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Crystal and Molecular Structures of Hypervalent Thia/Selena-pentalenes

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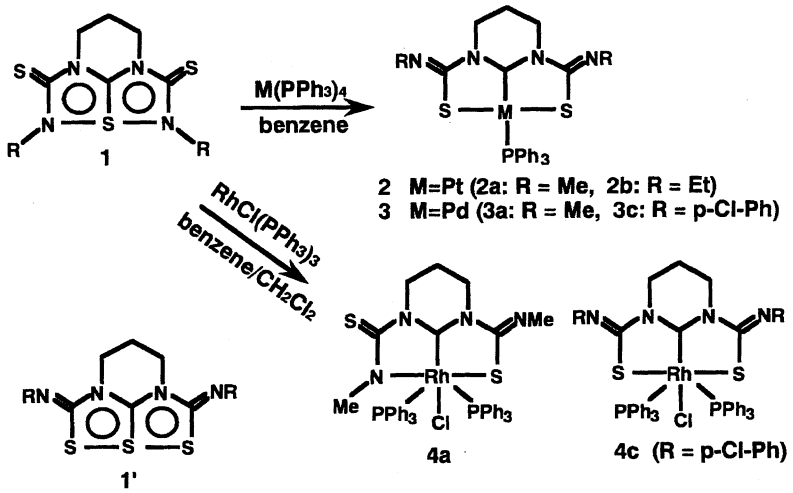
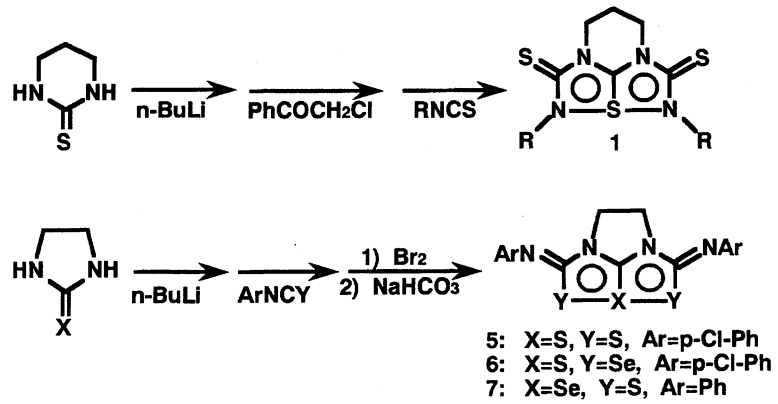
X-Ray structure analyses were performed on the 2,3,4,5-tetrahydro-3,4-dimethylene-2,5-bis(4-chlorophenylimino)-1,6,6aλ^4-trithia-3,4-diazapentalene (**5**), 2,5-bis(4-chlorophenylimino)-6aλ^4-thia-1,6-diselena-3,4-diazapentalene derivative (**6**) and 2,5-bis(phenylimino)-1,6-dithia-6aλ^4-selena-3,4-diazapentalene derivative (**7**). The lengths of the S–S bonds (mean value of 2.401 Å) for **5** and those of the Se–S bonds (mean value of 2.501 Å) for **6** and **7** are longer than that of the normal S–S or Se–S single bond (2.08 and 2.21 Å for S–S and Se–S bonds, respectively) by about 15%, which shows the hypervalent character of these S–S or Se–S bonds. In molecule **5**, a difference in the two S–S bonds (2.488 and 2.314 Å) is considered to be a reflection of the feature of a weak hypervalent bond, which is very liable with effects of the environment, such as substituents or packing. The same tendency was observed for molecule **6**. The crystal structures of **5** and **6**, both of which are *p*-Cl-phenylimino derivatives, are isomorphous with each other. The crystal structure of **7**, a phenylimino derivative, is different from those of **5** and **6**, and two Se–S bonds of **7** are almost similar. The diffraction intensities of **5** were measured by a Weissenberg-diffractometer with imaging-plates, because only very small crystals were obtained, the intensities of which could not be measured by a conventional four-circle diffractometer with a rotating anode generator.

Many studies have been performed on hypervalent sulfur compounds,[1] such as thiathiophthenes[2,3] and σ-sulfuranes,[4,5] and have stimulated great interest in structural chemistry and organic synthesis. We studied the structural features of 6a-thiatetraazapentalene derivatives (**1**), which contain a hypervalent sulfur atom with a 12π conjugated system.[6—8] In the course of studying the reactivity of **1**, novel metal–carbene complexes (**2**—**4**) were obtained from **1** by treating with [Pt(PPh_3)$_4$], [Pd(PPh_3)$_4$], and [RhCl(PPh_3)$_3$], respectively, the structures of which were determined by X-ray investigations (Scheme 1).[9—11] The formation mechanism of these metal–carbene complexes was proposed based on the structures of the complexes and the MO calculations of **1** and related compounds.[12] In this mechanism, the sulfur atoms of the thiocarbonyl groups of **1** play an important role as a nucleophilic ligand after cleaving the hypervalent S–N bonds. From this point of view, we have expected that a similar nucleophilic ligand would be obtained from **1′** after cleaving the hypervalent S–S bonds. A similar carbene complex should be obtained from **1′** with the hypervalent S–S–S system, instead of **1** with the N–S–N hypervalent system.

The N–S–N compounds (**1**) were obtained from perhy-



Scheme 1.



Scheme 2.

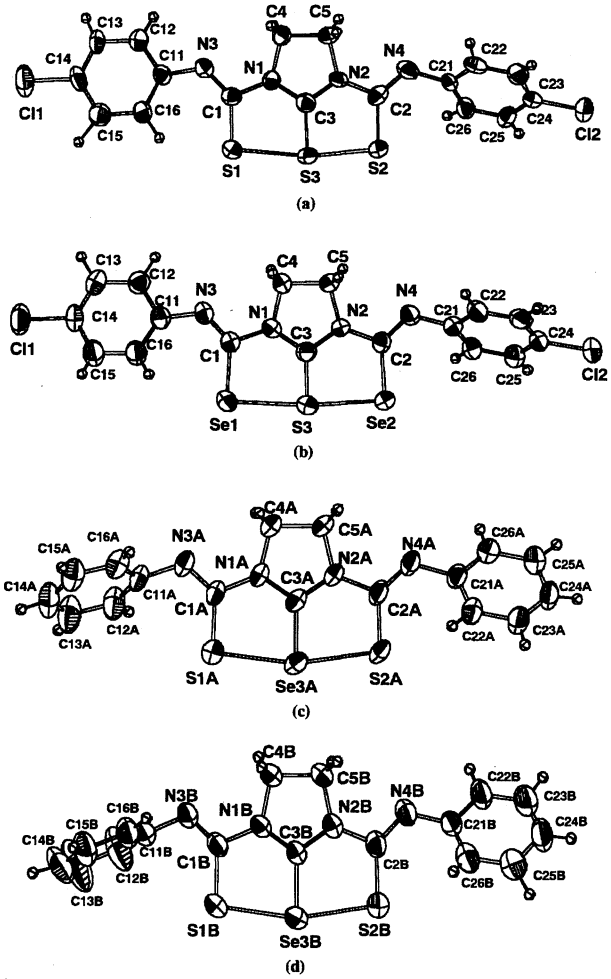


Fig. 1. ORTEP drawings of the molecules with the atom-numbering. The thermal ellipsoids for non-H atoms are drawn at 50% probability and the H atoms are drawn as spheres with a radius of 0.1 Å. (a) **5**, (b) **6**, (c) **7A**, and (d) **7B**.

