# Crystal and Molecular Structures of Novel Metal–Carbene Complexes III. Rh–Carbene Complexes and Cu Complex

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(Received March 13, 1996)

2,3,4,5-Tetrahydro-1,6-dialkyl-3,4-trimethylene-6a$\lambda^4$-thia-1,3,4,6-tetraazapentalene-2,5-dithiones (**1**), which contain a hypervalent sulfur atom, have been found to give novel metal–carbene complexes by treating with $RhCl(PPh_3)_3$. X-Ray investigations have revealed that the resultant complexes are novel Rh–carbene complexes: *trans*(*P*,*P*′)-(chloro){[3-(methylthiocarbamoyl-$\varkappa N$)perhydropyrimidine-1-yl-$\varkappa C^2$](methyliminomethanethiolato-$\varkappa S$)}-bis(triphenylphosphine)rhodium(III) (**4a**) and *trans*(*P*,*P*′)-(chloro){(perhydropyrimidine-1,3-diyl-$\varkappa C^2$)bis[(4-chlorophenylimino)methanethiolato-$\varkappa^2 SS'$]}bis(triphenylphosphine)rhodium(III) (**4c**). In these complexes, the central sulfur atom in **1** was substituted by a Rh atom. In **4a**, obtained from 1,6-dimethyl-pentalene (**1a**), only one of the sulfur atoms of the thioamide groups coordinates the Rh atom, while the other thioamide group coordinates Rh with the N atom. Rh is coordinated by S, N, C, and Cl atoms to form an equatorial plane, and is coordinated by two $PPh_3$ groups axially. In **4c**, obtained from the 4-chlorophenyl derivative (**1c**), two thioamide groups rotated to form an S–Rh–S bond. A reaction of **1a** with $Cu(ClO_4)_2$ gave a different kind of complex, bis (2,3,4,5-tetrahydro-1,6-dimethyl-3,4-trimethylene-6a$\lambda^4$-thia-1,3,4,6-tetraazapentalene-2,5-dithione-$\varkappa^2 S^4$)copper(I) (**7**). The framework of the starting tetraazathiapentalene **1** remained unsubstituted, and the sulfur atoms of the thiocarbonyl groups of **1** coordinated the Cu atom to form one-dimensional coordination polymers, where the Cu atom is coordinated tetrahedrally by four S atoms. Because of a difference in the changes of the oxidation numbers of the metals during the reactions, metal–carbene complexes could not be obtained in the case of the Cu-complex.

In a previous paper[1] we reported on the structures of novel Pt and Pd-carbene complexes derived from 6a-thiatetraazapentalene derivatives (**1**), which contain a hypervalent sulfur atom.[2—4] In these complexes the central sulfur atom in **1** was substituted by a metal atom, and the thioamide groups rotated to form metal–sulfur bonds in the resultant metallapentalene framework.[1,5] The reactions of **1a** and **1c** with $RhCl(PPh_3)_3$ also gave Rh complexes, **4a** and **4c**. A structure analysis was carried out to elucidate the coordination mode of these complexes. A Cu-complex **7** was also obtained from the reaction of **1a** with $Cu(ClO_4)_2$ (Scheme 1). An X-ray structure determination revealed that **7** was not a carbene complex, but a tetrahedral-coordination polymer.

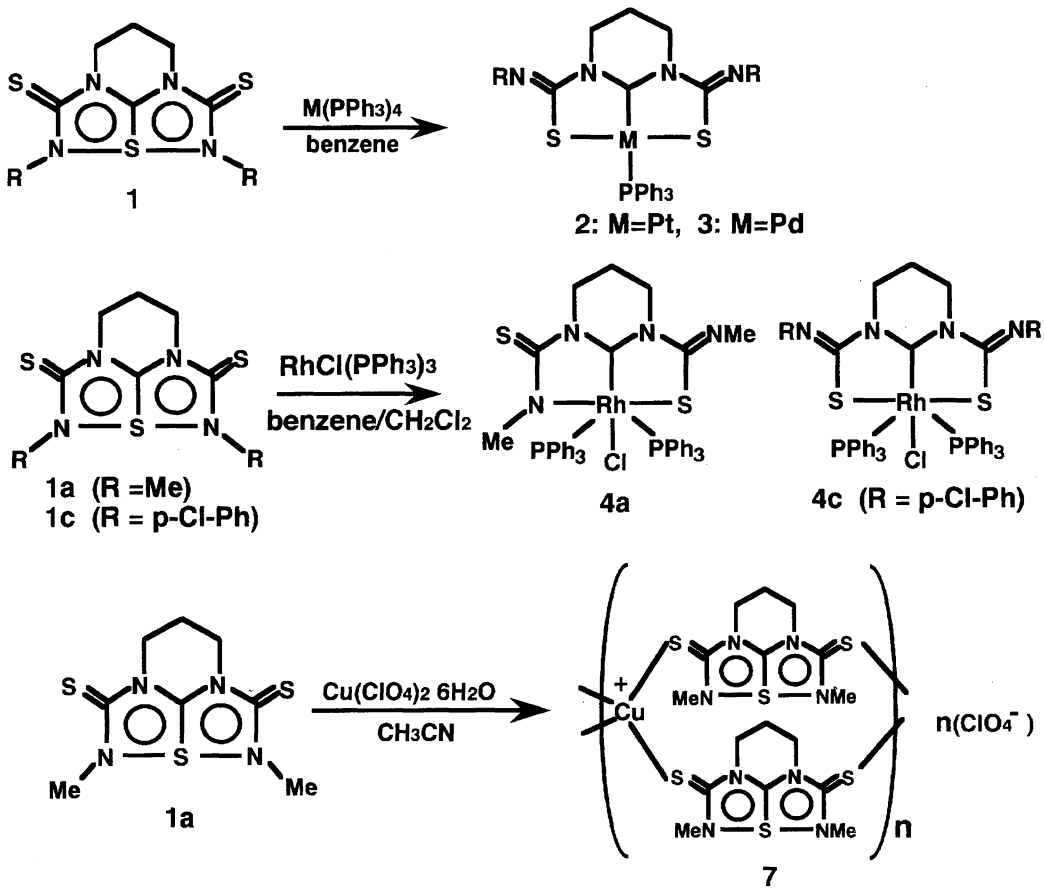
## Experimental

Crystals of **4a** and **4c** for X-ray analyses were grown from $CH_2Cl_2$/hexane and $CHCl_3$/hexane solutions, respectively. Crystals of **7** were grown from $CH_3CN$ solutions. For **4a** and **7**, intensity data were measured using a Rigaku diffractometer (AFC-5R) with a graphite monochromator. Absorption corrections were applied numerically. Crystal data, details of the data collection and structure refinements are listed in Table 1.

Two crystal modifications (**4c-1** and **4c-2**) of **4c** were grown from different batches, although the same solvents were used. Although crystals of **4c-1** were obtained soon from solution, those of **4c-2** were obtained after one week. Crystals of **4c-1** were very unstable in air. Diffraction data could not be measured using a conventional four-circle diffractometer, even in a thin glass capillary. We then used a new Weissenberg-type diffractometer (DIP-3000) with imaging plates as a two-dimensional detector.[6,7] Using this equipment, the intensities of 8542 independent reflections out of 37227 total and 12100 unique reflections could be observed. The total time of the intensity measurement was 7 h. The intensities of **4c-2** were also measured using DIP-3000 within 2 h. The intensities of 8333 independent reflections out of 20891 total and 10109 unique (82.5% of the total unique reflections with $2\theta_{max} = 55°$) reflections could be observed.

The structures were solved by a heavy-atom method, preceded by the Patterson function to locate the metal atom using the program SHELXS86.[8] For **4a**, a solvent molecule, $CH_2Cl_2$, was found in D-maps. The occupancy factor was set to 0.75 from the peak heights of the D-maps. For **4c-1**, peaks corresponding to two $CHCl_3$ molecules in an asymmetric unit were found in D-maps. One of the solvent molecules with an occupancy factor of 0.3 seemed to be rotating or greatly disordering. The positions of several H atoms were obtained from D-maps; the remaining H atoms were located from calculations, and were included in the refinements with restraint.

For **4c-2**, only one $CHCl_3$ molecule was found in an asymmetric unit from D-maps. For **4c-2** and **7**, almost all of the H atoms were located from D-maps; the remaining H atoms were obtained from




Scheme 1.

calculations.

The structures were refined by block-diagonal least-squares with anisotropic temperature factors for the non-H atoms and isotropic ones for the H atoms. The function $\Sigma w(|F_o| - k|F_c|)^2$ was minimized. The final $R$ values are 0.0664, 0.0847, 0.0602, and 0.0391 for **4a**, **4c-1**, **4c-2**, and **7**, respectively.

Atomic-scattering factors were used from the International Tables for X-Ray Crystallography.[9] All of the computations were performed with the programs SHELXS86, UNICS III,[10] ORTEP II.[11] The final atomic parameters are given in Table 2.[12]

## Discussion

**Structures of Rh Complexes.** The molecular structures of **4a**, **4c-1**, and **4c-2** with the atomic numbering are shown in Fig. 1. Selected bond distances and angles are listed in Table 3. In each **4a** and **4c**, the sulfur atom of the tetraazathiapentalene framework of **1** is substituted by the Rh atom, as in the case of the Pt and Pd complexes, **2** and **3**. In the case of **4a**, however, only one sulfur atom of the thioamide groups coordinates to the Rh atom. The other thioamide group coordinates Rh with the N atom. Therefore, Rh is coordinated by S, N, C, and Cl atoms to form an equatorial plane, and is coordinated by two $PPh_3$ groups apically. In the case of **4c**, two thioamide groups rotated to form an S–Rh–S bond, just like the Pt and Pd complexes. Rh–carbene complexes with a pentalene ring have been reported for $RhCl((C_6H_5)CONCS)_2(P(C_6H_5)_3)_2\cdot(C_2H_5)_2O$[13] and $RhCl(C_2H_5OCONCS)_3(P(C_6H_5)_3)_2\cdot(CH_3)_2CO$,[14] which were obtained from the reaction of $RhCl(PPh_3)_3$ with benzoyl isothiocyanate and ethoxycarbonyl isothiocyanate, respectively. The structural feature of **4a** with nearly linear S–Rh–N bonds is similar to that of $RhCl((C_6H_5)CONCS)_2(P(C_6H_5)_3)_2\cdot(C_2H_5)_2O$, which has S–Rh–O bonds. The feature of **4c** with the S–Rh–S system is similar to that of $RhCl(C_2H_5OCONCS)_3(P(C_6H_5)_3)_2\cdot(CH_3)_2CO$ with the S–Rh–S system.

