Dinuclear Complexes of Tetrathia[10]metallocenophanes with Silver(I) Ion: Slightly Distorted Square-Pyramidal Coordination of Ag(I) Ion

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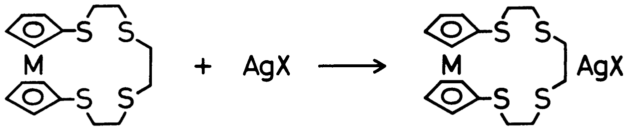
Tetrathia[10](1,1′)ferrocenophane reacts with silver(I) perchlorate and/or trifluoromethamesulfonate to form dimeric 1:1 complexes (**2c** and **2d**) in 73 and 60% yields, respectively. The corresponding complexes (**2a** and **2b**) of tetrathia[10](1,1′)ruthenocenophane were also obtained in 45 and 33% yields, respectively. The crystal structure of complex **2c** was determined by the X-ray method. The crystal data: monoclinic, space group $P2_1/a$, a=19.227(3), b=10.619(3), c=9.739(2) Å, β=91.71(2)°, U=1987.8 Å^3, D_c=2.02 g cm^{-3}, Z=4, μ(Mo $K\alpha$)=23 cm^{-1}, R=0.075. In complex **2c** the inner coordination sphere of the silver is completed by a sulfur atom of another ligand bonded axially to produce a five-coordinate silver ion with an overall slightly distorted square-pyramidal geometry. The temperature dependence of the ^{1}H NMR spectra of **2** was also examined. The rate between the silver free ligand **1a** and complex **2b** at room temperature was very first by the ^{1}H NMR scale.

Transition metal complexes with thioether ligands are of much current interest from the viewpoint of coordination chemistry and biological aspects. Such complexes have been extensively reviewed recently.[1] Of particular interest in coordination chemistry are the metal complexes of macrocyclic polythiaethers. For example, the polythiacrown ether ligands, such as 1,4,7-trithiacyclononane and 1,4,7,10,13,16-hexathiacyclooctadecane, often impose novel electronic properties on transition metal ions.[2,3] It is well-known that the complexes of silver(I) exhibit a preference for linear two coordination and occasionally, tetrahedral four coordination. Higher numbers of coordination can be forced by polydentate macrocyclic ligands, though such complexes generally show irregular geometries and ambiguous coordination numbers due to a poor fit between the metal ion and ligand.[4—13] For example, six and four coordination of Ag(I) are typical examples. However, to the best of the author's knowlege, no mention has been made in the literature about the fivehold coordination of thiaethers on Ag(I) ion. We have previously reported on the preparation of polythia[*n*]ruthenocenophanes,[14] -ferrocenophanes,[15] and 1,*n*-dioxathia[*n*]ruthenocenophanes,[16] which exhibited considerably enhanced Ag(I) cation binding compared with the corresponding ring membered crown ethers. We report here the preparation and the first novel structure of tetrathiaferrocenocrown ether complex of silver(I).

Silver(I) perchlorate or silver(I) trifluoromethanesulfonate (0.1 mmol) in acetonitrile (5 ml) was slowly added to a gently refluxing acetonitrile solution (10 ml) containing tetrathia[10]metallocenophane (**1**, 0.1 mmol). The resulting crystals were collected by filtration and washed with a small amount of acetonitrile to give 1:1 complexes (**2**) in 33—73% yields.

X-Ray Analyses. Recrystallization of **2c** from hot acetonitrile afforded brown crystals suitable for X-ray diffraction studies. The conformation of the complex (**2c**) is illustrated in Fig. 1, which also shows the atom