dropyrimidine-2-thiones with *n*-BuLi, $PhCOCH_2Cl$, and RNCS.[13] From perhydroimidazole-2-thione with *n*-BuLi, *p*-ClPhNCX (X = S or Se), Br_2, and $NaHCO_3$, **5** and **6** were synthesized, while **1′** couldn't be obtained from perhydropyrimidine-2-thiones by the same method for **5** (Scheme 2).[14]

Since the trithiapentalene derivative (**5**) was unstable in solution, thiadiselenapentalene (**6**) was used for the formation of metal-complexes. X-Ray structure analyses revealed that these complexes were also novel metal–carbene complexes coordinated by Se atoms. In this paper we report on the structure of the starting diselenathiapentalene **6**, as well as those of related compounds, trithiapentalene (**5**) and dithiaselenapentalene (**7**). The structures of metal–carbene complexes obtained from **6** will be presented in a following paper.[15]

Experimental

The crystals of **5**, **6**, and **7** for X-ray studies were grown from a $CHCl_3$ solution. For **5**, it was very difficult to measure the intensities using a conventional four-circle diffractometer with a rotating anode X-ray generator, because only very small crystals were obtained. The diffraction intensities were measured by a Weissenberg-diffractometer with imaging-plates (MacScience-DIP3000).[16,17] The intensities of **6** and **7** were measured using four-circle diffractometers (Rigaku-AFC4 and AFC7R, respectively). Crystal data, details of data collection, and structure refinements are listed in Table 1.

The structures of **5** and **7** were solved by a direct method using the programs SHELXS86[18] and SAPI91,[19] respectively. The structure of **6** was solved by the Patterson method using SHELXS86. For all structures, the positions of the H atoms, except for several on terminal positions, were obtained from D-maps. The remaining H atoms were located from calculations and included in refinements. The structures of **5** and **6** were refined by the block-diagonal least-squares, and that of **7** by the full-matrix least-squares with anisotropic temperature factors for non-H atoms and isotropic ones for H atoms. The function $\sum w(|F_o| - k|F_c|)^2$ was minimized. The final R values are 0.102, 0.057, and 0.052 for **5**, **6**, and **7**, respectively.

The atomic scattering factors were used from International Tables for X-Ray Crystallography.[20] Programs (UNICS III,[21] teXsan,[22] and ORTEP II[23]) were used for calculating refinements and structural geometries. The final atomic parameters are given in Table 2.[24]

Discussions

The molecular structures of **5**, **6**, and **7** along with the atomic numbering are shown in Fig. 1. Selected bond distances and angles are listed in Table 3.

Structures of 5 and 6. The molecular features of **5** and

Table 1. Crystal Data, Experimental Condition, and Details of Refinement

	5 $C_{17}H_{12}Cl_2N_4S_3$	**6** $C_{17}H_{12}Cl_2N_4SSe_2$	**7** $C_{17}H_{14}N_4S_2Se$
F.W.	439.41	533.20	417.42
Color	Yellow	Yellow	Yellow
Crystal Shape	Plates	Plates	Plates
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	8.735(1)	9.792(5)	12.109(4)
b/Å	11.173(1)	10.866(5)	18.796(6)
c/Å	11.194(1)	10.874(4)	8.261(2)
α/°	110.1(3)	109.41(3)	97.21(2)
β/°	103.8(2)	104.50(4)	107.42(3)
γ/°	106.0(1)	108.68(4)	101.88(3)
V/Å^3	917.7(16)	947.7(10)	1719.9(10)
Z	2	2	4
D_x/g cm^{-3}	1.589	1.868	1.613
μ/mm^{-1}	0.690	4.260	2.400
$F(000)$	448	520	840
Crystal size	$0.08\times0.03\times0.15$	$0.40\times0.10\times0.10$	$0.40\times0.10\times0.20$
Diffractometer	Mac-Science DIP3000	Rigaku-AFC4	Rigaku-AFC7R
Radiation	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
λ/Å	0.71073	0.71073	0.71073
Temperature/K	293	298	295
For cell dimensions			
No. of refs.	1374	21	24
2θrange/°	—	14.80—34.55	34.28—35.02
Scan mode	Weissenberg	ω–2θ	ω–2θ
$2\theta_{max}$/°	52.7	55.0	55
Scan width $\Delta\omega$/°	—	1.30+0.40tan θ	1.37+0.30tan θ
Scan speed ω/°min^{-1}	—	4	16
Rotation axis	a	—	—
$\Delta\phi$/°	220	—	—
No. of IPs	22	—	—
No. of standard refs.	—	3 (every 50 reflections)	3 (every 150 reflections)
Intensity variation	—	0.928—1.002	0.843—1.000
Range of hkl	−9—9, −13—13, −13—13	0—12, −14—13, −14—13	0—15, −24—23, −10—10
T_{max}, T_{min}	—	0.4269, 0.4860	0.9456, 0.9859
No. of reflections			
Measured	8213	4937	8288
Unique	3394	4342	7913
Observed ($\|F_o\| > 3\sigma(F)$)	2084	2709	4587
R_{int}	0.106	0.018	0.066
No. of parameters	283	283	545
S	1.283	1.071	1.56
Δ/σ	0.005	0.005	0.02
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$/e Å^{-3}	0.649, −0.614	0.729, −0.643	0.79, −1.28
Weighting scheme[a)]	1	2	3
R	0.102	0.057	0.052
wR	0.124	0.060	0.066

a) 1: $w=1/\{\sigma(F)^2+0.15316|F_o|-0.00099|F_o|^2\}$. 2: $w=1/\{\sigma(F)^2-0.04214|F_o|+0.00009|F_o|^2\}$. 3: $w=1/\{\sigma(F)^2\}$.

