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(η^5-Cyclopentadienyl)(Halo or Acido) (Substituted 1-Methylthio-$\varkappa S$-ethylene-2-thiolato)cobalt(III): Formation, Stereoisomers, and Isomerization

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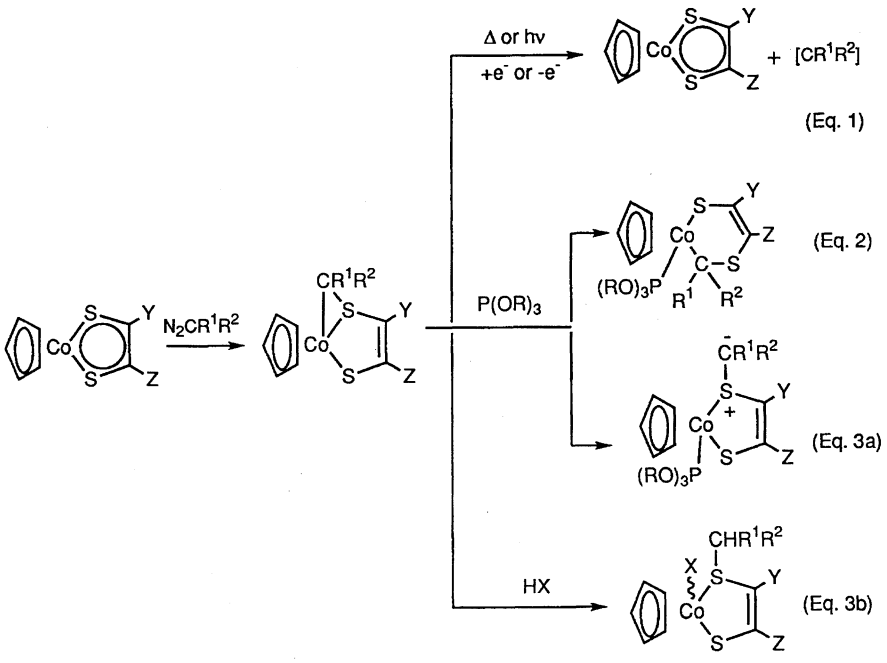
The addition of protic acids to (η^5-cyclopentadienyl)(1-methylenethio)-$\varkappa C,\varkappa S$-ethylene-2-thiolato)cobalt(III) complexes (**2**) causes a Co–C bond cleavage in the three-membered cobaltathiirane ring to give (η^5-cyclopentadienyl)(halo or acido)(1-methylthio-$\varkappa S$-ethylene-2-thiolato)cobalt(III) complexes (**3**). In the crystalline state, these complexes have either *syn*- or *anti*-configuration with respect to halo (or acido) and the methyl or substituted methyl group attached to S. In some cases, complexes **3** exist in equilibria between *syn*- and *anti*-stereoisomeric forms in solutions. In solutions, an exchange of the coordinated anions occurs very easily.

Metalladichalcogenolene (metalladithiolene and metalladiselenolene) rings[1] are very interesting conjugated metal chelate rings with 6π electrons. The coexistence of aromaticity and unsaturation is the origin of unique reactivities of this quasi-aromatic ring. Aromaticity is the origin of substitution reactions in electrophilic,[2] radical,[2—4] or other mechanism,[5] while the unsaturated character of the ring causes addition reactions.[6—10] The formation of a methylene bridge between metal and a chalcogen in the reaction with diazo compounds is a typical reaction due to unsaturation.[6,7]

The three-membered metallathiirane ring in the methylene-bridged complexes shows also interesting reactions. The reactions of three-membered metallathiirane rings, hitherto clarified, are classified into 3 types: 1) elimination of the alkylidene group in thermolysis, photolysis,[6b] or electrochemical redox reactions[11] (Eq. 1), 2) cleavage of the metal–sulfur bond to form six-membered dihydrocobaltadithiine ring (Eq. 2),[12,13] and 3) cleavage of metal–carbon bond (Eqs. 3a and 3b) (Scheme 1).[13] Case 3 is subdivided into 2 categories: a reaction to give ylide (Eq. 3a) and a reaction to



Scheme 1.

give an electrically neutral complex (Eq. 3b).