1a: M=Ru
1b: M=Fe

2a: M=Ru, X=ClO_4
2b: M=Ru, X=CF_3SO_3
2c: M=Fe, X=ClO_4
2d: M=Fe, X=CF_3SO_3

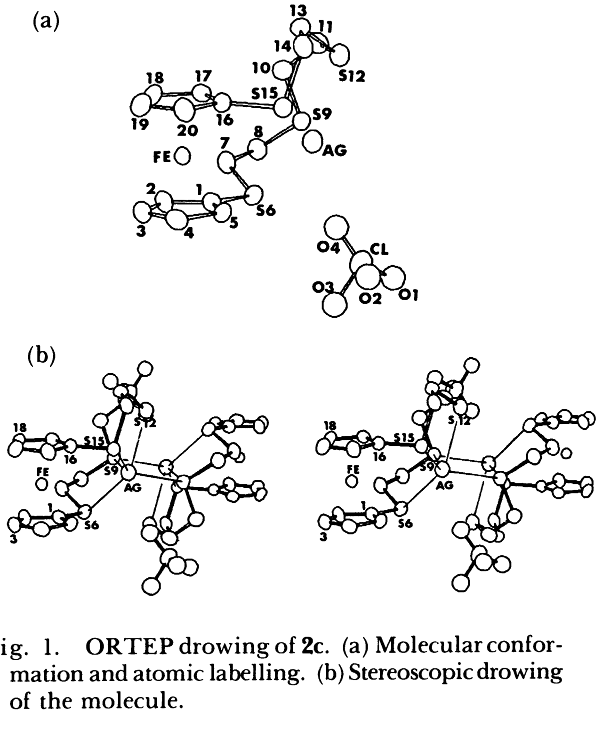


Fig. 1. ORTEP drowing of **2c**. (a) Molecular conformation and atomic labelling. (b) Stereoscopic drowing of the molecule.

labels used. The positional parameters for nonhydrogen atoms are listed in Table 1. Also, the bond lengths, bond angles and torsion angles are listed in Table 2.

As shown in Fig 1, **1b** forms a 1:1 complex with silver perchlorate which is dimeric in relation to the center of symmetry; two silver atoms are sandwiched between the two ferrocenophanes to yield a five-coordinated complex, in which each silver atom is coordinated with four sulfur atoms (S(6), S(9), S(12), and S(15)) of the organic ligand moiety and one sulfur atom (hereafter denoted as S(9′)) of another ligand. The deviations of the four sulfur atoms from their mean plane are between +0.14 and −0.11 Å, and such that the configuration of these four atoms is a very flattened tetrahedron. The Ag atom is 0.87 Å out of the plane. The inner coordination sphere of the silver atom is completed by the S(9′) atom bonded at the apex to produce a five-coordinate silver atom with overall square-pyramidal geometry. However, the line Ag···S(9′) is displaced from the normal square-pyramidal geometry, the angle S(9′)–Ag–X ranging from 77.3(4) to 133.4(4)°. The perchlorate ion does not appear to be coordinated to the silver ion, and the shortest interatomic distance between the Ag and O atoms is 3.035(18) Å. Silver–sulfur distances range from 2.629(4) to 2.883(4) Å. Although bond lengths of Ag–S(6)(2.668(4) Å), Ag–S(15)(2.629(4) Å) and Ag–S(9′)(2.474(4) Å) are in same range as those observed in bis(1,4,7-trithiacyclononane)silver(I) trifluoromethanesulfonate (which contains a six-coordinate silver atom)[17] and in 1,3,5-trithiane silver(I) perchlorate (which contains both four- and five-coordinate silver),[18] the bond lengths of Ag–S(9)(2.883(4) Å) and Ag–S(12)(2.805(4) Å) are comparable with that in μ-(1,3,5-trithiane-S^1,S^3)-bis[bis(1,3,5-trithiane)silver(I)] bis-[hexafluoroarsenate(V)]–sulfur dioxide (in which contains five-coordinate silver).[6] The Cp rings take an eclipsed conformation, in which the dihedral angle between them is 3.9(6)° and the torsion angle C(1)–Cp1–Cp2–C(16) (Cp1 and Cp2 being the centroids of the Cp rings) is 57.7(15)°. These results agree well with those in the platinum complex of 1,4,7,10-tetrathia[10](1,1′)ruthenocenophane.[19] The distances between the iron atom and the carbon atoms of the Cp rings range from 2.002(12) to 2.056(14) Å. The perpendicular distances from the iron atom to the least square planes of the two Cp rings, 1.631 and 1.636 Å, respectively, are both slightly shorter than those found in the NaSCN complex[20] of pentaoxa[12](1,1′)ferrocenophane but agree well with those of some bridged ferrocenophanes. The intramolecular atomic distances between the Fe and Ag(I) atoms is 4.101(2) Å. This value is much longer than the sum of the covalent radii of the Fe and Ag(I) atoms[21] and indicates no direct metal–metal interaction between the coordinated Ag(I) atom and the iron atom of the ferrocene nucleus in the complex **2c**.