6 are very similar because of the isomorphous structures. In these molecules, the pentalene rings are planar with the maximum deviations of 0.111(11) and 0.132(8) Å for **5** and **6**, respectively. The perhydroimidazole ring is also planar. The dihedral angles between the imidazole and pentalene rings are 2.9(3) and 2.2(2)° for **5** and **6**, respectively. For **5**, the lengths of S(1)–S(3) and S(2)–S(3) are 2.488(3) and 2.314(4) Å, respectively. These S–S lengths, which are longer than that of the normal S–S single bond (2.08 Å) by about 15% (19 and 11%, for S(1)–S(3) and S(2)–S(3), respectively) show hypervalency. The typical hypervalent S–S length is 2.40 Å, which corresponds to a Paulings' bond order of 0.5. The lengths of Se(1)–S(3) and Se(2)–S(3) of **6** are 2.590(2) and 2.466(2) Å, respectively, longer than that of the normal single Se–S bond of 2.21 Å by about 14%, so that these Se–S bonds also show the typical hypervalency. In these molecules, the hypervalent S–S or Se–S bonds show an asymmetry: The lengths of the S(1)/Se(1)–S(3) bond are longer than those of

Table 2. Positional Parameters and Equivalent Isotropic Temperature Factors (B_{eq}) for Non-H Atoms

$$B_{eg} = \frac{4}{3}\sum_i\sum_j \beta_{ij}\, \boldsymbol{a}_i \cdot \boldsymbol{a}_j$$

Atom	x	y	z	B_{eq}/Å^2	Atom	x	y	z	B_{eq}/Å^2
(1) **5**					(2) **6**				
S(1)	0.3526(4)	0.6268(3)	0.4437(3)	3.70(11)	Se(1)	0.33920(9)	0.61768(9)	0.39873(8)	4.18(3)
S(2)	0.7832(4)	0.8605(3)	0.8939(3)	4.00(11)	Se(2)	0.78616(9)	0.87383(9)	0.88227(8)	4.52(3)
S(3)	0.5885(3)	0.7624(3)	0.6721(3)	3.50(11)	S(3)	0.5761(2)	0.7585(2)	0.6427(2)	3.80(7)
Cl(1)	−0.4295(5)	0.1618(5)	−0.1256(3)	6.54(16)	Cl(1)	−0.4515(3)	0.1601(3)	−0.1225(2)	6.5(1)
Cl(2)	1.3274(4)	1.0854(3)	1.5505(3)	5.15(13)	Cl(2)	1.3002(3)	1.0616(3)	1.5417(2)	6.4(1)
N(1)	0.3407(10)	0.5196(8)	0.6145(8)	2.8(3)	N(1)	0.3342(6)	0.5136(6)	0.5959(6)	3.3(2)
N(2)	0.5420(11)	0.6206(8)	0.8191(8)	3.2(3)	N(2)	0.5288(6)	0.6230(6)	0.8065(6)	3.2(2)
N(3)	0.1041(11)	0.3938(9)	0.4219(9)	3.5(4)	N(3)	0.0990(7)	0.3861(6)	0.4121(6)	3.8(2)
N(4)	0.7401(12)	0.6979(9)	1.0323(9)	3.6(4)	N(4)	0.7154(7)	0.6881(6)	1.0187(6)	3.5(2)
C(1)	0.2459(13)	0.5004(10)	0.4825(10)	3.0(4)	C(1)	0.2352(8)	0.4879(8)	0.4623(7)	3.5(3)
C(2)	0.6915(13)	0.7203(11)	0.9271(11)	3.4(4)	C(2)	0.6763(8)	0.7199(7)	0.9162(7)	3.3(3)
C(3)	0.4872(13)	0.6279(11)	0.7040(10)	3.1(4)	C(3)	0.4767(8)	0.6256(7)	0.6825(7)	3.3(3)
C(4)	0.2831(14)	0.4277(11)	0.6792(10)	3.5(4)	C(4)	0.2763(9)	0.4306(9)	0.6707(8)	4.6(3)
C(5)	0.4331(14)	0.4925(11)	0.8174(11)	3.6(4)	C(5)	0.4200(8)	0.4920(8)	0.8074(7)	4.0(3)
C(11)	−0.0156(12)	0.3496(11)	0.2914(10)	3.1(4)	C(11)	−0.0247(8)	0.3385(8)	0.2812(7)	3.6(3)
C(12)	−0.1730(13)	0.2461(11)	0.2558(10)	3.1(4)	C(12)	−0.1760(9)	0.2554(8)	0.2668(8)	4.0(3)
C(13)	−0.2991(13)	0.1884(12)	0.1292(11)	3.7(4)	C(13)	−0.3077(8)	0.1992(8)	0.1434(8)	4.2(3)
C(14)	−0.2689(15)	0.2367(13)	0.0378(11)	4.1(5)	C(14)	−0.2880(8)	0.2282(9)	0.0348(7)	4.3(3)
C(15)	−0.1119(15)	0.3384(13)	0.0665(12)	4.4(5)	C(15)	−0.1419(9)	0.3065(10)	0.0427(8)	4.9(4)
C(16)	0.0143(14)	0.3943(12)	0.1961(10)	4.1(5)	C(16)	−0.0117(9)	0.3619(10)	0.1661(8)	4.6(3)
C(21)	0.8836(13)	0.7976(11)	1.1539(9)	2.9(4)	C(21)	0.8569(8)	0.7840(7)	1.1407(7)	3.4(3)
C(22)	0.9866(14)	0.7478(11)	1.2168(11)	3.6(5)	C(22)	0.9485(9)	0.7228(8)	1.1909(8)	3.9(3)
C(23)	1.1283(14)	0.8375(12)	1.3405(12)	4.0(5)	C(23)	1.0860(9)	0.8088(9)	1.3142(8)	4.5(4)
C(24)	1.1557(13)	0.9769(11)	1.3982(10)	3.1(4)	C(24)	1.1292(8)	0.9548(9)	1.3864(8)	4.4(3)
C(25)	1.0505(13)	1.0286(11)	1.3375(11)	3.5(4)	C(25)	1.0387(9)	1.0179(8)	1.3388(8)	4.5(3)
C(26)	0.9147(13)	0.9387(11)	1.2158(10)	3.4(4)	C(26)	0.9031(8)	0.9319(8)	1.2162(8)	3.8(3)
(3) **7**									
		Molecule A					Molecule B		
Se(3A)	0.31528(6)	0.48865(3)	0.80475(7)	4.49(1)	Se(3B)	0.00982(5)	0.07903(3)	0.29992(7)	4.13(1)
S(1A)	0.29079(17)	0.56669(9)	1.0509(2)	5.21(4)	S(1B)	0.08735(15)	−0.01669(10)	0.16605(18)	5.09(4)
S(2A)	0.35035(18)	0.38886(9)	0.61399(18)	5.21(4)	S(2B)	−0.02333(15)	0.17454(10)	0.5073(2)	5.16(4)
N(1A)	0.3638(4)	0.4477(3)	1.1289(5)	3.9(1)	N(1B)	0.1971(4)	0.0285(3)	0.5031(5)	3.7(1)
N(2A)	0.3850(4)	0.3671(2)	0.9320(5)	3.8(1)	N(2B)	0.1492(4)	0.1141(2)	0.6543(5)	3.8(1)
N(3A)	0.3142(4)	0.5077(3)	1.3431(5)	4.2(1)	N(3B)	0.2886(4)	−0.0448(3)	0.3740(6)	4.4(1)
N(4A)	0.4023(4)	0.2698(3)	0.7557(6)	4.1(1)	N(4B)	0.1303(4)	0.2039(3)	0.8454(6)	4.3(1)
C(1A)	0.3238(5)	0.5071(3)	1.1932(6)	3.8(1)	C(1B)	0.2023(5)	−0.0155(3)	0.3535(6)	3.8(1)
C(2A)	0.3804(5)	0.3334(3)	0.7660(7)	4.0(1)	C(2B)	0.0902(5)	0.1688(3)	0.6878(7)	3.9(1)
C(3A)	0.3574(5)	0.4309(3)	0.9653(6)	3.8(1)	C(3B)	0.1244(5)	0.0725(3)	0.4986(6)	3.5(1)
C(4A)	0.3931(6)	0.3880(3)	1.2225(7)	4.3(1)	C(4B)	0.2831(6)	0.0377(4)	0.6789(7)	4.1(1)
C(5A)	0.4150(7)	0.3341(4)	1.0878(7)	4.6(2)	C(5B)	0.2481(6)	0.0969(3)	0.7861(7)	4.1(1)
C(11A)	0.2707(5)	0.5632(3)	1.4173(6)	4.1(1)	C(11B)	0.2983(5)	−0.0851(4)	0.2244(7)	4.7(1)
C(12A)	0.3232(7)	0.6381(4)	1.4481(9)	5.6(2)	C(12B)	0.2260(8)	−0.1552(6)	0.1457(12)	8.7(3)
C(13A)	0.2768(9)	0.6880(5)	1.5275(11)	7.3(2)	C(13B)	0.2427(11)	−0.1913(8)	0.0000(18)	12.2(4)
C(14A)	0.1816(8)	0.6647(5)	1.5783(10)	6.6(2)	C(14B)	0.3296(8)	−0.1623(6)	−0.0590(11)	8.4(3)
C(15A)	0.1300(7)	0.5908(5)	1.5508(9)	5.6(2)	C(15B)	0.4024(8)	−0.0946(5)	0.0204(10)	6.4(2)
C(16A)	0.1734(6)	0.5402(4)	1.4690(8)	4.7(2)	C(16B)	0.3873(7)	−0.0556(4)	0.1639(9)	5.3(2)
C(21A)	0.3996(6)	0.2290(3)	0.5966(7)	4.0(1)	C(21B)	0.0881(5)	0.2638(3)	0.9041(7)	4.2(1)
C(22A)	0.3106(6)	0.2214(3)	0.4392(7)	4.3(1)	C(22B)	0.0785(6)	0.2687(4)	1.0698(8)	5.3(2)
C(23A)	0.3131(7)	0.1784(3)	0.2920(8)	4.8(2)	C(23B)	0.0475(7)	0.3288(5)	1.1398(10)	6.4(2)
C(24A)	0.4029(7)	0.1439(4)	0.3001(9)	5.3(2)	C(24B)	0.0241(7)	0.3830(5)	1.0522(11)	7.1(2)
C(25A)	0.4894(7)	0.1495(4)	0.4556(9)	5.6(2)	C(25B)	0.0352(8)	0.3806(5)	0.8884(10)	6.8(2)
C(26A)	0.4882(7)	0.1925(3)	0.6037(8)	4.9(2)	C(26B)	0.0678(7)	0.3197(4)	0.8164(10)	5.7(2)