We have preliminarily reported an example of the protic acid-induced cleavage of the Co–C bonds in a cobaltathiirane ring in the case of (η^5-cyclopentadienyl)[1-(trimethylsilyl)methylenethio-$\varkappa C,\varkappa S$-1-methoxycarbonylethylene-2-thiolato-$\varkappa S$]cobalt(III).[14] Here, we describe the details of the bond cleavage in three-membered cobaltathiirane rings by protic acids: structure determination of the formed three-component-adducts, existence of stereiomers, and exchange of anions coordinated to the cobalt atom.

Results and Discussion

Opening of Cobaltathiirane Ring by Protic Acids. The methylene-bridged cobaltadithiolene complexes [derivatives of (η^5-cyclopentadienyl)(1-methylenethio-$\varkappa C,\varkappa S$-ethylene-2-thiolato)cobalt(III): (**2**)] react easily with protic acid. Vigorous stirring of a suspension of a few drops of aqueous protic acid and the dichloromethane solution of **2** at room temperature gives product **3** (Scheme 2). The elemental analysis and MS of the isolated product **3** indicate that **3** is formally composed of 3 components: cobaltadithiolene complex, methylene (or substituted methylene), and protic acid. Thus, we call this type of complexes "three-component-adducts." As discussed below, the three-component-adducts have the structure of (η^5-cyclopentadienyl)(halo or acido)-(substituted 1-methylthio-$\varkappa S$-ethylene-2-thiolato)cobalt(III). Namely, the anioic part of protic acids is coordinated to the cobalt atom and the proton adds to the methylene carbon.

The results for the formation of the three-component-adducts are summarized in Table 1. Normally, the reactions proceed easily at room temperature within 30 min and give **3** in high yields. However, the reaction of **2c** (ethoxycarbonylmethylene-bridged complex) with HCl proceeds at a very slow rate and the yield of the three-component-adduct is low (36%).

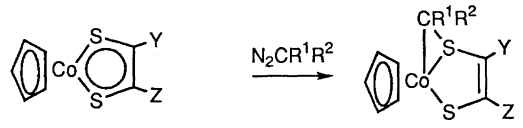
Stereoisomers of Three-Component Adducts. The structures of ten three-component-adducts (**3aCl**, **3aFA**, **3bFA**, **3cCl**, **3dCl**, **3dBr**, **3dI**, **3eCl**, **3fCl**, and **3gCl**) were determined by X-ray crystal analysis. The ORTEP drawings of these complexes (except that for **3eCl** which has been shown in Ref. 14) are shown in Fig. 1 and the selected bond lengths and bond angles are summarized in Table 2.

All of the three-component-adducts, whose X-ray structures have been determined, have structures in which the anionic part of protic acids is coordinated to the cobalt atom, and the proton attaches to the methylene carbon.

The structures of the three-component-adducts are classified into two groups: in the first group, (substituted) methyl group (CHR^1R^2) attached to S and halo or acido ligands are located at the opposite side of the dithiolene ring plane (*anti*-form); and in the second group of adducts, (substituted) methyl group (CHR^1R^2) attached to S and halo or acido ligands are located at the same side of the dithiolene ring plane (*syn*-form).

Either in the *syn*- or *anti*-form, the cobaltadithiolene rings are planar and the corresponding bond lengths and angles of the cobaltadithiolene rings in three-component-adducts are similar, independently of the *syn*- or *anti*-configuration and of the kind of anions.

The conformations around the cobalt atom are described fundamentarily as a piano-stool structure. The plane angles between Cp and dithiolene and the bond angles of ∠X–Co–S-(2) in the *syn*-forms are somewhat larger than those in the *anti*-forms. The substituted methyl groups attached to S

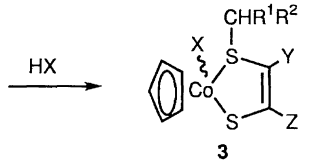


1

1a: Y=Z=COOMe
1b: Y=COOMe, Z=H
1c: Y=Z=CN
1d: Y=Z=Ph

2

2a: Y=Z=COOMe, R^1=R^2=H
2b: Y=Z=COOMe, R^1=H, R^2=$SiMe_3$
2c: Y=Z=COOMe, R^1=H, R^2=COOEt
2d: Y=COOMe, Z=H, R^1=R^2=H
2e: Y=COOMe, Z=H, R^1=H, R^2=$SiMe_3$
2f: Y=Z=CN, R^1=R^2=H
2g: Y=Z=Ph, R^1=R^2=H