Table 1. Fractional Atomic Coordinates (×10^4) and Thermal Parameters (Å^2), with Estimated Standard Deviations in Parentheses

Atom	x	y	z	B_{eq}[22]
Ag	4331(1)	4927(1)	6790(1)	2.55
Fe	2358(1)	5742(2)	8010(2)	3.01
Cl	4100(2)	1018(3)	7722(4)	2.89
C(1)	2497(6)	4519(12)	6443(12)	3.43
C(2)	1834(6)	5123(13)	6285(13)	2.81
C(3)	1467(6)	4826(12)	7500(13)	2.81
C(4)	1878(7)	4075(13)	8347(14)	2.98
C(5)	2545(6)	3871(12)	7713(13)	3.15
S(6)	3183(2)	4462(3)	5268(3)	3.09
C(7)	3060(6)	5936(13)	4327(12)	3.41
C(8)	3672(7)	6152(13)	3373(13)	3.68
S(9)	4512(2)	6223(3)	4225(4)	3.76
C(10)	4555(7)	7770(13)	5014(14)	3.07
C(11)	5210(7)	7898(13)	5866(14)	3.30
S(12)	5295(2)	6856(4)	7346(4)	2.78
C(13)	4803(6)	7695(12)	8630(13)	2.21
C(14)	4601(7)	6805(13)	9798(13)	2.63
S(15)	3967(2)	5572(3)	9274(3)	3.36
C(16)	3194(6)	6436(11)	9024(11)	3.24
C(17)	3026(6)	7225(11)	7914(12)	2.84
C(18)	2334(7)	7677(12)	8066(14)	3.37
C(19)	2092(7)	7162(13)	9313(13)	1.93
C(20)	2615(6)	6401(13)	9897(12)	3.90
O(1)	452(1)	36(2)	683(2)	10.8(0.4)
O(2)	402(1)	49(2)	900(2)	11.6(0.5)
O(3)	348(1)	33(2)	754(2)	15.6(0.6)
O(4)	401(1)	223(2)	759(2)	12.0(0.5)

^{1}H NMR Spectra. The 400 MHz ^{1}H NMR spectra of **1b** in acetonitrile-d_3 showed a pair of triplets corresponding to the α- and β-ring protons of the ferrocene nucleus at δ 4.29 (t, J=1.8 Hz, 4H) and 4.27 (t, J=1.8 Hz, 4H), in addition to a singlet at δ 3.05 (s, 4H, $-SCH_2CH_2S-$) and two triplets at δ 3.15 (t, J=7.0 Hz, 4H, $-SCH_2-$) and 2.85 (t, J=7.0 Hz, 4H, $-SCH_2-$). The ^{1}H NMR spectra of **2c** in acetonitrile-d_3 showed a pair of triplets due to the α- and β-protons of Cp-rings at δ 4.43 (t, J=1.8 Hz, 4H) and 4.36 (t, J=1.8 Hz, 4H) together with two broad singlets at δ 3.12 (8H) and 3.06 (4H) due to the methylene protons, although these peaks shifted downfield to about 0.12—0.29 ppm. This result suggests that the counter ion (ClO_4^-) of the complex **2c** is completely separated from the silver(I) ion and the Fe atom of the ferrocene nuclues, and that the anions are surrounded by the acetonitrile-d_3 in solution. Furthermore, the change in the methylene protons' absorption pattern upon complexing (compared with the corresponding silver free ligand) can be explained by the coordination of the sulfur atoms to the silver atom described below. That is, the methylene protons at 7-, 8-, 13-, and 14-, and 10- and 11-positions become equivalent to each other upon complexing. The ^{1}H NMR spectra of **2a** in acetonitrile-d_3 showed also a pair of triplets corresponding to the α- and β-ring protons of the

Table 2. Bond Lengths (Å), and Bond and Torsion Angles (°)