the S(2)/Se(2)–S(3) bonds by 0.174 and 0.124 Å for **5** and **6**, respectively. The sum of the asymmetrical hypervalent S–S or Se–S distances is almost equal to twice the typical symmetrical hypervalent length, like other examples with asymmetrical hypervalent bonds.[3,25]

The crystal structure of **5** is shown in Fig. 2. Crystals of **6** are isomorphous with those of **5**. Figure 3 shows the molecular overlapping in crystals of **5** and **6**. In the crystals of **5** and **6**, the pentalene frameworks related by the center of symmetry overlap with each other to form a dimer-like structure, with interplanar distances of 3.495(13) and 3.581(8) Å for **5** and **6**, respectively. The phenyl group, C(11)—C(16), which is almost parallel to the pentalene plane, slightly overlaps the pentalene plane of the adjacent molecule, while the other phenyl group, C(21)—C(26), which is inclined from the pentalene plane, does not overlap the adjacent molecule. The dihedral angles between the pentalene plane and the phenyl group (C11—C16) are 16.4(3) and 24.7(2)° for **5** and **6**, respectively, while those corresponding to the other phenyl group (C21—C26) are 49.6(3) and 55.9(2)° for **5** and **6**, respectively. Some bond angles also show an asymmetry under the influence of a steric effect between the phenyl and pentalene groups. The angles of S/Se(1)–C(1)–N(3) and C(1)–N(3)–C(11) are larger than the corresponding angles of S/Se(2)–C(2)–N(4) and C(2)–N(4)–C(21), respectively, because of the steric hindrance between S/Se(1) and the H atom attached to C(16) of the coplanar phenyl group. The asymmetry of the hypervalent S–S or Se–S bonds is ascribed to these packing effects. For the bond lengths, except for the hypervalent S–S or S–Se bonds, no such asymmetric features are observed. A weak hypervalent bond is very liable to environmental effects, such as substituents or packing.[25]

Structure of 7. The crystal structure and molecular overlapping of **7** are shown in Figs. 4 and 5, respectively. There are two independent molecules, **A** and **B**, in an asymmetric unit of the triclinic cell. Symmetric hypervalent Se–S bonds are observed in these molecules. For molecule **7A**, the dihedral angles between the pentalene plane and the phenyl groups of C11—C16 and C21—C26 are 61.8(2) and 41.3(2)°, respectively. The corresponding angles of **7B** are 80.1(3) and 41.8(2)° for C11—C16 and C21—C26, respectively. In these molecules, unlike those of **5** and **6**, the phenyl groups are not coplanar with the pentalene ring, and there are no steric effects between the phenyl and pentalene rings.