NMR spectroscopy revealed that S–Metal–N bonds were also found in solutions in the case of the Pt and Pd complexes. However, the S–Metal–N structure gradually transformed to the S–Metal–S structure in the solution. In the case of Pt and Pd complexes, only an S–M–S isomer has been obtained in the crystalline state.[5] It may be considered that the S–M–N isomer was protected among the bulky triphenylphosphine groups in the case of **4a** with a small N-methyl group. As for **4c**, the bulky 4-Cl-phenyl groups could no longer be accommodated between the triphenylphosphine groups because of steric crowding, so that only the S–Rh–S isomer could be obtained.

The metallapentalene frameworks of **4a** and **4c** are planar. The maximum deviations from the best plane, defined with eight atoms of the pentalene ring, are 0.081(5), 0.216(9), and 0.332(5) Å for **4a**, **4c-1**, and **4c-2**, respectively. In Table 4,

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

| | **4a** | **4c-1** | **4c-2** | **7** |
|---|---|---|---|---|
| | $C_{44}H_{42}ClN_4P_2RhS_2$ ·0.75($CH_2Cl_2$) | $C_{54}H_{44}Cl_3N_4P_2RhS_2$ ·1.3($CHCl_3$) | $C_{54}H_{44}Cl_3N_4P_2RhS_2$ ·$CHCl_3$ | $C_{16}H_{24}N_8S_6Cu^+$· $ClO_4^-$ |
| F.W. | 940.76 | 1239.15 | 1203.69 | 683.81 |
| Color | Yellow | Yellow | Yellow | Yellow |
| Crystal shape | Plate | Plate | Prism | Pillar |
| Crystal system | Monoclinic | Monoclinic | Monoclinic | Monoclinic |
| Space group | $P2_1/n$ | $P2_1/n$ | $P2_1/a$ | $P2_1/n$ |
| $a$/Å | 10.302(2) | 28.127(1) | 19.049(1) | 7.693(2) |
| $b$/Å | 36.241(5) | 16.797(1) | 15.762(1) | 9.848(1) |
| $c$/Å | 11.958(2) | 14.103(1) | 18.353(1) | 16.085(2) |
| $\beta$/° | 101.04(2) | 101.19(27) | 105.17(5) | 111.82(1) |
| $V$/Å$^3$ | 4382(1) | 6536(6) | 5318(1) | 2601.8(5) |
| $Z$ | 4 | 4 | 4 | 4 |
| $D_x$/g cm$^{-3}$ | 1.426 | 1.259 | 1.503 | 1.746 |
| $D_m$/g cm$^{-3}$ | — | 1.376 | — | — |
| $F$(000) | 1932 | 2516 | 2448 | 1400 |
| Crystal size | 0.075 × 0.15 × 0.45 | 0.33 × 0.26 × 0.15 | 0.30 × 0.30 × 0.60 | 0.20 × 0.20 × 0.25 |
| Radiation | Mo $K\alpha$ | Mo $K\alpha$ | Mo $K\alpha$ | Mo $K\alpha$ |
| $\lambda$/Å | 0.71069 | 0.71073 | 0.71073 | 0.71069 |
| $\mu$/mm$^{-1}$ | 0.736 | 0.685 | 0.795 | 1.448 |
| Temperature/K | 293 | 293 | 293 | 296 |
| Scan mode | $\omega$ | Weissenberg | Weissenberg | $\omega$–2$\theta$ |
| $2\theta_{max}$/° | 55.0 | 52.7 | 55.0 | 55.0 |
| Scan width $\Delta\omega$/° | 1.10+0.45tan $\theta$ | — | — | 1.40+0.5tan $\theta$ |
| Scan speed/°min$^{-1}$ | 4 | — | — | 4 |
| Rotation axis | — | $c$ | $a$ | — |
| $\Delta\phi$/° | — | 181 | 61 | — |
| No. of IPs | — | 20 | 20 | — |
| No. of standard refs. | 3 every 50 refls. | — | — | 3 every 100 refs. |
| Variation of intensities | 0.968—1.004 | — | — | 0.987—1.007 |
| Range of $h$ $k$ $l$ | 0—14 0—47 −16—16 | −35—35 −20—20 −8—15 | −17—17 −15—20 −17—23 | −23—23 0—13 0—21 |
| $T_{max}$, $T_{min}$ | 0.955, 0.926 | — | — | 0.881, 0.821 |
| No. of reflection | | | | |
| Measured | 11019 | 37227 | 20891 | 6377 |
| Unique | 10077 | 12100 | 10109 | 5981 |
| Observed ($\|F_o\| > 3\sigma(F)$) | 6174 | 8542 | 8333 | 4693 |
| Refinement | 6174 | 8542 | 8333 | 4693 |
| $R_{int}$ | 0.0665 | 0.059 | 0.030 | 0.015 |
| No. of parameters | 690 | 851 | 811 | 421 |
| $S$ | 1.858 | 5.532 | 1.540 | 1.163 |
| $\Delta/\sigma$ | 0.255 | 0.330 | 0.156 | 0.048 |
| $(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ | 1.188, −0.774 | 0.948, −1.260 | 1.036, −1.133 | 0.667, −0.640 |
| Weighting scheme[a)] | *1 | *2 | *3 | *4 |
| $R$ | 0.0664 | 0.0847 | 0.0602 | 0.0391 |
| $wR$ | 0.0694 | 0.1061 | 0.0942 | 0.0478 |

a) *1: $w = 1.7999/\{\sigma(F)^2 + 0.000628|F_o|^2\}$. *2: $w = 1$. *3: $w = 1/\{\sigma(F)^2 + 0.01177|F_o| + 0.00205|F_o|^2\}$. *4: $w = 1/\{\sigma(F)^2 + 0.02226|F_o| + 0.00030|F_o|^2\}$.

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

$$B_{eq} = 4/3 \sum_i \sum_j \beta_{ij} \boldsymbol{a}_i \cdot \boldsymbol{a}_j$$