1	2	3	4	1-2	1-2-3	1-2-3-4
Tetrathia-crown moiety						
S(6)	C(1)	C(2)	C(3)	1.775(13)	128.2(10)	177.0(6)
S(6)	C(1)	C(5)	C(4)		121.2(9)	176.6(8)
C(2)	C(1)	S(6)	C(7)			29.2(13)
C(5)	C(1)	S(6)	C(7)			−154.0(11)
C(1)	S(6)	C(7)	C(8)		102.1(6)	172.3(8)
S(6)	C(7)	C(8)	S(9)	1.825(14)	110.0(9)	−58.8(13)
C(7)	C(8)	S(9)	C(10)	1.538(19)	114.9(10)	−76.4(11)
C(8)	S(9)	C(10)	C(11)	1.795(14)	105.2(6)	174.9(8)
S(9)	C(10)	C(11)	S(12)	1.814(14)	110.1(10)	−64.4(13)
C(10)	C(11)	S(12)	C(13)	1.49(2)	116.0(10)	−82.6(11)
C(11)	S(12)	C(13)	C(14)	1.821(15)	102.1(6)	161.3(8)
S(12)	C(13)	C(14)	S(15)	1.823(14)	110.8(9)	−67.3(12)
C(13)	C(14)	S(15)	C(16)	1.538(19)	114.2(9)	−71.6(11)
C(14)	S(15)	C(16)	C(17)	1.850(14)	102.5(6)	74.9(12)
C(14)	S(15)	C(16)	C(20)			−108.3(11)
S(15)	C(16)	C(17)	C(18)	1.757(12)	126.5(9)	176.3(7)
S(15)	C(16)	C(20)	C(19)		125.3(9)	−176.9(5)
Cyclopentadienyl ring						
C(1)	C(2)	C(3)	C(4)	1.431(18)	105.6(11)	−0.6(16)
C(2)	C(3)	C(4)	C(5)	1.431(19)	109.5(12)	1.1(16)
C(3)	C(4)	C(5)	C(1)	1.379(19)	109.2(12)	−1.1(15)
C(4)	C(5)	C(1)	C(2)	1.457(19)	105.2(11)	0.7(15)
C(5)	C(1)	C(2)	C(3)	1.411(18)	110.5(11)	−0.1(15)
C(16)	C(17)	C(18)	C(19)	1.398(17)	108.5(11)	1.2(15)
C(17)	C(18)	C(19)	C(20)	1.425(19)	106.8(12)	−1.0(16)
C(18)	C(19)	C(20)	C(16)	1.423(19)	108.7(12)	0.4(16)
C(19)	C(20)	C(16)	C(17)	1.397(19)	108.0(11)	0.4(15)
C(20)	C(16)	C(17)	C(18)	1.422(18)	108.1(11)	−1.0(15)
Ag coordination						
S(6)	Ag	S(9)		2.668(4)	74.1(1)	
S(9)	Ag	S(12)		2.853(4)	73.9(1)	
S(12)	Ag	S(15)		2.805(4)	80.0(1)	
S(15)	Ag	S(9)*		2.629(4)	133.4(1)	
S(9)*	Ag			2.747(4)		*: 1−*x*, 1−*y*, 1−*z*
O(4)	Ag			3.035(18)		
Fe	Ag			4.101(2)		
Cl	Ag			4.275(4)		
Ag*	Ag			4.393(2)		

ruthenocene nucleus at δ 4.84 (J=1.7 Hz, 4H) and 4.76 (t, J=1.7 Hz, 4H), in addition to a broad singlet at δ 3.03 (bs, 4H) and a multiplet at δ 3.05—3.14 (m, 8H). The peak due to the methylene protons at the 7-, 8-, 13-, and 14-positions of the ruthenocenophane complex **2a** is broadened and appears as a multiplet, although the chemical shift value is very similar to that of the ferrocenophane complex **2c**. Furthermore, the methylene protons at the 10- and 11-positions of **2a** and **2c** also showed nearly the same chemical shift values. These results suggest that **2a** in solution forms a 1 : 1 complex similar to that of **2c**, but the methylene protons at 7- and 8- (and/or 13- and 14-) positions become nonequivalent environments due to the long distance between the two Cp-rings of the ruthenocene nucleus in **2a** compared with that of the ferrocene nucleus in **2c**. A similar relationship is observed between **2b** and **2d**.