In the crystals, the pentalene ring of molecule **A** overlaps the phenyl ring (C21—C26) of molecule **B**, with the distance between the planes equal to 3.598(10) Å and a dihedral angle of 8.9(2)°. The pentalene ring of **A** also overlaps that of molecule $\mathbf{A}^{i}$ (a symmetry code: i=1−x, 1−y, 2−z) with a distance of 3.657(6) Å. For molecule **B**, the distance between the pentalene ring and the phenyl ring (C21—C26) of molecule **A** and that between pentalene planes **B** and $\mathbf{B}^{ii}$ (ii=−x, −y, 1−z) are 3.546(9) and 3.668(6) Å, respectively. The dihedral angle between the pentalene ring of **B** and the phenyl ring of **A** is 171.9(2)°. It is very interesting that the existence of the terminal chlorine atoms attached to the phenyl groups affects the difference in the molecular packing. From the dimensions of the unit cell and the space group, crystals of the trithiadiazapentalene derivative with the phenyl groups are considered to be isomorphous with those of **7**.[26] Unfortunately, no atomic parameters have been listed in the Cambridge Structural Database (CSD)[27] and the original paper.

Table 3. Selected Bond Lengths (l) and Bond Angles (θ) of Non-H Atoms (Y(1)–X(3)–Y(2))

	5	**6**	**7A**	**7B**
X	S	S	Se	Se
Y	S	Se	S	S
Lengths	l/Å	l/Å	l/Å	l/Å
Y(1)–X(3)	2.488(3)	2.590(2)	2.484(2)	2.482(2)
Y(2)–X(3)	2.314(4)	2.466(2)	2.484(2)	2.501(2)
Y(1)–C(1)	1.716(13)	1.894(9)	1.741(6)	1.738(5)
Y(2)–C(2)	1.757(13)	1.883(8)	1.734(6)	1.731(6)
X(3)–C(3)	1.720(13)	1.716(9)	1.839(5)	1.841(5)
N(1)–C(1)	1.420(14)	1.407(9)	1.411(7)	1.423(6)
N(1)–C(3)	1.346(10)	1.345(7)	1.324(6)	1.323(6)
N(1)–C(4)	1.494(17)	1.479(12)	1.483(7)	1.476(7)
N(2)–C(2)	1.390(10)	1.394(7)	1.417(6)	1.412(7)
N(2)–C(3)	1.301(16)	1.330(11)	1.328(7)	1.333(6)
N(2)–C(5)	1.476(15)	1.485(10)	1.480(7)	1.480(7)
N(3)–C(1)	1.284(11)	1.261(8)	1.277(6)	1.258(7)
N(3)–C(11)	1.402(13)	1.416(9)	1.415(7)	1.415(7)
N(4)–C(2)	1.285(17)	1.279(11)	1.274(7)	1.280(7)
N(4)–C(21)	1.429(10)	1.415(7)	1.425(6)	1.420(7)
C(4)–C(5)	1.543(14)	1.525(10)	1.530(8)	1.541(8)
Angles	θ/°	θ/°	θ/°	θ/°
X(3)–Y(1)–C(1)	95.3(4)	89.7(3)	94.9(2)	95.9(2)
X(3)–Y(2)–C(2)	94.8(4)	89.9(2)	96.2(2)	96.0(2)
Y(1)–X(3)–Y(2)	170.3(2)	174.0(1)	164.89(6)	164.30(5)
Y(1)–X(3)–C(3)	83.7(4)	85.9(3)	82.8(2)	82.5(2)
Y(2)–X(3)–C(3)	86.7(4)	88.1(3)	82.2(2)	81.8(2)
C(1)–N(1)–C(3)	125.6(10)	127.3(7)	123.1(5)	124.0(4)
C(1)–N(1)–C(4)	124.4(9)	121.3(7)	124.5(4)	123.7(4)
C(3)–N(1)–C(4)	109.8(9)	110.5(7)	111.3(4)	111.9(4)
C(2)–N(2)–C(3)	122.7(10)	124.7(7)	124.0(4)	124.1(5)
C(2)–N(2)–C(5)	124.8(10)	123.2(6)	124.5(4)	124.5(4)
C(3)–N(2)–C(5)	112.4(10)	111.6(6)	111.4(4)	111.4(4)
C(1)–N(3)–C(11)	125.7(11)	126.3(7)	120.3(5)	117.4(5)
C(2)–N(4)–C(21)	122.6(11)	120.9(7)	121.6(5)	122.9(5)
Y(1)–C(1)–N(1)	111.0(8)	111.4(6)	114.2(3)	112.8(4)
Y(1)–C(1)–N(3)	135.9(10)	134.3(7)	130.2(4)	130.2(4)
N(1)–C(1)–N(3)	113.1(10)	114.3(7)	115.6(5)	117.0(5)
Y(2)–C(2)–N(2)	111.9(9)	112.8(5)	112.9(4)	113.4(4)
Y(2)–C(2)–N(4)	130.6(10)	131.3(6)	131.7(4)	132.7(4)
N(2)–C(2)–N(4)	117.5(11)	115.9(7)	115.4(5)	113.9(5)
X(3)–C(3)–N(1)	124.1(9)	125.1(6)	124.2(4)	124.1(4)
X(3)–C(3)–N(2)	123.7(9)	124.1(6)	124.4(4)	124.6(4)
N(1)–C(3)–N(2)	112.1(10)	110.7(7)	111.4(5)	111.2(4)
N(1)–C(4)–C(5)	102.9(9)	103.5(7)	102.9(4)	102.8(4)
N(2)–C(5)–C(4)	102.3(9)	102.0(7)	102.8(4)	102.7(4)

Comparison of the Structures. In Table 4, a comparison of the bond lengths and angles of these compounds is listed

