethiolato)tin(IV) [17], 2.721(6) Å. The establishment of such intramolecular tin–

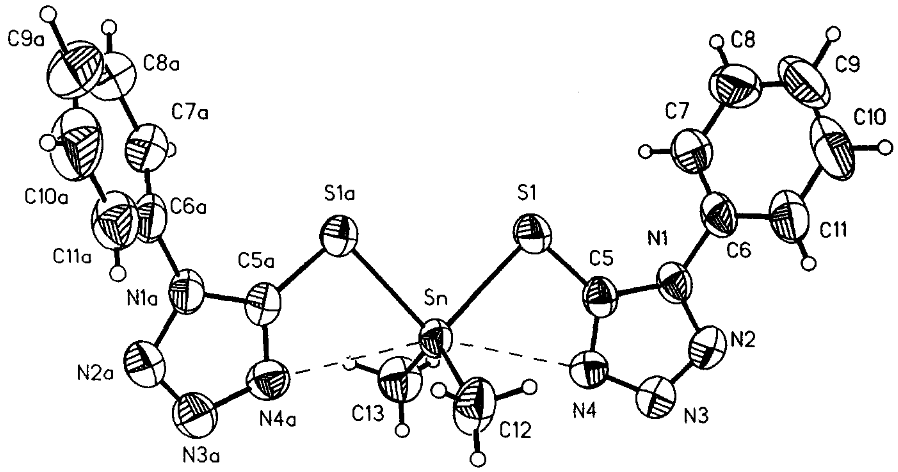


Fig. 1. Thermal ellipsoid plots of the molecular structure of dimethylbis(1-phenyl-1H-tetrazole-5-thiolate)tin(IV), **2**, scaled to the 50% probability level.

Table 1. Selected bond lengths (Å) and angles (°) for dimethylbis(1-phenyl-1H-tetrazole-5-thiolate)tin(IV), **2**

Sn—S(1)	2.481(2)
Sn—C(12)	2.105(8)
Sn—C(13)	2.120(10)
S(1)—C(5)	1.719(5)
N(1)—C(5)	1.354(6)
N(1)—C(6)	1.443(6)
N(1)—N(2)	1.366(6)
N(2)—N(3)	1.288(6)
N(3)—N(4)	1.360(6)
C(5)—N(4)	1.322(7)
S(1)—Sn—C(13)	111.4(2)
S(1)—Sn—C(12)	106.4(2)
C(12)—Sn—C(13)	126.7(4)
S(1)—Sn—S(1a)	87.5(1)
Sn—S(1)—C(5)	92.2(2)
N(2)—N(1)—C(6)	121.0(4)
N(1)—N(2)—N(3)	106.1(4)
N(3)—N(4)—C(5)	106.5(4)
S(1)—C(5)—N(4)	125.6(4)
N(2)—N(1)—C(5)	108.3(4)
C(5)—N(1)—C(6)	130.6(4)
N(2)—N(3)—N(4)	111.4(4)
S(1)—C(5)—N(1)	126.6(4)
N(1)—C(5)—N(4)	107.8(4)

nitrogen interactions brings the present structure rather far from a regular tetrahedron, i.e. despite the fact that two of the complex core angles [S(1)—Sn—C(12) = 106.4(2)° and S(1)—Sn—C(13) = 111.4(2)°] are close to the expected tetrahedral value, the C(12)—Sn—C(13) angle [126.7(4)°] is more obtuse due to the occurrence of the Sn—N secondary interactions in a plane bisecting it, with the concomitant decrease of the S(1)—Sn—S(1a) angle to 87.5(1)°. The geometry around the metal may thus be viewed, alternatively, as a distorted trapezoidal bipyramid, with the two methyl carbons in bent axial positions and the trapezoidal plane being defined by the two Sn—S covalent bonds and the two Sn—N secondary interactions. The five equatorial atoms are nearly coplanar, the maximum deviation from the calculated least-squares plane being that of the metal center (0.065 Å). It should be mentioned that notably similar *trans*-$R_2SnS_2N_2$ coordination geometries are found in analogous systems of 2-pyridinethiolato ligands [15–17].

As in the case of the analog with the considerably bulkier di-*n*-butyl ligands [22], short tin–heteroatom intermolecular distances are absent in the crystal lattice of **2**, Fig. 2, the shortest being 4.756(4) Å between a tin atom and a neighbouring molecule nitrogen, N(2). This fact suggests that the presence of two bulky thiotetrazolato rings, and not the organic groups, is the important factor in precluding the establishment of intermolecular associations in complexes of the SnR_2L_2 type.