In order to investigate the stability of the silver complex, the VT NMR technique was used. According to the rise in temperature the spectral pattern and chemical shift of **2b** in DMSO-d_6 changed. At 65 °C a sharp singlet due to the methylene protons at the 7-, 8-, 13-, and 14-positions became a broad singlet and then the broad singlet separated completely to two multiplet peaks at 90 °C. Furthermore the methylene protons at the 7-, 8-, 13-, and 14-positions became a pair of A_2B_2 triplets at δ 3.11 (J=6.6 Hz) and 2.94 (J=6.6 Hz), and the peaks of the Cp ring protons shifted up-field and showed a pair of AA′BB′ triplets at δ 4.82 and 4.68 at 170 °C. The spectrum of **2b** at 170 °C is very similar to that found in the silver-free ligand **1a** at room temperature. These results suggest that the dissociation of **2b** to (**1a**+$AgCF_3SO_3$) began at 65 °C and finished completely at about 170 °C. In order to calculate the formation energy of **2b** from **1a**

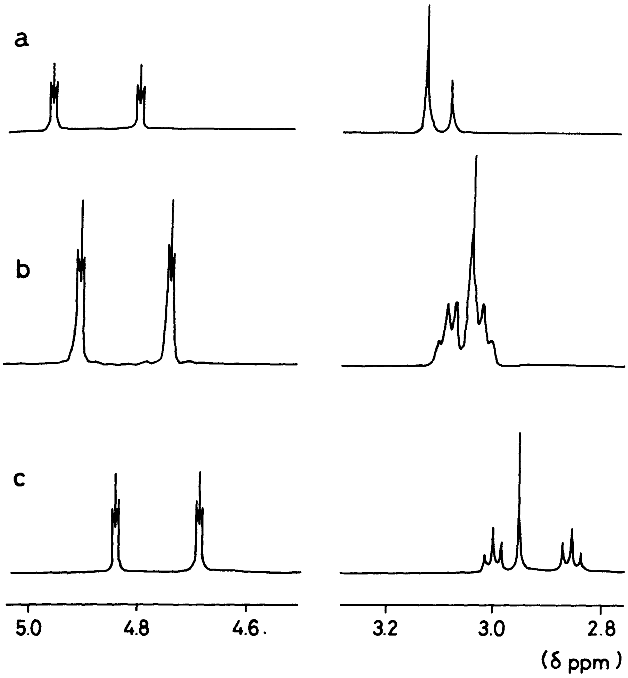


Fig. 2. ^{1}H NMR spectra (in DMSO-d_6) of (a) **2b**, (b) an equimolar mixture of **1a**+**2b**, and (c) **1a**.

and $AgCF_3SO_3$, a VT NMR measurement of the 1 : 1 mixture of **1a** and **2b** was carried out. First, the 1 : 1 mixture of the complex **2b** and silver free ligand **1a** in DMSO-d_6 was measured at room temperature. The spectrum showed a pair of AA′BB′ triplets corresponding to the α- and β-ring protons at δ 4.91 (J=1.8 Hz) and 4.74 (J=1.8 Hz), a singlet due to the methylene protons at the 10- and 11-positions, together with a broad pair of triplets due to the methylene protons at the 7-, 8-, 13-, and 14-positions. However the spectrum did not show any peaks due to the methylene protons at the 7-, 8-, 13-, and 14-positions of **1a** and **2a** at room temperature. These results showed that there is a relatively fast equilibrium by ^{1}H NMR scale between the following equations. Then, low-temperature measurements of the mixture in various solvents were attempted. Unfortunately, though, they failed because of the low solubility of the samples at low temperatures.

Experimental

The melting points are uncorrected. The IR spectra were measured on a JASCO IRA-2 Diffraction Grating Infrared Spectrometer. The ^{1}H NMR spectra were obtained on a JEOL GX400 spectrometer with TMS as the internal standard. Elemental analyses of **2b** and **2d** were not carried out because of the explosive property of these complexes at high temperature.

Materials. 1,4,7,10-Tetrathia[10]ruthenocenophane[19] and 1,4,7,10-tetrathia[10]ferrocenophane[23] were prepared according to a method discussed in the previous papers. Silver(I) perchlorate and trifluoromethanesulfonate (triflate) were commercially available. The solvents used were reagents grade and/or purified by distillation.