3

3aCl: Y=Z=COOMe, R^1=R^2=H, X=Cl
3aBr: Y=Z=COOMe, R^1=R^2=H, X=Br
3aI: Y=Z=COOMe, R^1=R^2=H, X=I
3aFA: Y=Z=COOMe, R^1=R^2=H, X=CF_3COO
3bFA: Y=Z=COOMe, R^1=H, R^2=$SiMe_3$, X=CF_3COO
3cCl: Y=Z=COOMe, R^1=H, R^2=COOEt, X=Cl
3dCl: Y=COOMe, Z=H, R^1=R^2=H, X=Cl
3dBr: Y=COOMe, Z=H, R^1=R^2=H, X=Br
3dI: Y=COOMe, Z=H, R^1=R^2=H, X=I
3eCl: Y=COOMe, Z=H, R^1=H, R^2=$SiMe_3$, X=Cl
3fCl: Y=Z=CN, R^1=R^2=H, X=Cl
3gCl:Y=Z=Ph, R^1=R^2=H, X=Cl

Scheme 2.

Table 1. Reactions between Alkylidene-Adducts of Cobaltadithiolene Complexes with Protic Acids

	Alkylidene adduct				Reaction conditions			Product		
	Cobaltadithiolene		Alkylidene		Protic acid	Temp	Time	Product	Yield	Isomer ratio
	Y	Z	R^1	R^2	X	°C	h		%	
2a	COOMe	COOMe	H	H	Cl	r.t.	0.5	**3aCl**	96	1 : 4
2a	COOMe	COOMe	H	H	Br	r.t.	0.5	**3aBr**	85	1 : 2
2a	COOMe	COOMe	H	H	I	r.t.	0.5	**3aI**	94	1 : 1
2a	COOMe	COOMe	H	H	CF_3COO	r.t.	0.5	**3aFA**	96	1 : 0
2b	COOMe	COOMe	H	$SiMe_3$	CF_3COO	r.t.	0.5	**3bFA**	91	1 : 0
2c	COOMe	COOMe	H	COOEt	Cl	r.t.	17.0	**3cCl**	36	1 : 0
2d	COOMe	H	H	H	Cl	r.t.	0.5	**3dCl**	83	1 : 4
2d	COOMe	H	H	H	Br	r.t.	0.5	**3dBr**	91	1 : 2
2d	COOMe	H	H	H	I	r.t.	0.5	**3dI**	91	1 : 1
2e	COOMe	H	H	$SiMe_3$	Cl	r.t.	1.0	**3eCl**	73	1 : 0
2e	CN	CN	H	H	Cl	r.t.	0.5	**3fCl**	97	1 : 0
2f	Ph	Ph	H	H	Cl	r.t.	0.5	**3gCl**	95	1 : 0

and the anionic ligands coordinated to the cobalt atom are perpendicular to the five-membered cobaltadithiolene ring.

Previously we have reported that the five-membered cobaltadithiolene ring (Co–S(1)–C(1)–C(2)–S(2) ring) of **1a** is almost planar due to its aromaticity, that its plane is perpendicular to that of Cp ring, and that the Co–S(1)–C(1)–C(2)–S(2) ring of the methylene-bridged complex, **2a**, is also almost planar and that the three-membered cobaltathiirane ring formed by the insertion of a CH_2 into the Co–S bond of the cobaltadithiolene ring is almost perpendicular to the plane of the cobaltaithiolene ring (dihedral angle against the Cp plane, 82.09°).[11]

The X-ray structures of the complexes **3aFA**, **3bFA**, **3cCl**, **3eCl**, **3fCl**, and **3gCl** show the *syn*-configuration, while those of **3aCl**, **3dCl**, **3dBr**, and **3dI** show the *anti*-configuration. There is no three-component-adduct in which both *syn*- and *anti*-isomers have been identified by X-ray crystal structure analysis. However, in some cases (**3aCl**, **3aBr**, **3aI**, **3dCl**, **3dBr**, and **3dI**), the ^{1}H NMR specra of the three-component adducts in $CDCl_3$ solutions are composed of two sets of signals, although elemental analyses of these complexes agree with those calculated for the 1 : 1 : 1 adducts of the cobaltadithiolene complex, alkylidene moiety, and hydrogen halide. A typical example is illustrated in Fig. 2 by **3aBr**. These facts indicate that the three-component adduct exists in two kinds of isomeric species in solutions. These two species can be assigned to *syn*- and *anti*-stereoisomers. {The exsistence of some chemical species other than the *syn*- and *anti*-isomers in solution may be conceivable. However, the similarity of ^{13}C NMR in the solid state and in a solution (in the cases of **3aFA** and **3aI**) suggests that the three-component adducts in a solution have only *syn*- and *anti*-stuctures similar to those in the solid state.} In the other cases (in the cases of **3aFA**, **3bFA**, **3cCl**, **3eCl**, **3fCl**, and **3gCl**), ^{1}H NMR spectra show that a single species exists in solutions.