On the other hand, inspection of the geometrical parameters of the thiotetrazolate moiety (Table 1) reveals an extensive π-electron delocalization over the five-membered polyaza ring and the exocyclic C—S bond, as in fact occurs in neutral and anionic 1-organyl-1H-tetrazole-5-thiolate systems [22,31].

Table 2 also collects the tin–nitrogen distances shorter than the sum of van der Waals radii [25], (3.75 Å), *inter*- and/or *intra*-molecular, which are found in the organotin(IV) complexes of 1-phenyl-1H-tetrazole-5-thiolate (L) characterized by us, including those in **2**. Although the metal–ligand primary bonding occurs through sulfur, such interactions play an important role in the coordination scheme of these complexes and even the weaker intramolecular Sn···N interactions exert an effect in the geometry of the coordination polyhedra which cannot be ignored [21–24]. An analysis of such distances reveals several interesting features. In the compounds of the SnR_3L series, when no restrictions due to steric crowding are

Table 2. Comparative tin–sulfur and tin–nitrogen distances (Å) in organotin(IV) complexes of 1-phenyl-1H-tetrazole-5-thiolato (L)

Compound	Sn—S	Sn—N (*intra*molecular)	Sn—N (*inter*molecular)
$SnMe_3L^a$	2.565(4)	3.285(12)	2.747(14)
$SnBz_3L^b$	2.589(av.)	3.18(av.)	2.617(av.)
$SnPh_3L^c$	2.487(1)	3.283(3)	3.491(4)
$Sn(n\text{-}Bu)_2L_2{}^d$	2.474(3)	2.975(5)	—
$SnMe_2L_2$ (**2**)^e	2.481(2)	2.947(4)	—

[a] Ref. [23].
[b,d] Ref. [22].
[c] Ref. [24].
[e] This work.

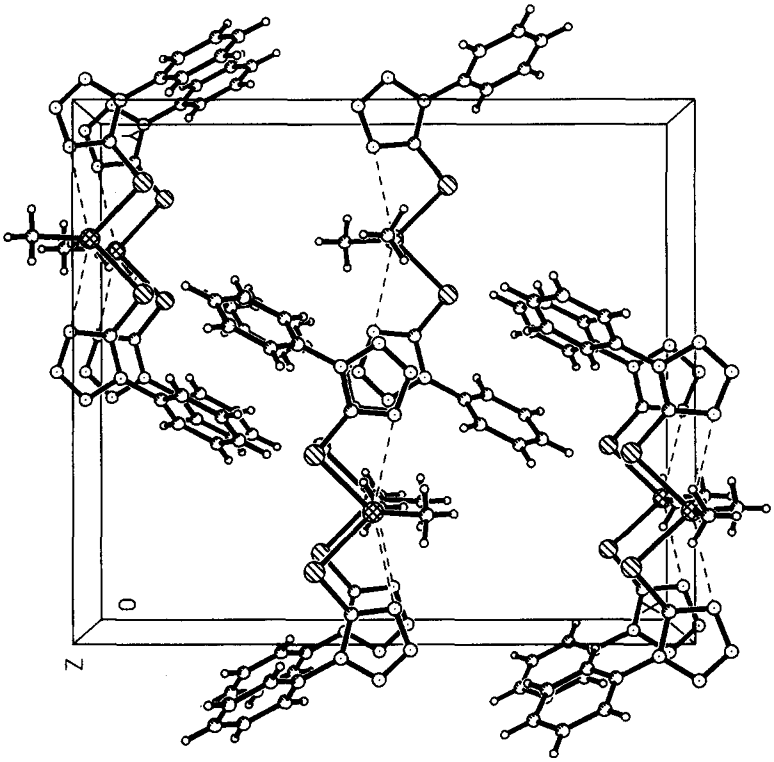
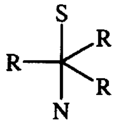


Fig. 2. Unit cell view of dimethylbis(1-phenyl-1H-tetrazole-5-thiolate)tin(IV), **2**.

imposed at the metal center, namely in $SnMe_3L$ and $SnBz_3L$, relatively strong (coordinative) *inter*-molecular Sn—N bonds (2.6–2.75 Å) are formed, in clear preference over *intra*molecular bonding (around 3.2 Å). The resulting geometry is virtually *trans*-S,N trigonal-bipyramidal in both complexes, confirming what had been supposed for the trimethyl derivative on the basis of Mössbauer quadrupole splitting data [21].