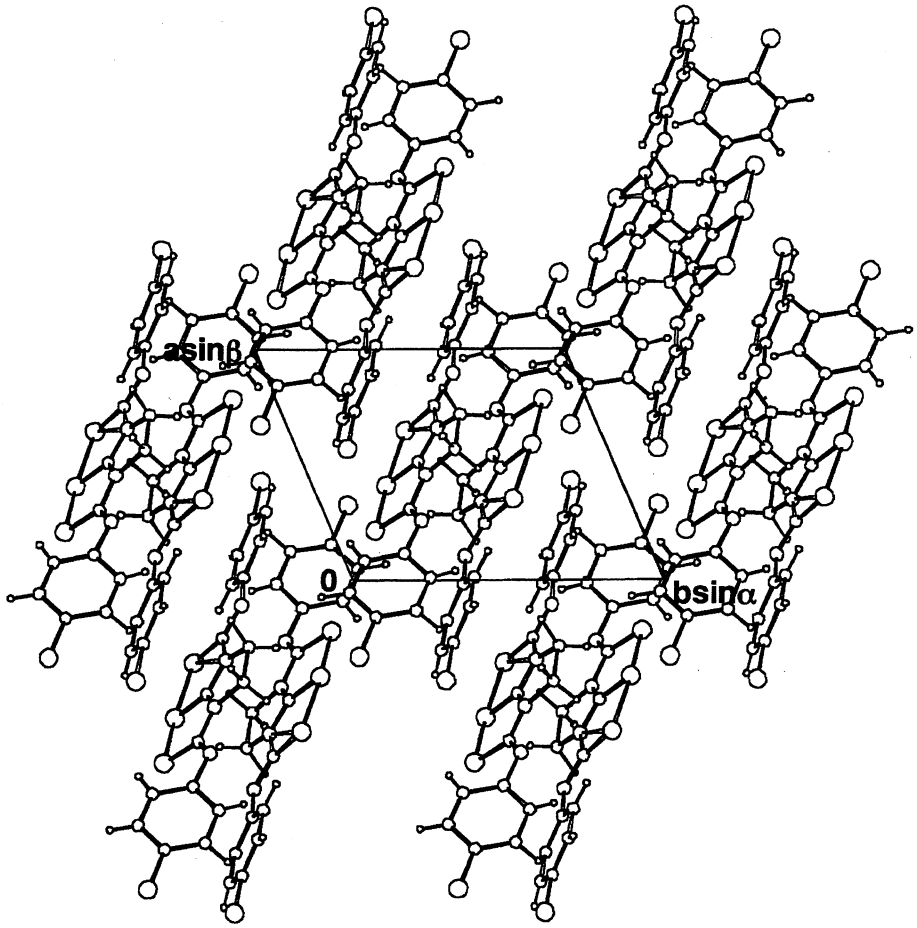


Fig. 2. Projection of the crystal structure of **5** viewed along the *c* axis.

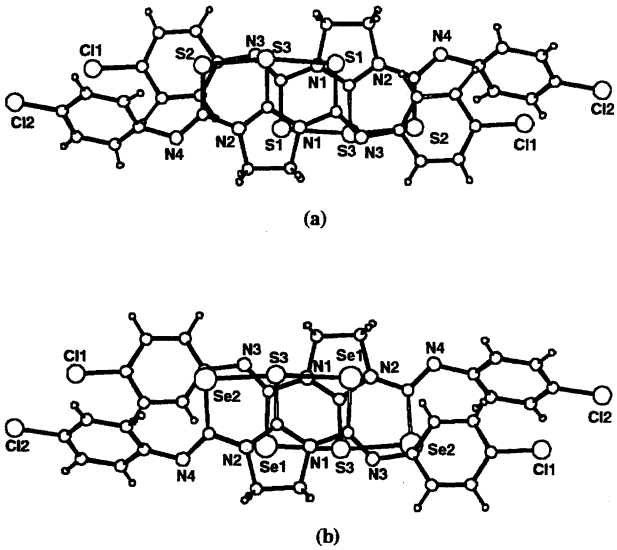


Fig. 3. Overlappings of the molecules related with the center of symmetry. (a) **5** and (b) **6**.

along with those of some trithia/selena-diazapentalenes. In the case of **5**, **6**, **7**, **A**,[26] and **B**,[28] which have a perhydroimidazole moiety, the outer C–N bond (bond **d**) is significantly longer than the inner C–N bond (bond **e**), because of the effect of the exocyclic C–N double bond (bond **f**). (The symbols, **A** and **B** in this section denote the different molecules from **7A** and **7B**, respectively, in the previous section. See Table 4). The same tendency has been observed in the thia/selena-tetraazapentalenes (**F**—**K**),[7,13,28,29] which have a perhydropyrimidine moiety. In **C**,[30] **D**,[31] and **E**,[32] no such differences between bonds **d** and **e** are observed. The lengths of the S–C bonds (Y–C, bond **c**) of the latter group are significantly shorter than those of **5**, **7**, and **A**. The endopentalene angles (especially γ, δ, and ε angles) are significantly affected by the perhydroimidazole ring. The smaller γ, and the greater δ and ε angles are observed in the molecules with a perhydroimidazole ring (**5**, **6**, **7**, and **B**), rather than those in the molecules without a ring (**C**—**E**). The exopentalene angles (ϕ, ψ, and $\varkappa$) also show the differences between these two groups, and between groups with the imidazole ring and with the pyrimidine ring (**F**—**K**).

A calculation of the frontier electron densities of **5** using the PM3 method[33] shows large HOMO electron densities on the side S atoms, like thiocarbonyl S atoms of **1**, and the large LUMO density on the central C atom, as shown in Fig. 6. Therefore, the side S atoms are expected to work as a nucleophilic ligand, similar to the thiocarbonyl S atoms, to form a metallapentalene complex.

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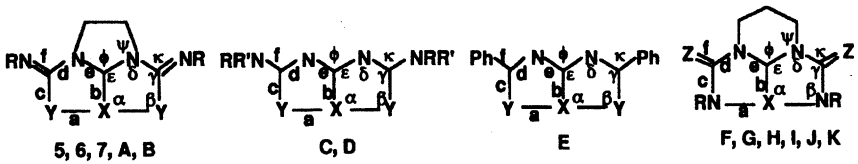
Table 4. Comparison of Bond Lengths and Angles of 6a-Thia/Selena-pentalenes