| Atom | $x$ | $y$ | $z$ | $B_{eq}$/Å$^2$ | Atom | $x$ | $y$ | $z$ | $B_{eq}$/Å$^2$ |
|---|---|---|---|---|---|---|---|---|---|
| (1) **4a** | | | | | (2) **4c-1** | | | | |
| Rh(1) | 0.27822(4) | 0.35961(1) | 0.45522(4) | 2.18(1) | Rh(1) | 0.31446(3) | 0.09642(5) | 0.57287(6) | 3.20(2) |
| S(1) | 0.50039(15) | 0.37076(4) | 0.53652(16) | 2.96(4) | Cl(1) | 0.31286(10) | 0.05304(18) | 0.7375(2) | 4.65(8) |
| S(2) | −0.11494(18) | 0.41796(6) | 0.3394(2) | 4.84(5) | Cl(11) | 0.05623(17) | −0.2092(3) | 0.3487(4) | 10.8(2) |
| Cl(1) | 0.27693(18) | 0.29229(4) | 0.43949(16) | 3.64(4) | Cl(21) | 0.61759(16) | 0.3125(3) | 0.6792(5) | 11.7(2) |
| P(1) | 0.33850(16) | 0.36431(5) | 0.27249(15) | 2.77(4) | S(1) | 0.23782(9) | 0.04354(16) | 0.51227(19) | 3.85(7) |
| P(2) | 0.23012(16) | 0.34901(4) | 0.63806(15) | 2.56(4) | S(2) | 0.39056(9) | 0.15915(18) | 0.6013(2) | 4.26(8) |
| N(1) | 0.3640(5) | 0.43463(13) | 0.5132(4) | 2.57(9) | P(1) | 0.27698(9) | 0.21865(16) | 0.6022(2) | 3.69(7) |
| N(2) | 0.1402(5) | 0.42705(13) | 0.4394(5) | 2.79(9) | P(2) | 0.35477(9) | −0.02613(16) | 0.55120(19) | 3.40(7) |
| N(3) | 0.5866(5) | 0.44063(14) | 0.5845(5) | 3.54(10) | N(1) | 0.2772(3) | 0.1012(5) | 0.3674(6) | 3.9(2) |
| N(4) | 0.0811(5) | 0.36774(14) | 0.3825(5) | 2.91(9) | N(2) | 0.3509(3) | 0.1651(5) | 0.4117(6) | 4.0(3) |
| C(1) | 0.4926(6) | 0.41882(16) | 0.5481(6) | 2.79(10) | N(3) | 0.2110(3) | 0.0213(5) | 0.3186(6) | 4.6(3) |
| C(2) | 0.0405(6) | 0.40223(19) | 0.3855(6) | 3.18(10) | N(4) | 0.4261(3) | 0.2189(6) | 0.4493(8) | 5.6(3) |
| C(3) | 0.2631(6) | 0.41255(16) | 0.4712(5) | 2.42(10) | C(1) | 0.2401(3) | 0.0517(6) | 0.3927(7) | 3.6(3) |
| C(4) | 0.3504(7) | 0.47460(18) | 0.5243(7) | 3.79(10) | C(2) | 0.3927(4) | 0.1845(6) | 0.4855(7) | 4.0(3) |
| C(5) | 0.2144(8) | 0.4836(2) | 0.5397(8) | 5.30(11) | C(3) | 0.3142(3) | 0.1254(6) | 0.4404(7) | 3.5(3) |
| C(6) | 0.1098(7) | 0.46625(19) | 0.4522(7) | 4.21(10) | C(4) | 0.2741(4) | 0.1185(7) | 0.2647(8) | 5.0(4) |
| C(7) | 0.7189(6) | 0.4250(2) | 0.6173(7) | 4.67(11) | C(5) | 0.3032(5) | 0.1913(8) | 0.2533(9) | 5.8(4) |
| C(8) | −0.0132(7) | 0.3400(2) | 0.3283(7) | 4.28(11) | C(6) | 0.3535(4) | 0.1861(8) | 0.3108(9) | 5.2(4) |
| C(11) | 0.3724(6) | 0.41194(18) | 0.2418(6) | 3.25(10) | C(11) | 0.1742(4) | −0.0332(7) | 0.3319(8) | 4.6(3) |
| C(12) | 0.5044(7) | 0.4239(2) | 0.2530(7) | 4.49(11) | C(12) | 0.1839(4) | −0.1010(7) | 0.3861(9) | 5.2(4) |
| C(13) | 0.5289(9) | 0.4610(2) | 0.2348(8) | 5.83(11) | C(13) | 0.1480(4) | −0.1561(7) | 0.3925(10) | 5.5(4) |
| C(14) | 0.4263(10) | 0.4858(2) | 0.2058(7) | 6.22(11) | C(14) | 0.1022(5) | −0.1404(8) | 0.3415(11) | 7.0(5) |
| C(15) | 0.2994(9) | 0.4743(2) | 0.1972(7) | 5.41(11) | C(15) | 0.0928(5) | −0.0742(10) | 0.2842(13) | 8.7(6) |
| C(16) | 0.2712(8) | 0.4375(2) | 0.2167(6) | 4.14(11) | C(16) | 0.1288(5) | −0.0206(9) | 0.2788(11) | 7.0(5) |
| C(21) | 0.4854(6) | 0.33831(19) | 0.2497(6) | 3.44(10) | C(21) | 0.4710(4) | 0.2388(8) | 0.5119(10) | 5.8(4) |
| C(22) | 0.5267(7) | 0.3429(2) | 0.1479(7) | 4.58(11) | C(22) | 0.5005(5) | 0.1905(9) | 0.5696(12) | 7.4(5) |
| C(23) | 0.6375(8) | 0.3243(3) | 0.1263(8) | 5.82(11) | C(23) | 0.5456(5) | 0.2110(8) | 0.6207(12) | 6.9(5) |
| C(24) | 0.7028(7) | 0.3001(3) | 0.2077(9) | 5.83(11) | C(24) | 0.5622(5) | 0.2802(9) | 0.6145(14) | 8.9(6) |
| C(25) | 0.6601(7) | 0.2953(2) | 0.3075(8) | 5.22(11) | C(25) | 0.5381(8) | 0.3291(13) | 0.5552(23) | 16.2(12) |
| C(26) | 0.5517(7) | 0.3144(2) | 0.3291(7) | 3.99(10) | C(26) | 0.4911(8) | 0.3091(13) | 0.5040(25) | 18.4(14) |
| C(31) | 0.2127(6) | 0.34795(18) | 0.1526(6) | 3.17(10) | C(31) | 0.2664(4) | 0.2800(6) | 0.4953(8) | 4.1(3) |
| C(32) | 0.1798(8) | 0.3111(2) | 0.1510(7) | 4.52(11) | C(32) | 0.3005(4) | 0.3319(7) | 0.4744(9) | 5.2(4) |
| C(33) | 0.0802(8) | 0.2964(2) | 0.0667(7) | 4.88(11) | C(33) | 0.2931(5) | 0.3783(7) | 0.3952(10) | 5.7(4) |
| C(34) | 0.0163(8) | 0.3185(3) | −0.0194(7) | 4.85(11) | C(34) | 0.2501(5) | 0.3713(9) | 0.3279(10) | 6.7(5) |
| C(35) | 0.0530(8) | 0.3545(2) | −0.0215(7) | 4.92(11) | C(35) | 0.2157(5) | 0.3190(8) | 0.3439(9) | 6.1(4) |
| C(36) | 0.1520(8) | 0.3696(2) | 0.0627(7) | 4.49(11) | C(36) | 0.2241(4) | 0.2729(7) | 0.4260(8) | 4.8(4) |
| C(41) | 0.3415(6) | 0.31899(16) | 0.7357(6) | 2.74(10) | C(41) | 0.2183(4) | 0.2160(6) | 0.6419(8) | 3.9(3) |
| C(42) | 0.4449(7) | 0.29905(19) | 0.7059(6) | 3.45(10) | C(42) | 0.1888(4) | 0.2828(7) | 0.6311(10) | 5.5(4) |
| C(43) | 0.5200(7) | 0.2757(2) | 0.7838(7) | 4.59(11) | C(43) | 0.1474(5) | 0.2847(9) | 0.6680(10) | 6.3(5) |
| C(44) | 0.4924(7) | 0.2707(2) | 0.8906(6) | 4.13(11) | C(44) | 0.1353(5) | 0.2199(9) | 0.7175(12) | 7.2(5) |
| C(45) | 0.3887(7) | 0.2901(2) | 0.9208(6) | 4.06(10) | C(45) | 0.1643(5) | 0.1536(8) | 0.7284(12) | 7.0(5) |
| C(46) | 0.3154(7) | 0.31415(19) | 0.8447(6) | 3.32(10) | C(46) | 0.2053(4) | 0.1519(7) | 0.6895(10) | 5.4(4) |
| C(51) | 0.0698(6) | 0.32693(18) | 0.6343(6) | 2.98(10) | C(51) | 0.3104(4) | 0.2851(6) | 0.6946(7) | 4.0(3) |
| C(52) | 0.0617(6) | 0.29069(17) | 0.6684(6) | 3.23(10) | C(52) | 0.3439(4) | 0.2544(7) | 0.7730(8) | 4.6(3) |
| C(53) | −0.0591(8) | 0.2742(2) | 0.6657(7) | 4.76(11) | C(53) | 0.3649(5) | 0.3034(9) | 0.8488(10) | 6.6(5) |
| C(54) | −0.1738(7) | 0.2926(2) | 0.6283(7) | 4.82(11) | C(54) | 0.3522(6) | 0.3815(9) | 0.8490(10) | 7.1(5) |
| C(55) | −0.1697(7) | 0.3279(2) | 0.5889(8) | 5.34(11) | C(55) | 0.3194(6) | 0.4121(8) | 0.7754(12) | 7.5(5) |
| C(56) | −0.0479(7) | 0.34573(18) | 0.5892(7) | 4.27(10) | C(56) | 0.2981(5) | 0.3643(7) | 0.6989(10) | 5.6(4) |
| C(61) | 0.2305(7) | 0.39031(17) | 0.7268(6) | 3.25(10) | C(61) | 0.4066(3) | −0.0569(6) | 0.6456(7) | 3.6(3) |
| C(62) | 0.3490(8) | 0.4021(2) | 0.7881(7) | 5.13(11) | C(62) | 0.4232(4) | −0.0145(7) | 0.7280(8) | 4.5(3) |
| C(63) | 0.3560(9) | 0.4327(3) | 0.8611(8) | 6.59(11) | C(63) | 0.4612(4) | −0.0438(8) | 0.7974(8) | 5.6(4) |
| C(64) | 0.2425(10) | 0.4518(2) | 0.8679(8) | 6.83(11) | C(64) | 0.4820(4) | −0.1139(8) | 0.7859(9) | 5.6(4) |
| C(65) | 0.1237(11) | 0.4410(3) | 0.8050(9) | 7.20(11) | C(65) | 0.4663(4) | −0.1567(7) | 0.7026(9) | 5.4(4) |
| C(66) | 0.1189(8) | 0.4108(2) | 0.7340(7) | 5.31(11) | C(66) | 0.4285(4) | −0.1286(7) | 0.6339(9) | 5.0(4) |
| | | | | | C(71) | 0.3812(3) | −0.0238(6) | 0.4420(7) | 3.4(3) |
| Cl(91) | −0.2849(5) | 0.4033(2) | −0.0805(4) | 17.89(11) | C(72) | 0.3536(4) | −0.0378(7) | 0.3513(8) | 4.3(3) |
| Cl(92) | −0.0922(5) | 0.45647(14) | 0.0310(4) | 12.59(10) | C(73) | 0.3736(4) | −0.0319(7) | 0.2705(9) | 4.9(4) |
| C(9) | −0:2051(10) | 0.4223(3) | 0.0466(7) | 12.52(12) | C(74) | 0.4204(4) | −0.0088(7) | 0.2772(9) | 5.0(4) |

Table 2. (Continued)

| Atom | x | y | z | $B_{eq}$/Å$^2$ |
|---|---|---|---|---|
| C(75) | 0.4478(4) | 0.0086(8) | 0.3649(9) | 5.2(4) |
| C(76) | 0.4288(4) | 0.0001(7) | 0.4473(8) | 4.4(3) |
| C(81) | 0.3180(3) | −0.1176(6) | 0.5397(7) | 3.7(3) |
| C(82) | 0.2866(4) | −0.1288(6) | 0.6035(8) | 4.4(3) |
| C(83) | 0.2613(4) | −0.1985(7) | 0.6030(9) | 5.2(4) |
| C(84) | 0.2659(4) | −0.2575(7) | 0.5398(10) | 5.5(4) |
| C(85) | 0.2965(5) | −0.2481(7) | 0.4747(10) | 5.6(4) |
| C(86) | 0.3229(4) | −0.1776(7) | 0.4722(9) | 4.9(4) |
| Cl(1A) | 0.6301(2) | −0.1214(3) | 0.9580(4) | 11.3(2) |
| Cl(1B) | 0.7088(2) | −0.0139(4) | 0.9912(4) | 10.8(3) |
| Cl(1C) | 0.6150(2) | 0.0419(3) | 0.9976(4) | 11.6(2) |
| C(1A) | 0.6557(6) | −0.0387(10) | 1.0238(11) | 8.0(6) |
| Cl(2A)[a] | 0.4500(5) | 0.5563(12) | 0.7035(14) | 10.8(7) |
| Cl(2B)[a] | 0.3764(7) | 0.5185(13) | 0.5605(14) | 12.5(8) |
| Cl(2C)[a] | 0.4382(10) | 0.4040(19) | 0.6481(24) | 19.7(15) |
| C(2A)[a] | 0.4183(25) | 0.4909(32) | 0.6539(66) | 13.6(35) |

a) Occupancy factor: 0.3.