In Table 1, the stereoisomeric compositions (determined by ^{1}H NMR) of the three-component-adducts are summarized.

Among the three-component-adducts which show dual sets of NMR signals in solutions, we succeeded in the determination of X-ray structure for **3aCl**, **3dCl**, **3dBr**, and **3dI**. Interestingly all of them have *anti*-configuration.

At present, we can not assign the NMR spectra of the mixtures of stereoisomers to the *syn*- or *anti*-isomer with sufficient reliability, because we have not yet succeeded in the separate crystallization of these isomers. The fact that **3bCl** having a bulky trimethylsilyl group at the *S*-methyl moiety shows a single set of NMR and has the *syn*-structure may suggest that the bulky groups preferably take the *syn*-configuration.[14] However, **3fCl**, in which only a small steric hindrace is presumed, shows also *syn*-configuration.

When we fix the group attached to S as CH_3 and the substituent in the cobaltadithiolene ring as two COOMe's, the isomer ratios change depending on the anions. When chloride anion is coordinated, the isomer ratio is 4 : 1. In the case of bromide, the ratio is 2 : 1, and in the case of iodide it is 1 : 1. In the case of trifluoroacetate, no isomer is seen and only *syn*-isomer is present. The isomer ratios for the chloro, bromo, and iodo complexes of *S*-methylmono(methoxycarbonyl)cobaltadithiolenes (**3dCl**, **3dBr**, and, **3dI**) are 4 : 1, 2 : 1, and 1 : 1, respectively. These ratios are the similar to those of the corresponding bis(methoxycarbonyl)cobaltadithiolenes (**3aCl**, **3aBr**, and **3aI**).

All of the three-component-adducts, analyzed as *syn*-configuration by X-ray structural analysis, show a single set of ^{1}H NMR spectra in solutions. The three-component-adducts analyzed as *anti*-configuration by X-ray structural analysis show dual sets of ^{1}H NMR.

As described earlier, there has been no case for which we could succeed in preparing single crystals of both *syn*- and *anti*-isomers. In order to examine the possibility of separate crystallization of the stereoisomers, we submitted 5 pieces each of single crystals of **3aCl** and **3dCl**, which show dual sets of ^{1}H NMR signals in solutions, on X-ray structure analysis. However, all of the crystals of each complex showed the same crystal parameters (namely the same crystal structure). This strongly suggests that **3aCl** and **3dCl** crystallizes preferentially in the form of the *syn*-configuration under the conditions for single-crystal preparation.