	5	6	7	A[b)]	B[b)]	C	D	E	F	G	H	I	J	K
Reference				26	28	30	31	32	7	7	13	28	7	29
Ref. code[a)]				EHPIZP	HABGUM	ANAZTP10	MAZPEN	PAZTPN10	KIPRAC	KIPREG	FIVZEP10	SONHIM	KIPRIK	HABGOG
X	S	S	Se	S	Se	S	S	S	S	S	S	S	Se	Se
Y	S	Se	S	S	Se	S	S	S	N	N	N	N	N	N
R	*p*-Cl-Ph	*p*-Cl-Ph	Ph	Ph	Et	Ph, H	Me, Me		Ph	Et	Et	*cy*-Hx	Et	Et
Z									O	O	S	Se	S	Se
a(X–Y)/Å	2.401	2.528	2.488	2.391	2.627	2.350	2.346	2.325	1.959	1.927	1.909	1.933	2.034	2.049
b(X–C)/Å	1.720	1.716	1.840	1.693	1.874	1.789	1.856	1.779	1.717	1.717	1.705	1.726	1.852	1.860
c(Y–C)/Å	1.737	1.889	1.736	1.736	1.888	1.712	1.705	1.696	1.328	1.324	1.300	1.317	1.294	1.291
d(N–C)/Å	1.405	1.401	1.416	1.409	1.424	1.340	1.347	1.327	1.437	1.438	1.423	1.395	1.432	1.463
e(N–C)/Å	1.324	1.338	1.327	1.329	1.322	1.329	1.309	1.335	1.324	1.333	1.333	1.349	1.329	1.330
f(N–C)/Å	1.285	1.270	1.272		1.266	1.343	1.333	1.493	1.219	1.220	1.679	1.835	1.689	1.829
Y–X–Y/°	170.3	174.0	164.6		167.6	174.3	174.4	174.6	165.0	165.2	165.5	164.8	158.5	159.4
α(Y–X–C)/°	85.2	87.0	82.3		83.7	87.2	87.2	87.3	82.6	82.4	82.8	82.4	79.3	79.7
β(X–Y–C)/°	95.1	89.8	95.6		91.2	91.1	91.7	91.5	114.6	116.0	115.9	114.6	116.0	115.6
γ(Y–C–N)/°	111.5	112.1	113.3		113.6	121.0	120.9	121.7	107.9	107.5	108.6	110.4	110.7	110.8
δ(C–N–C)/°	124.2	126.0	123.8		127.8	119.1	121.1	117.9	116.3	115.4	114.7	114.7	116.6	116.2
ε(X–C–N)/°	123.9	124.6	124.4		123.8	121.5	118.9	121.5	118.4	118.4	118.1	117.9	117.6	117.6
ϕ(N–C–N)/°	112.1	110.7	111.3		112.5	117.1	122.3	116.9	123.3	123.2	123.8	124.0	124.9	124.8
ψ(C–N–C)/°	111.1	111.1	111.5		111.3				121.9	121.5	121.4	121.1	120.2	120.1
$\varkappa$(N–C–N)/°	115.3	115.1	115.5		115.5	115.7	117.5	116.9	120.3	120.6	120.6	120.9	120.5	120.4

a) Reference code in Cambridge Structural Database. b) These molecules are different from **7A** and **7B**.



5, 6, 7, A, B C, D E F, G, H, I, J, K

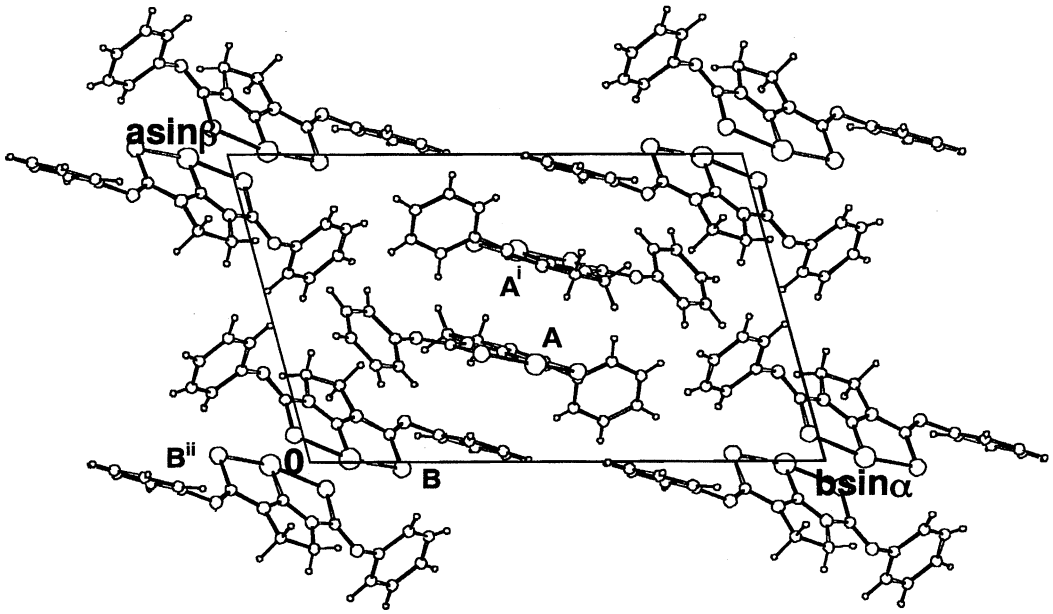


Fig. 4. Projection of the crystal structure of **7** viewed along the *c* axis.

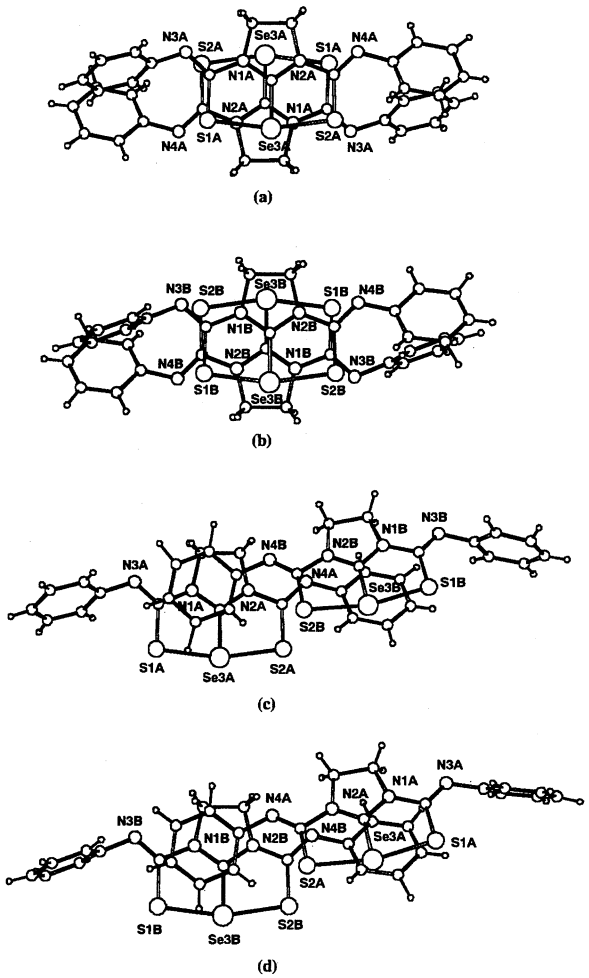


Fig. 5. Overlappings of the molecules of **7**. (a) Molecules **A** related by the center of symmetry. (b) Molecules **B** related by the center of symmetry. (c) Molecules **A** and **B**: Projection onto the **A** molecule. (d) Molecules **A** and **B**: Projection onto the **B** molecule.