(3) **4c-2**

| | | | | |
|---|---|---|---|---|
| Rh(1) | 0.12672(2) | 0.12602(2) | 0.27434(2) | 2.00(1) |
| Cl(1) | −0.00343(6) | 0.11980(8) | 0.26116(7) | 3.08(3) |
| Cl(11) | 0.29553(13) | 0.12871(13) | 0.78644(10) | 6.49(7) |
| Cl(21) | 0.03651(10) | 0.32969(15) | −0.19538(10) | 6.15(6) |
| S(1) | 0.17078(6) | 0.11872(8) | 0.40621(6) | 2.68(3) |
| S(2) | 0.11055(6) | 0.13999(8) | 0.14391(6) | 2.62(3) |
| P(1) | 0.11760(6) | −0.02613(8) | 0.27274(6) | 2.36(3) |
| P(2) | 0.12153(6) | 0.27585(8) | 0.28891(6) | 2.22(3) |
| N(1) | 0.2835(2) | 0.1167(3) | 0.3408(2) | 3.04(12) |
| N(2) | 0.2525(2) | 0.1477(3) | 0.2139(2) | 2.83(11) |
| N(3) | 0.3174(2) | 0.1111(3) | 0.4700(2) | 3.42(12) |
| N(4) | 0.2240(2) | 0.1997(3) | 0.0935(2) | 3.29(12) |
| C(1) | 0.2631(2) | 0.1133(3) | 0.4107(3) | 2.64(12) |
| C(2) | 0.1989(2) | 0.1672(3) | 0.1455(3) | 2.65(12) |
| C(3) | 0.2288(3) | 0.1299(3) | 0.2770(3) | 2.47(12) |
| C(4) | 0.3619(3) | 0.1166(4) | 0.3456(3) | 4.24(18) |
| C(5) | 0.3790(3) | 0.1014(5) | 0.2696(4) | 4.7(2) |
| C(6) | 0.3291(3) | 0.1575(4) | 0.2122(3) | 4.06(17) |
| C(11) | 0.3083(3) | 0.1133(3) | 0.5443(3) | 3.05(14) |
| C(12) | 0.2592(3) | 0.0642(4) | 0.5696(3) | 4.23(16) |
| C(13) | 0.2560(4) | 0.0680(4) | 0.6438(4) | 4.75(19) |
| C(14) | 0.3017(3) | 0.1211(4) | 0.6935(3) | 4.04(17) |
| C(15) | 0.3520(4) | 0.1681(5) | 0.6701(4) | 5.2(2) |
| C(16) | 0.3563(3) | 0.1632(4) | 0.5962(3) | 4.38(18) |
| C(21) | 0.1749(3) | 0.2296(3) | 0.0253(3) | 3.19(14) |
| C(22) | 0.1223(3) | 0.2899(4) | 0.0243(3) | 3.52(15) |
| C(23) | 0.0805(3) | 0.3212(4) | −0.0435(3) | 4.16(17) |
| C(24) | 0.0923(3) | 0.2926(4) | −0.1104(3) | 4.20(17) |
| C(25) | 0.1440(4) | 0.2331(5) | −0.1112(3) | 5.0(2) |
| C(26) | 0.1877(3) | 0.2023(4) | −0.0433(3) | 4.14(17) |
| C(31) | 0.0536(3) | −0.0665(3) | 0.3243(3) | 2.84(13) |
| C(32) | −0.0095(4) | −0.1077(5) | 0.2862(3) | 5.0(2) |
| C(33) | −0.0613(5) | −0.1331(6) | 0.3239(4) | 6.9(3) |
| C(34) | −0.0503(3) | −0.1212(4) | 0.3993(4) | 4.6(2) |
| C(35) | 0.0138(3) | −0.0820(4) | 0.4379(3) | 3.77(16) |
| C(36) | 0.0632(3) | −0.0537(4) | 0.4011(3) | 3.50(15) |
| C(41) | 0.0845(3) | −0.0766(3) | 0.1802(3) | 2.69(12) |
| C(42) | 0.0265(3) | −0.0418(3) | 0.1281(3) | 3.27(14) |
| C(43) | −0.0017(3) | −0.0820(4) | 0.0588(3) | 4.09(16) |
| C(44) | 0.0287(3) | −0.1560(4) | 0.0422(3) | 4.33(17) |
| C(45) | 0.0859(4) | −0.1918(4) | 0.0945(4) | 4.83(19) |
| C(46) | 0.1139(3) | −0.1526(4) | 0.1632(3) | 3.64(15) |
| C(51) | 0.2033(3) | −0.0810(3) | 0.3123(3) | 2.97(13) |
| C(52) | 0.2191(4) | −0.1302(4) | 0.3768(3) | 4.50(19) |
| C(53) | 0.2846(4) | −0.1731(5) | 0.3996(4) | 6.1(2) |
| C(54) | 0.3349(3) | −0.1687(5) | 0.3599(4) | 5.6(2) |
| C(55) | 0.3222(4) | −0.1186(4) | 0.2954(4) | 5.3(2) |
| C(56) | 0.2558(3) | −0.0750(4) | 0.2717(3) | 4.20(17) |
| C(61) | 0.2126(2) | 0.3216(3) | 0.3132(3) | 2.49(12) |
| C(62) | 0.2471(3) | 0.3479(4) | 0.2589(3) | 3.19(14) |
| C(63) | 0.3175(3) | 0.3758(4) | 0.2786(4) | 4.09(18) |
| C(64) | 0.3568(3) | 0.3765(4) | 0.3540(4) | 3.87(17) |
| C(65) | 0.3238(3) | 0.3496(4) | 0.4089(3) | 3.47(15) |
| C(66) | 0.2523(2) | 0.3223(3) | 0.3885(3) | 3.00(13) |
| C(71) | 0.0843(2) | 0.3149(3) | 0.3663(3) | 2.70(12) |
| C(72) | 0.0444(2) | 0.2631(3) | 0.4019(3) | 2.88(13) |
| C(73) | 0.0168(3) | 0.2955(4) | 0.4594(3) | 3.67(15) |
| C(74) | 0.0271(3) | 0.3801(4) | 0.4806(4) | 4.16(18) |
| C(75) | 0.0676(3) | 0.4309(4) | 0.4461(4) | 4.13(18) |
| C(76) | 0.0948(3) | 0.3991(3) | 0.3882(3) | 3.57(16) |
| C(81) | 0.0690(3) | 0.3384(3) | 0.2088(3) | 2.71(12) |
| C(82) | 0.0058(3) | 0.3038(3) | 0.1624(3) | 3.19(14) |
| C(83) | −0.0380(3) | 0.3528(4) | 0.1045(3) | 3.95(17) |
| C(84) | −0.0171(3) | 0.4352(4) | 0.0935(4) | 5.0(2) |
| C(85) | 0.0443(3) | 0.4697(4) | 0.1385(4) | 4.8(2) |
| C(86) | 0.0871(3) | 0.4226(4) | 0.1967(4) | 4.12(17) |
| Cl(1A) | 0.2808(2) | −0.0157(2) | −0.0693(2) | 10.37(12) |
| Cl(1B) | 0.1472(2) | −0.1057(3) | −0.0831(2) | 12.91(17) |
| Cl(1C) | 0.2088(2) | −0.0195(2) | 0.0520(2) | 11.19(14) |
| C(1A) | 0.2298(4) | −0.0744(6) | −0.0194(5) | 6.7(3) |

(4) **7**

| | | | | |
|---|---|---|---|---|
| Cu(1) | 0.77549(2) | 0.22316(4) | 0.04806(3) | 2.72(1) |
| S(1A) | 0.47630(4) | −0.04425(7) | −0.13237(5) | 2.02(2) |
| S(2A) | 0.22451(4) | −0.03228(8) | −0.13884(6) | 2.58(2) |
| S(3A) | 0.64481(5) | 0.30321(8) | −0.03597(6) | 2.67(2) |
| N(1A) | 0.36649(14) | 0.1045(2) | −0.10184(16) | 1.99(7) |
| N(2A) | 0.49435(14) | 0.2052(2) | −0.07124(16) | 1.99(7) |
| N(3A) | 0.36858(15) | −0.1046(3) | −0.15151(17) | 2.22(7) |
| N(4A) | 0.57654(14) | 0.0588(3) | −0.10006(17) | 2.18(7) |
| C(1A) | 0.44301(17) | 0.1012(3) | −0.09916(18) | 1.88(7) |
| C(2A) | 0.32260(17) | −0.0176(3) | −0.13193(19) | 2.07(8) |
| C(3A) | 0.57354(16) | 0.1804(3) | −0.07022(19) | 1.99(8) |
| C(4A) | 0.33429(19) | 0.2277(3) | −0.0747(2) | 2.62(9) |
| C(5A) | 0.46876(19) | 0.3362(3) | −0.0449(2) | 2.60(9) |
| C(6A) | 0.37767(20) | 0.3507(3) | −0.0912(2) | 2.89(10) |
| C(7A) | 0.34158(21) | −0.2374(4) | −0.1917(2) | 3.05(10) |
| C(8A) | 0.64692(19) | 0.0050(4) | −0.1159(2) | 2.75(9) |
| S(1B) | 0.93397(4) | 0.51510(8) | −0.13788(5) | 2.25(2) |
| S(2B) | 1.18205(5) | 0.57336(9) | −0.13463(7) | 3.07(3) |
| S(3B) | 0.85864(5) | 0.15285(8) | −0.02821(6) | 2.85(3) |
| N(1B) | 1.07981(15) | 0.4102(3) | −0.08956(18) | 2.31(7) |
| N(2B) | 0.98149(14) | 0.2832(2) | −0.05663(17) | 2.15(7) |
| N(3B) | 1.02317(15) | 0.6022(3) | −0.15574(18) | 2.44(7) |
| N(4B) | 0.86481(15) | 0.3946(3) | −0.10701(19) | 2.63(8) |
| C(1B) | 1.00490(17) | 0.3916(3) | −0.0905(2) | 2.04(8) |
| C(2B) | 1.09102(18) | 0.5335(3) | −0.1285(2) | 2.32(8) |
| C(3B) | 0.89863(18) | 0.2840(3) | −0.0665(2) | 2.18(8) |
| C(4B) | 1.14120(20) | 0.3017(4) | −0.0572(3) | 3.30(11) |
| C(5B) | 1.03815(21) | 0.1683(3) | −0.0194(3) | 3.10(10) |
| C(6B) | 1.12500(22) | 0.2185(4) | 0.0128(3) | 3.70(12) |
| C(7B) | 1.01285(22) | 0.7344(4) | −0.1989(2) | 3.17(10) |
| C(8B) | 0.77807(21) | 0.4254(4) | −0.1369(3) | 4.19(13) |
| Cl(1) | 0.56210(7) | 0.61774(10) | −0.21074(7) | 4.31(3) |
| O(1) | 0.5224(3) | 0.7360(4) | −0.2561(2) | 6.68(14) |
| O(2) | 0.5874(3) | 0.5313(4) | −0.2634(3) | 7.93(16) |
| O(3) | 0.6237(3) | 0.6467(4) | −0.1288(3) | 10.06(20) |
| O(4) | 0.5012(3) | 0.5410(6) | −0.1889(4) | 11.36(26) |