(1,4,7,10-Tetrathia[10]ruthenocenophane)silver(I) Perchlorate (2a). To a solution of **1a** (11.0 mg, 2.5×10^{-2} mmol) in acetonitrile (2 cm^3) was added a solution of silver(I) perchlorate (5.2 mg, 2.5×10^{-2} mmol) in acetonitrile (1 cm^3). After the solution was refluxed for 3 min, it was diluted with diethyl ether (1 cm^3). The solution was kept overnight in a refrigerator. The resulting crystals were collected by filtration and washed with small amounts of acetonitrile to give **2a** in 45% yield as white needles. Mp 170 °C (decomp). ^{1}H NMR (in CD_3CN) δ=4.84 (t, J=1.7 Hz, 4H), 4.76 (t, J=1.7 Hz, 4H), 3.14—3.05 (m, 8H), and 3.04—3.01 (m, 4H). IR (KBr) 3090, 2910, 1410, 1090, 1050, 820, 618, and 490 cm^{-1}.

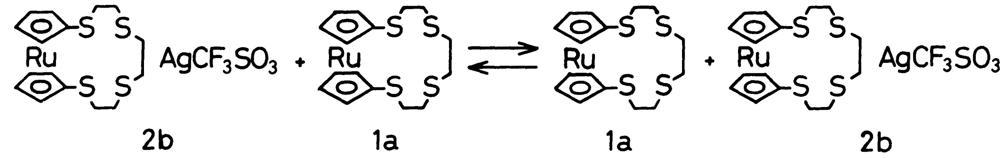
(1,4,7,10-Tetrathia[10]ruthenocenophane)silver(I) Triflate (2b). Complex **2b** was prepared using the same method as described above. Yield 33%. Mp 190 °C (decomp). Found: C, 29.59; H, 2.90%. Calcd for $C_{17}H_{20}AgF_3O_3RuS_5$: C, 29.23; H, 2.89%. ^{1}H NMR (in CD_3CN) δ=4.84 (t, J=1.7 Hz, 4H), 4.76 (t, J=1.7 Hz, 4H), 3.14—3.05 (m, 8H), and 3.03 (s, 4H). IR (KBr) 3100, 2910, 1410, 1280, 1110, 810, 625, and 570 cm^{-1}.

(1,4,7,10-Tetrathia[10]ferrocenophane)silver(I) Perchlorate and Triflate (2c and 2d). Complexes **2c** and **2d** were prepared using a method described in a previous paper.[15]

2c was identified by a comparison with melting point and the spectral data of an authentic sample.

2d. Yield 60%. Mp 195 °C (decomp). Found: C, 31.16; H, 3.06%. Calcd for $C_{17}H_{20}AgF_3FeO_3S_5$; C, 31.25; H, 3.06%. ^{1}H NMR (in CD_3CN) δ=4.43 (t, J=1.8 Hz, 4H), 4.36 (t, J=1.8 Hz, 4H), 3.12 (s, 8H), and 3.06 (s, 4H). IR (KBr) 3090, 2910, 1410, 1275, 1250, 1023, 622, and 510 cm^{-1}.

X-Ray Crystallography of 2c. Lattice constants were determined by a least-squares fit of angular settings of 2θ reflections within the range 15<2θ<25°. Intensity data were obtained on a Rigaku AFC-5R apparatus equipped with graphite monochromated Mo $K\alpha$ radiation and using the ω–2θ scan technique (2θ≤50°). During data collection three standards (measured g before every 200 reflections) showed no significant variation. Of 3510 independent reflections measured, only 3122 were considered as being observed on the basis of the criterion $F_o > 2\sigma(F_o)$. All intensities were corrected for Lorentz and polarization effects, but not for absorption. Crystal data: $C_{16}H_{20}S_4FeAgClO_4$, Mw=603.8, crystal size 0.5×0.5×0.15 mm, monoclinic, space group $P2_1/a$, a=19.227(3), b=10.619(3), c=9.739(2) Å, β=91.71(2)°, U=1987.8 Å^3, Z=4, D_c=2.02 g cm^{-3}, μ(Mo $K\alpha$)=23 cm^{-1}, T=



297 K. The structure was solved by heavy-atom methods, and refined by block-diagonal least-squares methods. The positions of the hydrogen atoms were estimated from standard geometry. The final refinements with anisotropic temperature factors for the nonhydrogen atoms and isotropic temperature factors for the hydrogen atoms lowered the R value to 0.075 (R_w=0.086, $w=1/\sigma^2(F_o)$). The goodness of fit was 5.6. The excursions in the final difference Fourier synthesis were within ±0.7 e Å^{-3}.

The complete F_o-F_c data are deposited as Document No. 8868 at the office of the editor of Bull. Chem. Soc. Jpn.

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