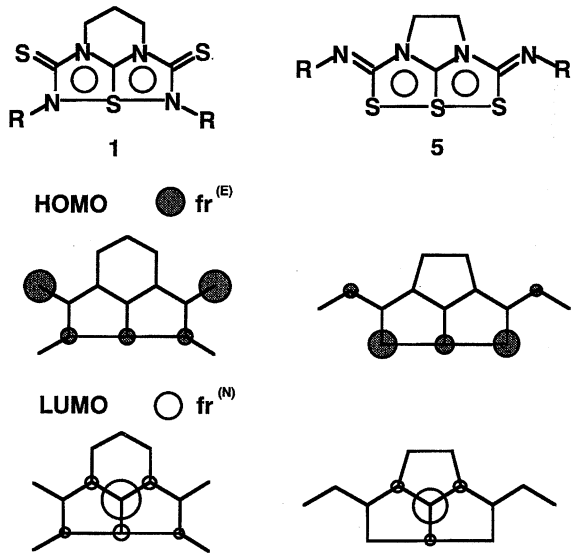


Fig. 6. Schematic drawings of frontier electron densities of thiatetraazapentalene (**1**) and trithiadiazapentalene (**5**) calculated by PM3 method. The size of the circles is proportional to the densities.

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References

1) J. I. Musher, *Angew. Chem., Int. Ed. Engl.*, **8**, 54 (1969).
2) S. Bezzi, M. Mammi, and C. Garbuglio, *Nature*, **182**, 247 (1958).
3) A. Hordvik and K. Julshamn, *Acta Chem. Scand.*, **26**, 343 (1972).
4) A. Kálmán, K. Sásvári, and I. Kapovits, *Acta Crystallogr., Sect. B*, **B29**, 355 (1973).
5) I. C. Paul, J. C. Martin, and E. F. Perozzi, *J. Am. Chem. Soc.*, **94**, 5010 (1972).
6) N. Matsumura, M. Tomura, S. Yonéda, and K. Toriumi,

Chem. Lett., **1986**, 1047.

7) F. Iwasaki, H. Murakami, N. Yamazaki, M. Yasui, M. Tomura, and N. Matsumura, *Acta Crystallogr., Sect. C*, **C47**, 998 (1991).

8) F. Iwasaki, S. Yoshida, S. Kakuma, T. Watanabe, and M. Yasui, *J. Mol. Struct.*, **352/353**, 203 (1995).

9) N. Matsumura, J. Kawano, N. Fukunishi, H. Inoue, M. Yasui, and F. Iwasaki, *J. Am. Chem. Soc.*, **117**, 3623 (1995).

10) M. Yasui, S. Yoshida, S. Kakuma, S. Shimamoto, N. Matsumura, and F. Iwasaki, *Bull. Chem. Soc. Jpn.*, **69**, 2739 (1966).

11) F. Iwasaki, M. Yasui, S. Yoshida, H. Nishiyama, S. Shimamoto, and N. Matsumura, *Bull. Chem. Soc. Jpn.*, **69**, 2759 (1996).

12) N. Manabe, M. Yasui, H. Nishiyama, S. Shimamoto, N. Matsumura, and F. Iwasaki, *Bull. Chem. Soc. Jpn.*, **69**, 2771 (1996).

13) N. Matsumura, M. Tomura, O. Mori, Y. Tsuchiya, S. Yoneda, and K. Toriumi, *Bull. Chem. Soc. Jpn.*, **61**, 2419 (1988).

14) N. Matsumura, M. Kusamiya, H. Inoue, M. Yasui, and F. Iwasaki, *J. Heterocycl. Chem.*, **32**, 1269 (1995).

15) F. Iwasaki, H. Nishiyama, M. Yasui, and N. Matsumura, *Bull. Chem. Soc. Jpn.*, **70**, 1277 (1997).

16) F. Iwasaki, M. Sakuratani, H. Kaneko, M. Yasui, N. Kamiya, and H. Iwasaki, *Acta Crystallogr., Sect. B*, **B51**, 1028 (1995).

17) N. Kamiya and H. Iwasaki, *J. Appl. Crystallogr.*, **28**, 745 (1995).

18) G. M. Sheldrick, "SHELXS86. Program for Crystal Structure Determination," University of Göttingen, Germany (1986).

19) H.-F. Fan, "SAPI91, Structure Analysis Programs with Intelligent Control," Tokyo, Japan (1991).

20) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham (Present distributor D. Reidel, Dordrecht) (1974), Vol. IV.

21) T. Sakurai and K. Kobayashi, *Rikagaku Kenkyusho Hokoku*, **55**, 69 (1979).

22) MSC, "teXsan, Crystal Structure Analysis Package," Texas, USA (1992).

23) C. K. Johnson, "ORTEP II, Report ORNL-5138," Oak Ridge National Laboratory, Tennessee, USA (1976).

24) Lists of structure factors, anisotropic temperature factors for non-hydrogen atoms, atomic parameters for H-atoms, and all bond lengths and angles have been deposited as Document No. 70018 at the Office of the Editor of Bull. Chem. Soc. Jpn.

25) L. Hansen and A. Hordvik, *J. Chem. Soc., Chem. Commun.*, **1972**, 222.

26) K.-T. Wei, I. C. Paul, R. J. S. Beer, and A. Naylor, *J. Chem. Soc., Chem. Commun.*, **1975**, 265.

27) F. H. Allen, O. Kennard, and R. Taylor, *Acc. Chem. Res.*, **16**, 146 (1983).

28) D. G. Billing, E. E. Freg, L.-L. Lai, D. C. Levendis, and D. H. Reid, *Acta Crystallogr., Sect. C*, **C49**, 917 (1993).

29) D. G. Billing, J. C. A. Boeyens, L. Denner, M. D. Hellyar, L.-L. Lai, A. J. Matthee, and D. H. Reid, *Acta Crystallogr., Sect. C*, **C47**, 2564 (1991).

30) A. Hordvik and P. Oftedal, *Acta Chem. Scand., Ser. A*, **A35**, 663 (1981).

31) B. Stelander, H. G. Viehe, M. v. Meerssche, G. Germain, and J. P. Declercq, *Bull. Soc. Chim. Belg.*, **86**, 291 (1977).

32) A. Hordvik and L. M. Milje, *Acta Chem. Scand.*, **27**, 510 (1973).

33) J. J. P. Stewart, *J. Comput. Chem.*, **10**, 209 (1989).