Table 3. Selected Bond Lengths ($l$) and Bond Angles ($\theta$) of **4a** and **4c**

| | **4a** | | **4c-1** | **4c-2** |
|---|---|---|---|---|
| Lengths | $l$/Å | | $l$/Å | $l$/Å |
| Rh(1)–S(1) | 2.344(2) | Rh(1)–S(1) | 2.335(3) | 2.348(1) |
| Rh(1)–N(4) | 2.071(5) | Rh(1)–S(2) | 2.350(3) | 2.342(1) |
| Rh(1)–C(3) | 1.937(6) | Rh(1)–C(3) | 1.930(10) | 1.933(5) |
| Rh(1)–C1(1) | 2.447(1) | Rh(1)–Cl(1) | 2.442(3) | 2.429(1) |
| Rh(1)–P(1) | 2.389(2) | Rh(1)–P(1) | 2.380(3) | 2.404(1) |
| Rh(1)–P(2) | 2.364(2) | Rh(1)–P(2) | 2.398(3) | 2.382(1) |
| S(1)–C(1) | 1.750(6) | S(1)–C(1) | 1.705(10) | 1.741(5) |
| S(2)–C(2) | 1.689(6) | S(2)–C(2) | 1.700(11) | 1.730(5) |
| N(1)–C(1) | 1.430(8) | N(1)–C(1) | 1.434(13) | 1.436(7) |
| N(1)–C(3) | 1.332(7) | N(1)–C(3) | 1.375(11) | 1.363(6) |
| N(1)–C(4) | 1.464(8) | N(1)–C(4) | 1.464(14) | 1.473(7) |
| N(2)–C(2) | 1.424(8) | N(2)–C(2) | 1.447(12) | 1.428(5) |
| N(2)–C(3) | 1.356(7) | N(2)–C(3) | 1.357(13) | 1.379(7) |
| N(2)–C(6) | 1.469(8) | N(2)–C(6) | 1.480(15) | 1.476(7) |
| N(3)–C(1) | 1.261(8) | N(3)–C(1) | 1.300(12) | 1.290(6) |
| N(3)–C(7) | 1.458(8) | N(3)–C(11) | 1.421(15) | 1.420(7) |
| N(4)–C(2) | 1.321(9) | N(4)–C(2) | 1.289(15) | 1.281(7) |
| N(4)–C(8) | 1.461(8) | N(4)–C(21) | 1.433(15) | 1.432(6) |
| C(4)–C(5) | 1.484(11) | C(4)–C(5) | 1.498(18) | 1.531(10) |
| C(5)–C(6) | 1.489(10) | C(5)–C(6) | 1.489(16) | 1.508(9) |
| Angles | $\theta$/° | | $\theta$/° | $\theta$/° |
| S(1)–Rh(1)–Cl(1) | 101.2(1) | S(1)–Rh(1)–Cl(1) | 92.8(1) | 100.42(5) |
| S(1)–Rh(1)–P(1) | 87.9(1) | S(1)–Rh(1)–P(1) | 89.0(1) | 88.22(4) |
| S(1)–Rh(1)–P(2) | 90.3(1) | S(1)–Rh(1)–P(2) | 93.0(1) | 86.96(4) |
| S(1)–Rh(1)–N(4) | 161.9(2) | S(1)–Rh(1)–S(2) | 168.2(1) | 166.90(5) |
| S(1)–Rh(1)–C(3) | 83.1(2) | S(1)–Rh(1)–C(3) | 84.9(3) | 83.6(1) |
| Cl(1)–Rh(1)–P(1) | 90.0(1) | Cl(1)–Rh(1)–P(1) | 90.1(1) | 83.68(4) |
| Cl(1)–Rh(1)–P(2) | 84.8(1) | Cl(1)–Rh(1)–P(2) | 87.8(1) | 88.85(4) |
| Cl(1)–Rh(1)–N(4) | 96.8(2) | Cl(1)–Rh(1)–S(2) | 99.0(1) | 92.53(5) |
| Cl(1)–Rh(1)–C(3) | 174.7(2) | Cl(1)–Rh(1)–C(3) | 177.0(3) | 175.9(1) |
| P(1)–Rh(1)–P(2) | 174.1(1) | P(1)–Rh(1)–P(2) | 177.1(1) | 170.24(4) |
| P(1)–Rh(1)–N(4) | 90.7(2) | S(2)–Rh(1)–P(1) | 90.2(1) | 95.25(4) |
| P(1)–Rh(1)–C(3) | 93.4(2) | P(1)–Rh(1)–C(3) | 91.8(3) | 95.8(1) |
| P(2)–Rh(1)–N(4) | 92.8(2) | S(2)–Rh(1)–P(2) | 88.2(1) | 91.34(4) |
| P(2)–Rh(1)–C(3) | 92.0(2) | P(2)–Rh(1)–C(3) | 90.4(3) | 92.1(1) |
| N(4)–Rh(1)–C(3) | 79.0(2) | S(2)–Rh(1)–C(3) | 83.4(3) | 83.4(1) |
| Rh(1)–S(1)–C(1) | 98.5(2) | Rh(1)–S(1)–C(1) | 97.1(4) | 97.8(2) |
| Rh(1)–N(4)–C(2) | 114.4(5) | Rh(1)–S(2)–C(2) | 98.6(4) | 98.0(2) |
| Rh(1)–N(4)–C(8) | 127.1(4) | | | |
| C(1)–N(1)–C(3) | 118.8(5) | C(1)–N(1)–C(3) | 117.9(8) | 116.7(4) |
| C(1)–N(1)–C(4) | 118.0(5) | C(1)–N(1)–C(4) | 117.1(9) | 116.9(4) |
| C(3)–N(1)–C(4) | 123.2(6) | C(3)–N(1)–C(4) | 124.9(9) | 125.9(5) |
| C(2)–N(2)–C(3) | 115.9(5) | C(2)–N(2)–C(3) | 117.1(8) | 117.8(4) |
| C(2)–N(2)–C(6) | 120.5(6) | C(2)–N(2)–C(6) | 117.0(9) | 116.3(4) |
| C(3)–N(2)–C(6) | 123.5(6) | C(3)–N(2)–C(6) | 125.8(9) | 125.6(5) |
| C(1)–N(3)–C(7) | 117.7(6) | C(1)–N(3)–C(11) | 120.5(9) | 122.5(5) |
| | | C(2)–N(4)–C(21) | 118.9(11) | 119.9(5) |
| S(1)–C(1)–N(1) | 115.4(5) | S(1)–C(1)–N(1) | 117.5(7) | 117.5(4) |
| S(1)–C(1)–N(3) | 127.4(5) | S(1)–C(1)–N(3) | 128.8(8) | 128.2(4) |
| N(1)–C(1)–N(3) | 117.2(6) | N(1)–C(1)–N(3) | 113.7(9) | 114.2(4) |
| S(2)–C(2)–N(2) | 119.4(5) | S(2)–C(2)–N(2) | 117.4(8) | 115.5(4) |
| S(2)–C(2)–N(4) | 126.6(5) | S(2)–C(2)–N(4) | 131.0(9) | 129.6(4) |
| N(2)–C(2)–N(4) | 113.9(6) | N(2)–C(2)–N(4) | 111.6(10) | 114.9(4) |
| Rh(1)–C(3)–N(1) | 124.1(5) | Rh(1)–C(3)–N(1) | 120.7(7) | 123.7(4) |
| Rh(1)–C(3)–N(2) | 116.4(4) | Rh(1)–C(3)–N(2) | 123.6(7) | 122.2(4) |
| N(1)–C(3)–N(2) | 119.5(6) | N(1)–C(3)–N(2) | 115.6(9) | 114.1(4) |
| N(1)–C(4)–C(5) | 109.7(7) | N(1)–C(4)–C(5) | 109.9(10) | 113.6(5) |
| C(4)–C(5)–C(6) | 113.2(8) | C(4)–C(5)–C(6) | 112.0(11) | 107.4(6) |
| N(2)–C(6)–C(5) | 109.9(7) | N(2)–C(6)–C(5) | 108.7(10) | 111.7(6) |