In the case of $SnPh_3L$, where the steric hindrance around the metal is increased by the presence of three phenyl ligands, the *inter*molecular association is severely hampered (Sn $\cdots$ N 3.491(4) Å) but, remarkably, the *intra*molecular Sn $\cdots$ N distance (3.283(3) Å) is not reduced, remaining nearly the same as in the pentacoordinated complexes, in spite of its slightly increased Lewis acidity (in comparison with the trialkyl analogues).

These data indicate that intermolecular and *not* intramolecular bonding is preferred in the triorganotin(IV) compounds of this heterocyclic ligand, SnR_3L, in the solid state, on undergoing the well-known expansion of the tin(IV) coordination sphere beyond four. In other words, the *trans*-S,N trigonal-bipyramidal geometry, **2**, is preferred over the *cis* fashion, **3**. The former is in agreement with Bent's rule, in the sense that the most electronegative ligands occupy the axial positions, while the least ones lie in



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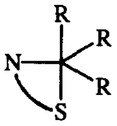

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equatorial positions, on the basis of the amount of *s* character of the metal hybrid orbitals used in bonding [32]. furthermore, the latter stereochemistry is unfortunate due to the fact that it involves the formation of four-membered Sn,S,C,N chelate rings, which display an important degree of strain [33,34].

In the present case, the electron distribution of the ligand does not seem to be an important factor in the bonding observed behaviour, since *ab initio* MO calculations of the anionic ligand performed by us (at the 6–31G*//3–21G* level) [35] have shown, somewhat surprisingly, a higher electron density on N(4) (-0.45), which is involved in the intramolecular interactions, than on N(3) (-0.08), which participates in the intermolecular bonding.

The bond angles in the structures of $SnMe_3L$ [S_{ax}—Sn—N_{ax} 173.8(4)°; mean C_{eq}—Sn—C_{eq} 117.97°] [23] and $SnBz_3L$ [S_{ax}—Sn—N_{ax} 178.0°; mean C_{eq}—Sn—C_{eq} 119.17°] [22] suggest that the bonding in the preferred *trans*-S,N trigonal–bipyramidal geometry may essentially involve metal sp^2 hybrid orbitals for the trigonal bonds and p_z orbitals, combined with two orbitals of the proper symmetry, one each from the sulfur and nitrogen atoms, to yield the three-centre, four-electron, axial bonding system.

A similar conclusion regarding the plausibility of the *trans* rather than the *cis* coordination geometry, could be drawn from a molecular orbital analysis of related MY_2Z_3 systems that employed the tin valence shell orbitals (5*s* and 5*p*) [34], the authors pointing out that when the former geometry is sterically prevented for a complex with highly electronegative Y ligands, even a tetrahedral arrangement may be more likely than the five-coordinated *cis* structure, in keeping with our results. Experimentally, the less effective ligand-to-metal bonding in the four-membered chelate fashion is further supported by the tin–sulfur distance in the distorted octahedral structure of Sn(pyridinethiolato)$_4$, since those in the chelate rings (2.48 and 2.54 Å) are slightly longer than those of the monodentate ligands (2.46 and 2.475 Å) [10]. It is also interesting to mention that the bonding pattern in several organotin(IV) complexes of dithiocarbamate ligands, i.e. one strong and one considerably weaker Sn—S bond in each Sn,S,C,S chelate ring formed [36], parallels the behaviour observed here. A similar 'reluctance' to form four-atom rings has been noted in analogous triphenyltin systems toward ligands containing the O$\overset{...}{—}$C$\overset{...}{—}$S and O$\overset{...}{—}$C$\overset{...}{—}$O coordinating units, namely 1-pyrrolethiocarboxylato [37] and 2-pyrimidylthioacetato [38], respectively. Thus, on the basis of the herein evidence, the structural assignment of the closely related complex $SnMe_3$(pyrimidine-2-thiolato), which was considered to display a *cis* trigonal-bipyramidal arrangement, involving the formation of a Sn,S,C,N ring [39], ought to be considered more carefully.