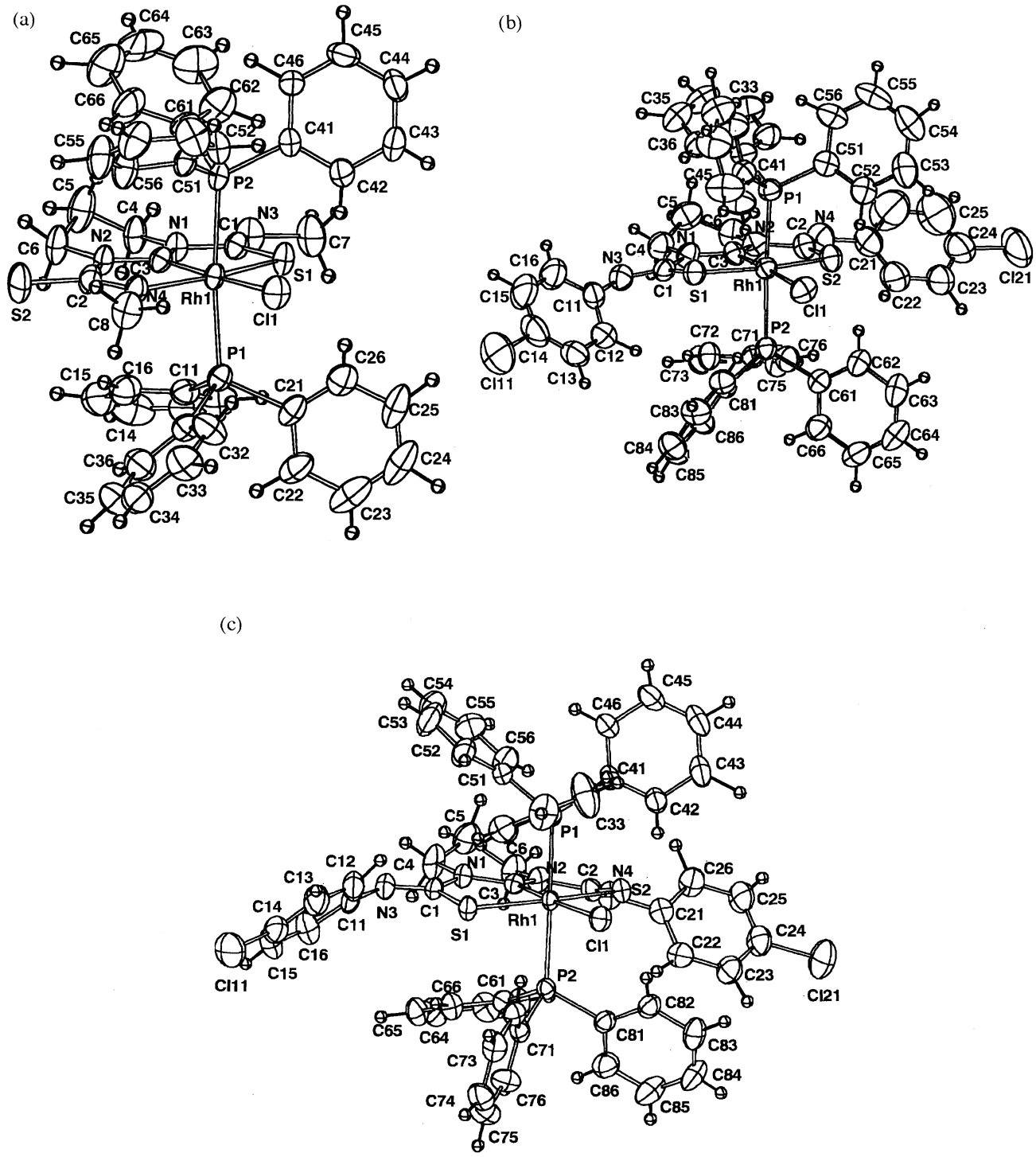


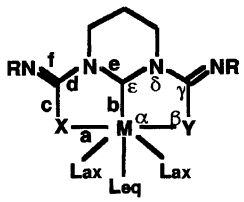

Fig. 1. ORTEP drawings of Rh-carbene complexes with the atom-numbering. The thermal ellipsoids for non-H atoms are drawn at 50% probability and the H atoms are drawn as spheres with a radius of 0.1 Å. (a) **4a**, (b) **4c-1**, and (c) **4c-2**.

some bond distances and angles of metallapentalenes, as well as those of tetraazathiapentalenes are summarized. The distances of the Rh–C bonds are 1.937(6), 1.930(10), and 1.933(5) Å for **4a**, **4c-1**, and **4c-2**, respectively, which are similar to those of Rh–carbene complexes reported so far, and shorter than those of the Pt–C and Pd–C bonds in **2** and **3**. The distances of the Rh–S bonds are 2.344(2) Å for **4a**, 2.335(3) and 2.350(3) Å for **4c-1**, and 2.348(1) and 2.342(1) Å for **4c-2**, which are longer than those of the Pt–S and Pd–S bonds of **2** and **3**, although these values are the same as those of the Rh–carbene complexes referred to above. The S–C lengths of **4c** (mean value: 1.703 Å for **4c-1** and 1.736 Å for **4c-2**) are shorter than that of **4a** (1.750 Å). However, such a difference has not been observed between **3a** and **3c** of the Pd complexes. The S–Rh–N angle of **4a** is 161.9(2)°, which is smaller than those of S–M–S (168° for all

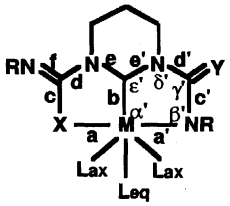
Table 4. Summary of Bond Lengths and Angles of Metallapentalenes and Tetraazathiapentalenes

| | **2a** | **2b** | **3a** | **3c** | **6** | **4c-1** | **4c-2** | **4a** | **10** | **11** | **9c′** [b] | **9b**[b] | **1b**[b] | **7**[b] | **12**[c] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ref. | 1) | 1) | 1) | 1) | 15) | | | | 16) | 16) | 3) | 3) | 2) | | 16) |
| M | Pt | Pt | Pd | Pd | Pd | Rh | Rh | Rh | Pt | Rh | S | S | S | S | Rh |
| R | Me | Et | Me | *p*-Cl-Ph | Me | *p*-Cl-Ph | *p*-Cl-Ph | Me | Me | Et | Ph | Et | Et | Me | Ph |
| Leq | $PPh_3$ | $PPh_3$ | $PPh_3$ | $PPh_3$ | Py | Cl | Cl | Cl | $PPh_3$ | Cl | | | | | Cl |
| Lax | | | | | | $(PPh_3)_2$ | $(PPh_3)_2$ | $(PPh_3)_2$ | | $(PPh_3)_2$ | | | | | $(PPh_3)_2$ |
| X,Y[a] | S,S | S,S | S,S | S,S | S,S | S,S | S,S | S,S | S,O | S,O | O,O | O,O | S,S | S,S | O,O |
| *a*(M–S)/Å | 2.282 | 2.287 | 2.288 | 2.287 | 2.285 | 2.343 | 2.345 | 2.344 | 2.281 | 2.335 | | | | | 2.376 |
| *b*(M–C)/Å | 2.001 | 1.992 | 2.005 | 1.990 | 1.944 | 1.930 | 1.933 | 1.937 | 1.961 | 1.940 | 1.717 | 1.717 | 1.705 | 1.709 | 1.745 |
| *c*(S–C)/Å | 1.760 | 1.757 | 1.757 | 1.743 | 1.743 | 1.703 | 1.736 | 1.750 | 1.761 | 1.744 | | | | | |
| *d*(N–C)/Å | 1.416 | 1.426 | 1.425 | 1.434 | 1.429 | 1.441 | 1.432 | 1.430 | 1.446 | 1.419 | | | | | |
| *e*(N–C)/Å | 1.345 | 1.340 | 1.339 | 1.345 | 1.350 | 1.366 | 1.371 | 1.332 | 1.327 | 1.346 | | | | | 1.281 |
| *f*(N–C)/Å | 1.279 | 1.269 | 1.261 | 1.273 | 1.266 | 1.295 | 1.286 | 1.261 | 1.238 | 1.281 | | | | | |
| *a*′(M–N)/Å | | | | | | | | 2.071 | 2.064 | 2.100 | 1.959 | 1.927 | 1.909 | 1.914 | 2.018 |
| *c*′(N–C)/Å | | | | | | | | 1.321 | 1.312 | 1.361 | 1.328 | 1.324 | 1.300 | 1.297 | 1.345 |
| *d*′(N–C)/Å | | | | | | | | 1.424 | 1.419 | 1.443 | 1.437 | 1.438 | 1.423 | 1.414 | 1.387 |
| *e*′(N–C)/Å | | | | | | | | 1.356 | 1.346 | 1.321 | 1.324 | 1.333 | 1.333 | 1.334 | 1.394 |
| C–Y/Å | | | | | | | | 1.689 | 1.244 | 1.221 | 1.219 | 1.220 | 1.679 | 1.695 | |
| M–Leq/Å | 2.304 | 2.315 | 2.331 | 2.333 | 2.106 | 2.442 | 2.429 | 2.447 | 2.318 | 2.446 | | | | | 2.377 |
| M–Lax/Å | | | | | | 2.389 | 2.393 | 2.377 | | 2.373 | | | | | 2.387 |
| S–M–S/° | 169.5 | 168.9 | 169.3 | 169.1 | 170.6 | 168.2 | 166.9 | | | | | | | | |
| S–M–N/° | | | | | | | | 161.9 | 162.7 | 161.7 | | | | | |
| $\alpha$(S–M–C)/° | 84.7 | 84.5 | 84.6 | 84.6 | 85.4 | 84.2 | 83.5 | 83.1 | 83.8 | 83.7 | | | | | |
| $\beta$(M–S–C)/° | 99.0 | 99.2 | 99.0 | 99.3 | 98.5 | 97.9 | 97.9 | 98.5 | 99.5 | 98.4 | | | | | |
| $\gamma$(S–C–N)/° | 116.5 | 115.7 | 116.2 | 116.2 | 115.8 | 117.5 | 116.0 | 115.4 | 115.3 | 115.6 | | | | | |
| $\delta$(C–N–C)/° | 119.6 | 119.8 | 119.9 | 119.1 | 119.3 | 117.5 | 117.3 | 118.8 | 117.5 | 119.5 | | | | | |
| $\varepsilon$(M–C–N)/° | 120.2 | 120.6 | 120.1 | 120.6 | 120.7 | 122.2 | 123.0 | 124.1 | 123.8 | 122.4 | | | | | |
| $\alpha$′(N–M–C)/° | | | | | | | | 79.0 | 79.0 | 79.1 | 82.6 | 82.4 | 82.8 | 82.7 | |
| $\beta$′(M–N–C)/° | | | | | | | | 114.4 | 114.5 | 112.9 | 114.6 | 116.0 | 115.9 | 115.4 | |
| $\gamma$′(N–C–N)/° | | | | | | | | 113.9 | 114.3 | 112.9 | 107.9 | 107.5 | 108.6 | 109.3 | |
| $\delta$′(C–N–C)/° | | | | | | | | 115.9 | 116.5 | 117.8 | 116.3 | 115.4 | 114.7 | 114.5 | |
| $\varepsilon$′(M–C–N)/° | | | | | | | | 116.4 | 115.5 | 117.0 | 118.4 | 118.4 | 118.2 | 118.1 | |
| C–M–Leq/° | 177.5 | 176.3 | 178.3 | 176.5 | 178.3 | 177.0 | 175.9 | 174.7 | 177.7 | 172.7 | | | | | |
| S–M–Leq/° | 95.3 | 95.5 | 95.4 | 95.5 | 94.6 | 95.9 | 96.5 | 101.2 | 96.7 | 100.4 | | | | | |
| N–M–Leq/° | | | | | | | | 96.8 | 100.6 | 97.3 | | | | | |

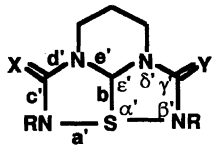
a) X and Y show the thiocarbonyl or carbonyl groups of the starting tetraazathiapentalenes. b) In these compounds (tetraazathiapentalenes), M means S. c) The corresponding lengths and angles are listed for **12**, which has not a pentalene framework.




**2a, 2b, 3a, 3c, 6, 4c**




**4a, 10, 11**




**9c', 9b, 1b, 7**

Pt, Pd, and Rh complexes). The dihedral angles between the pentalene plane and the phenyl groups of **4c-1** are 45.3(4) and 51.0(6)° for C(11)—C(16) and C(21)—C(26), respectively. The corresponding angles are 40.1(2) and 46.6(2)° for **4c-2**.

The crystal structures of **4a**, **4c-1**, and **4c-2** are shown in Figs. 2, 3, and 4, respectively. In **4a** and **4c-1**, crystal solvents are loosely surrounded by $PPh_3$ groups. On the other hand, the crystal solvent of **4c-2** are near to the pentalene plane with the van der Waals contacts. The molecules in the crystal of **4c-2** are tightly packed, rather than those of **4c-1**, as can be seen from the densities.

**Structure of Cu Complex.** The molecular structure of **7** with the atomic numbering is shown in Fig. 5. Selected bond distances and angles are listed in Table 5.

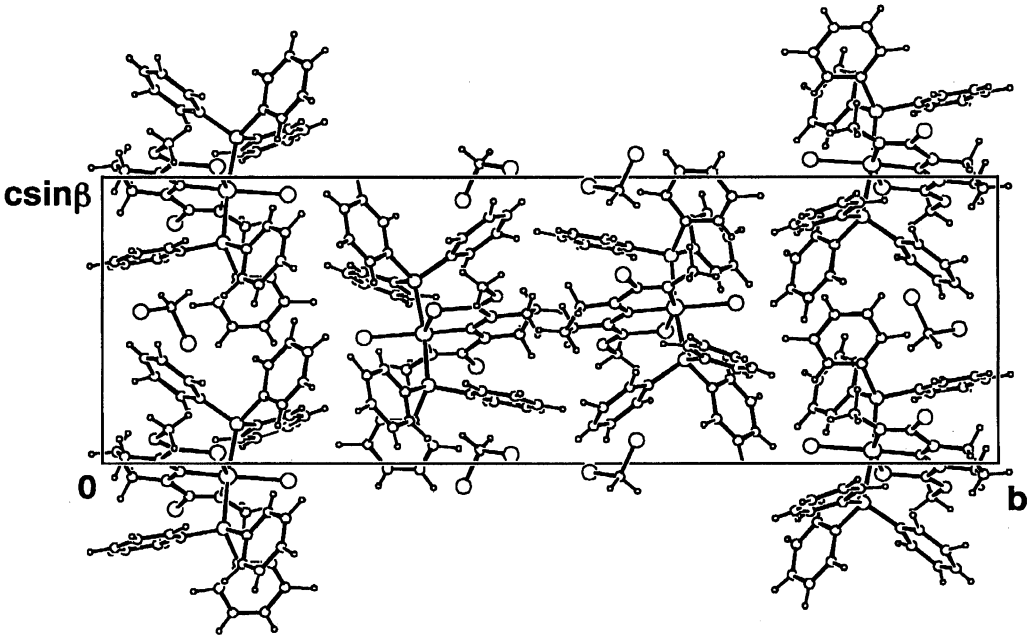



Fig. 2. Projection of the crystal structure of **4a** viewed along the *a* axis.

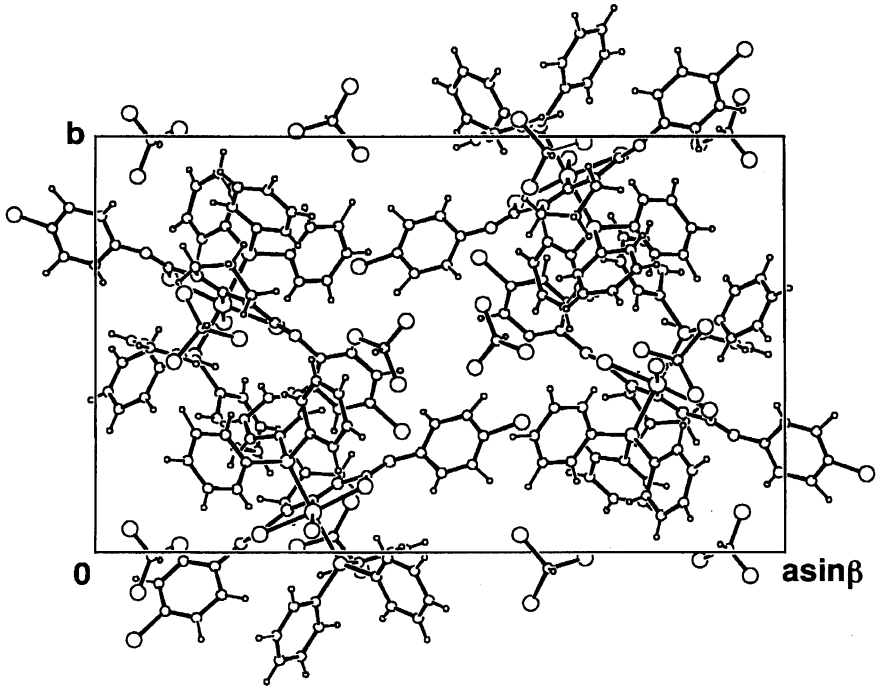



Fig. 3. Projection of the crystal structure of **4c-1** viewed along the *c* axis.

From the reaction of **1** with $Cu(ClO_4)_2$, a metallapentalene complex like **2**—**4** has not been obtained. The framework of the starting tetraazathiapentalene **1** remained unsubstituted, and the sulfur atoms of the thiocarbonyl groups of **1** coordinated the Cu atom. In the crystallographic asymmetric unit, there are two tetraazathiapentalenes (**A** and **B**), one Cu atom and one $ClO_4^-$ anion. One-dimensional coordination polymers are formed like a double chain, where a Cu atom is tetrahedrally coordinated by four S atoms belonging to the four tetraazathiapentalenes. The chains elongate along the [110] and [1$\bar{1}$0] directions alternately. In the coordination-polymer, two parallel tetraazathiapentalenes bridge the Cu atoms, as shown in Fig. 6. The distances between parallel tetraazathiapentalene rings are 3.405(3) and 3.468(4) Å, for $\mathbf{A}\cdots\mathbf{A}^{i}$ (i=1$-x$, $-y$, $-z$) and $\mathbf{B}\cdots\mathbf{B}^{ii}$ (ii=2$-x$, 1$-y$, $-z$), respectively. In the

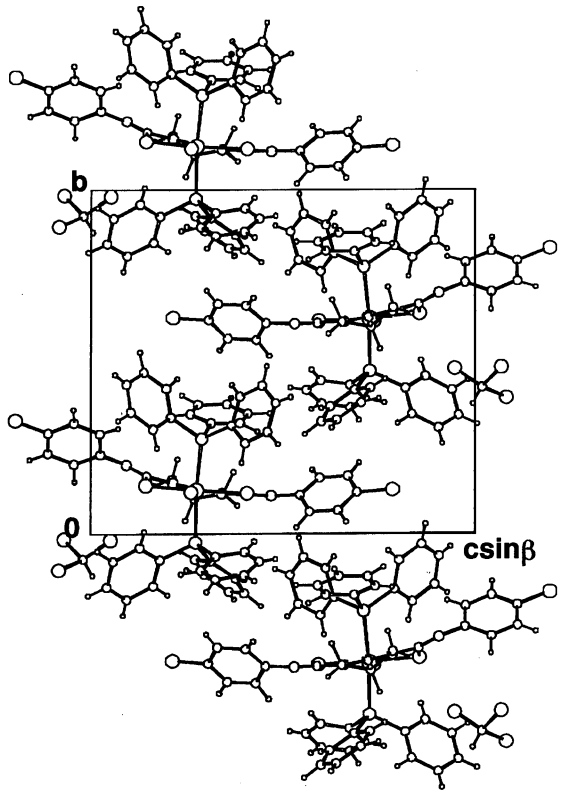



Fig. 4. Projection of the crystal structure of **4c-2** viewed along the *a* axis. A half of the *a* axis were shown for clarity.

molecular pair of $\mathbf{A}\cdots\mathbf{A}^{i}$, C(6) atoms of the trimethylenes of both molecules are folded outside with each other, while in $\mathbf{B}\cdots\mathbf{B}^{ii}$, are folded inside. This is related to the difference in the distances between the molecular planes.

The bond length and angles of tetraazathiapentalenes are similar to those of the starting molecule **1** and related molecules, as shown in Table 4. The lengths of the thiocarbonyl S=C bonds (1.69—1.70 Å) are slightly longer than those of **1** (1.68 Å). Two kinds of Cu–S distances are observed: 2.34 Å for Cu–S(3A) and Cu–S(3B) (2.339(1) and 2.343(1) Å, respectively) and 2.39 Å for Cu–S($2A^{i}$) and Cu–S($2B^{ii}$) (2.380(1) and 2.396(1) Å, respectively). The S–Cu–S angles are 95—118°. The smaller angles (94.8° for S(3A)–Cu–S($2B^{ii}$) and 103.4° for S(3B)–Cu–S($2A^{i}$)) correspond to the non-crowding parts of the pentalene molecules.