On the other hand, the formation of such chelate rings is not likely to be particularly favoured in the diorganotin derivatives of 1-phenyl-1H-tetrazole-5-thiolate, either, but rather the conjunction of two factors, the increased Lewis acidity arising from the presence of only two electron-releasing alkyl groups (instead of three) and the preclusion of the intermolecular interactions by the two bulky tetrazole rings, should be responsible for the ring 'closure' with the Sn—N intramolecular secondary bonds [2.975(5) Å in Sn(n-Bu)$_2$L$_2$ and 2.947(4) Å in **2**]. Extending this conclusion to similar SnR_2(Ligand)$_2$ systems, variations in such chelating Sn—N distances [15–17] (2.636–2.77 Å) are hence attributed mainly to differences in the electronic effects of both the organic and the heterocyclic ligands on the metal.

As regards monoorganotin(IV) derivatives, the structural information comes from the crystal and molecular structures of some SnR(Ligand)$_3$ complexes (R = *n*-Bu and Ligand = 2-pyrimidinethiolato; R = *p*-Tol, Me and Ligand = 2-pyridinethiolato) [26], which display distorted pentagonal–bipyramidal geometries, with the establishment of strong (coordinative), chelating N → Sn bonds in the 2.416–2.612 Å range. Such intramolecular bonds are shorter than in the di- and, of course, the tri-organo species. Therefore, the tendency to form four-membered Sn,S,C,N chelate rings in complexes of this class appears to follow the order **RSn(Ligand)$_3$ > R$_2$Sn(Ligand)$_2$ > R$_3$Sn(Ligand)**. This order seems to be defined by the Lewis acidity of the tin center, and it must also reflect the availability of the tin *d* orbitals for bonding, since the increase in number of highly electronegative atoms or groups approaching the metal, results in a considerable contraction of the otherwise high-energy and diffuse metal *d* orbitals, allowing thus a better metal–ligand overlap [40]. In the present case, such electronegative atoms are the nitrogens adjacent to the bonded sulfur atoms [N(4)], i.e. the more heterocyclic ligands bind to tin, the stronger are the tin–nitrogen interactions and hence, the chelate rings. Similar bonding considerations might also apply in the case of complexes of the form SnR_{4-n}(1-pyrrolethiocarboxylato)$_n$, where a parallel Sn···O bond length shortening in the Sn,S,C,O moiety, on passing from $n = 1$ to $n = 3$, has been observed [37].

EXPERIMENTAL

Details of the synthetic method and spectroscopic characterization of compound **2** have been published elsewhere [22]. Single-crystals suitable for X-ray measurements were obtained from a CH_2Cl_2/cyclohexane mixture, by the solvent diffusion method. Melting point measurements of the crystals (142–143°C) proved that the product remained unchanged upon the crystallization process.

Crystal structure determination of dimethylbis(1-*phenyl*-1*H-tetrazole*-5-*thiolate*)*tin*(*IV*), 2

Crystal and collection data. $C_{16}H_{16}N_8S_2Sn$, colourless prism with dimensions $0.40 \times 0.26 \times 0.08$ nm, orthorhombic, $a = 18.891(2)$, $b = 16.541(2)$, $c = 6.844(1)$ Å, $V = 2138.7(5)$ Å^3 (by least-squares refinement of diffractometer angles from 39 reflections, $4.27 < 2\theta < 25.02°$), $T = 293$ K, space group $Pnma$, $Z = 4$; Siemens $P4$ diffractometer, parallel-graphite crystal radiation ($\lambda = 0.71073$ Å), ω scans, data collection range $3.0 < 2\theta < 50°$, $h+22$, $k+19$, $l+8$, three standard reflections measured every 97 showed no significant variation in intensity; 1950 reflections measured, 1950 unique ($R_{int} = 0.0\%$) and 1538 ($F > 3\sigma F$) observed reflections were used for all calculations; analytical absorption correction (face-indexed numerical), min./max. transmission factors 0.646/0.8925. Solution and refinement: The structure was solved by the heavy-atom method and Fourier difference techniques; all non-hydrogen atoms were refined using anisotropic displacement parameters, while hydrogens were calculated as a riding model with isotropic U, using full matrix least-squares, on F (SHELXTL-PC) [41]. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.0003F^2$; 128 parameters refined, final R indices $R = 0.037$, $wR = 0.039$ (obs. data) and $R = 0.049$, $wR = 0.039$ (all data). GOF = 1.05, max./min. $\Delta\rho$ $0.56/-0.43$ eÅ^{-3}.

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