The formal charge of $Cu(S_3N_4C_8H_{12})_2$ is +1, because in the crystals the ratio of $Cu(S_3N_4C_8H_{12})_2$ to $ClO_4^-$ is 1 : 1. The tetrahedral coordination structure is a characteristic of $d^{10}$ Cu(I) complexes. The reason why metal–carbene complexes, such as **2**—**4**, could not be obtained in the case of the Cu-complex is considered to be because the change in the oxidation number of Cu during the reaction is different from those of Pd, Pt, and Rh. In the case of Pd and Pt complexes the oxidation number changed from 0 to II with the formation of carbene complexes and from I to III for the Rh complexes, while the oxidation number was reduced from II to I for the Cu complex. The formation mechanism of the metal–carbene complexes (**2**—**4**) will be proposed in the

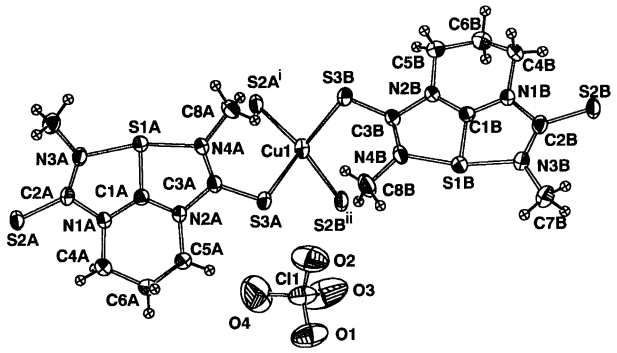



Fig. 5. ORTEP drawing of **7** with the atom-numbering. The thermal ellipsoids for non-H atoms are drawn at 50% probability and the H atoms are drawn as spheres with a radius of 0.1 Å.

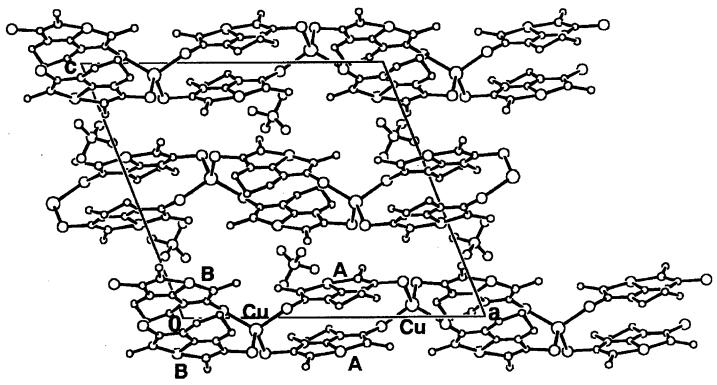



Fig. 6. Projection of the crystal structure of **7** viewed along the *b* axis.

Table 5. Bond Lengths ($l$) and Bond Angles ($\theta$) of **7**

| Lengths | $l$/Å | Lengths | $l$/Å |
|---|---|---|---|
| Cu(1)–S(3A) | 2.339(1) | Cu(1)–S(3B) | 2.343(1) |
| Cu(1)–S(2A$^{i}$) | 2.380(1) | Cu(1)–S(2B$^{ii}$) | 2.396(1) |
| S(1A)–N(3A) | 1.909(3) | S(1B)–N(3B) | 1.909(3) |
| S(1A)–N(4A) | 1.939(3) | S(1B)–N(4B) | 1.898(3) |
| S(1A)–C(1A) | 1.708(3) | S(1B)–C(1B) | 1.710(3) |
| S(2A)–C(2A) | 1.703(3) | S(2B)–C(2B) | 1.696(4) |
| S(3A)–C(3A) | 1.685(3) | S(3B)–C(3B) | 1.694(3) |
| N(1A)–C(1A) | 1.339(4) | N(1B)–C(1B) | 1.332(4) |
| N(1A)–C(2A) | 1.416(4) | N(1B)–C(2B) | 1.413(4) |
| N(1A)–C(4A) | 1.474(4) | N(1B)–C(4B) | 1.474(4) |
| N(2A)–C(1A) | 1.332(4) | N(2B)–C(1B) | 1.333(4) |
| N(2A)–C(3A) | 1.416(4) | N(2B)–C(3B) | 1.415(4) |
| N(2A)–C(5A) | 1.480(4) | N(2B)–C(5B) | 1.483(4) |
| N(3A)–C(2A) | 1.298(4) | N(3B)–C(2B) | 1.304(4) |
| N(3A)–C(7A) | 1.458(4) | N(3B)–C(7B) | 1.454(4) |
| N(4A)–C(3A) | 1.299(4) | N(4B)–C(3B) | 1.297(4) |
| N(4A)–C(8A) | 1.460(4) | N(4B)–C(8B) | 1.459(4) |
| C(4A)–C(6A) | 1.509(5) | C(4B)–C(6B) | 1.504(6) |
| C(5A)–C(6A) | 1.510(4) | C(5B)–C(6B) | 1.511(5) |
| Angles | $\theta$/° | Angles | $\theta$/° |
| S(3A)–Cu(1)–S(3B) | 118.37(4) | S(2A$^{i}$)–Cu(1)–S(2B$^{ii}$) | 112.05(4) |
| S(3A)–Cu(1)–S(2A$^{i}$) | 113.28(4) | S(3B)–Cu(1)–S(2B$^{ii}$) | 115.41(4) |
| S(3A)–Cu(1)–S(2B$^{ii}$) | 94.76(4) | S(3B)–Cu(1)–S(2A$^{i}$) | 103.36(4) |
| Cu(1)–S(3A)–C(3A) | 113.9(1) | Cu(1)–S(3B)–C(3B) | 113.2(1) |
| Cu(1)–S(2A$^{i}$)–C(2A$^{i}$) | 105.0(1) | Cu(1)–S(2B$^{ii}$)–C(2B$^{ii}$) | 105.0(1) |
| N(3A)–S(1A)–N(4A) | 164.8(1) | N(3B)–S(1B)–N(4B) | 165.8(1) |
| N(3A)–S(1A)–C(1A) | 82.6(1) | N(3B)–S(1B)–C(1B) | 82.9(1) |
| N(4A)–S(1A)–C(1A) | 82.2(1) | N(4B)–S(1B)–C(1B) | 82.9(1) |
| C(1A)–N(1A)–C(2A) | 114.2(3) | C(1B)–N(1B)–C(2B) | 114.6(3) |
| C(1A)–N(1A)–C(4A) | 120.5(3) | C(1B)–N(1B)–C(4B) | 120.2(3) |
| C(2A)–N(1A)–C(4A) | 125.3(3) | C(2B)–N(1B)–C(4B) | 125.0(3) |
| C(1A)–N(2A)–C(3A) | 114.7(3) | C(1B)–N(2B)–C(3B) | 114.6(3) |
| C(1A)–N(2A)–C(5A) | 121.6(3) | C(1B)–N(2B)–C(5B) | 120.7(3) |
| C(3A)–N(2A)–C(5A) | 123.6(3) | C(3B)–N(2B)–C(5B) | 124.5(3) |
| S(1A)–N(3A)–C(2A) | 115.7(2) | S(1B)–N(3B)–C(2B) | 115.2(2) |
| S(1A)–N(3A)–C(7A) | 119.6(2) | S(1B)–N(3B)–C(7B) | 120.6(2) |
| C(2A)–N(3A)–C(7A) | 124.6(3) | C(2B)–N(3B)–C(7B) | 124.2(3) |
| S(1A)–N(4A)–C(3A) | 115.0(2) | S(1B)–N(4B)–C(3B) | 115.8(2) |
| S(1A)–N(4A)–C(8A) | 121.2(2) | S(1B)–N(4B)–C(8B) | 119.0(3) |
| C(3A)–N(4A)–C(8A) | 123.6(3) | C(3B)–N(4B)–C(8B) | 124.9(3) |
| S(1A)–C(1A)–N(1A) | 118.2(2) | S(1B)–C(1B)–N(1B) | 118.0(2) |
| S(1A)–C(1A)–N(2A) | 118.6(2) | S(1B)–C(1B)–N(2B) | 117.6(2) |
| N(1A)–C(1A)–N(2A) | 123.1(3) | N(1B)–C(1B)–N(2B) | 124.4(3) |
| S(2A)–C(2A)–N(1A) | 120.7(2) | S(2B)–C(2B)–N(1B) | 121.2(2) |
| S(2A)–C(2A)–N(3A) | 130.1(3) | S(2B)–C(2B)–N(3B) | 129.5(3) |
| N(1A)–C(2A)–N(3A) | 109.3(3) | N(1B)–C(2B)–N(3B) | 109.4(3) |
| S(3A)–C(3A)–N(2A) | 119.8(2) | S(3B)–C(3B)–N(2B) | 120.7(2) |
| S(3A)–C(3A)–N(4A) | 130.9(2) | S(3B)–C(3B)–N(4B) | 130.3(3) |
| N(2A)–C(3A)–N(4A) | 109.3(3) | N(2B)–C(3B)–N(4B) | 109.0(3) |
| N(1A)–C(4A)–C(6A) | 109.3(3) | N(1B)–C(4B)–C(6B) | 109.8(3) |
| N(2A)–C(5A)–C(6A) | 108.9(3) | N(2B)–C(5B)–C(6B) | 109.7(3) |
| C(4A)–C(6A)–C(5A) | 110.9(3) | C(4B)–C(6B)–C(5B) | 112.0(4) |

Symmetry code: i=1/2−$x$, 1/2+$y$, 1/2−$z$; ii=$x$−1/2, 3/2−$y$, $z$+1/2.

following paper (IV).[16]

This work was supported in part by a Grant-in-Aid for Scientific Research for Developmental Scientific Research No. 04504002 from the Ministry of Education, Science and Culture.

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