This leads further to another question as to whether both

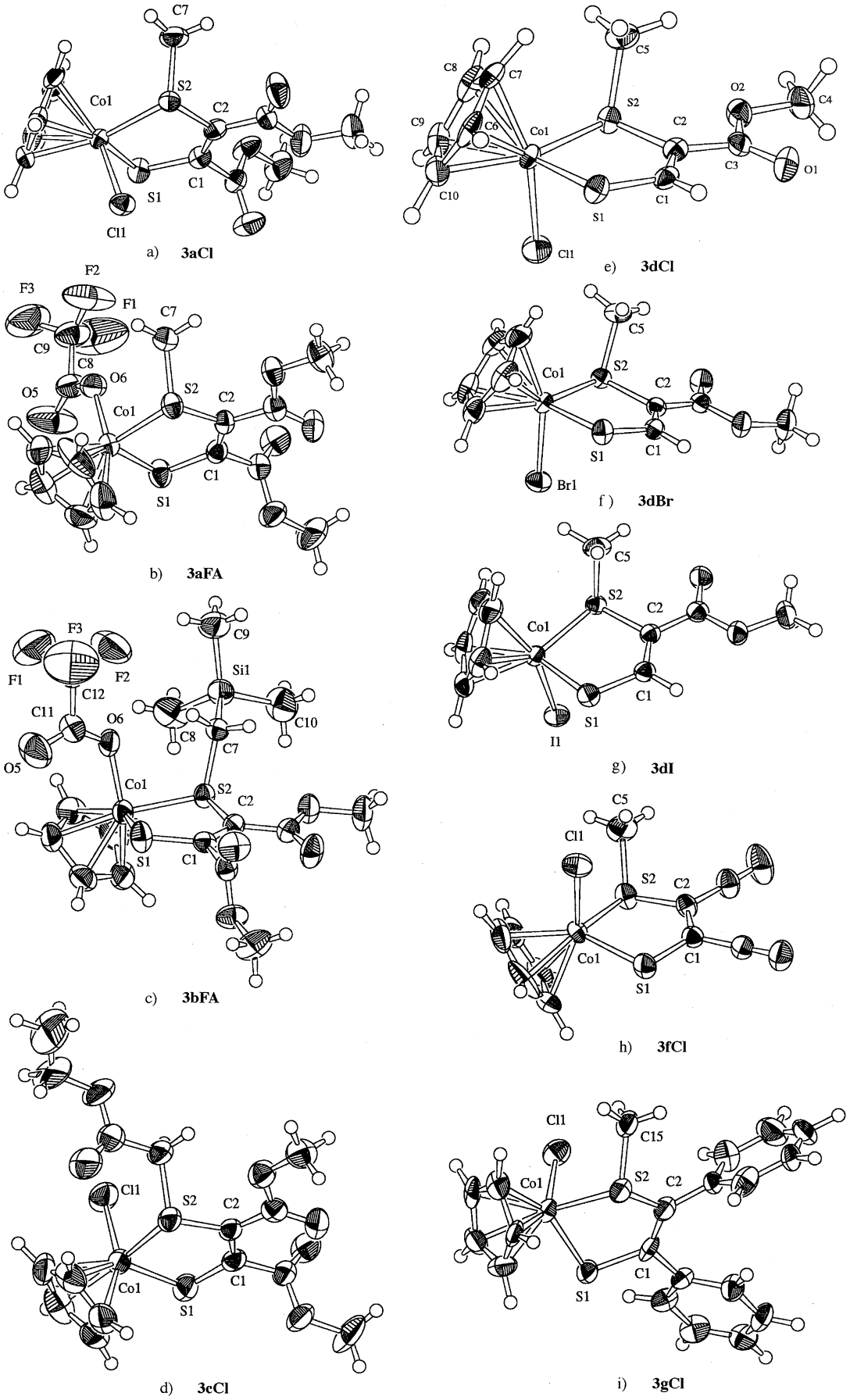


Fig. 1. ORTEP drawings of three-component-adducts.

Table 2. Selected Bond Lengths (Å), Bond Angles (deg), and Dihedral Angles (deg)

Complex Configuration	**1a**	**2a**	**3aCl** *anti-*	**3aFA** *syn-*	**3bFA** *syn-*	**3cCl** *syn-*	**3dCl** *anti-*	**3dBr** *anti-*	**3dI** *anti-*	**3eCl**[14] *syn-*	**3fCl** *syn-*	**3gCl** *syn-*
Bond distance												
Co–S(1)	2.108(2)	2.216(1)	2.229(2)	2.227(1)	2.233(1)	2.231(1)	2.228(2)	2.2361(8)	2.233(1)	2.240(3)	2.244(1)	2.239(3)
Co–S(2)	2.104(2)	2.182(1)	2.234(2)	2.241(1)	2.251(1)	2.238(2)	2.246(2)	2.227(39)	2.225(2)	2.260(2)	2.247(2)	2.227(3)
C(1)–C(2)	1.369(6)	1.361(3)	1.350(10)	1.341(4)	1.347(4)	1.337(5)	1.346(8)	1.347(4)	1.355(5)	1.32(1)	1.362(4)	1.370(1)
S(1)–C(1)	1.716(4)	1.703(2)	1.706(8)	1.713(3)	1.714(3)	1.702(4)	1.688(7)	1.704(3)	1.705(4)	1.70(1)	1.713(4)	1.76(1)
S(2)–C(2)	1.718(5)	1.765(2)	1.784(8)	1.775(3)	1.774(3)	1.786(4)	1.770(6)	1.776(3)	1.774(4)	1.770(8)	1.756(4)	1.79(1)
S(2)–C(7)			1.798(9)	1.801(3)	1.812(4)	1.809(4)	1.809(8)[c]	1.813(3)[c]	1.816(4)[c]	1.814(7)[c]	1.793(4)[e]	1.78(1)[d]
Co–X[a]			2.265(2)	1.936(2)	1.945(3)	2.264(2)	2.273(2)	2.4144(6)	2.5978(7)	2.238(3)	2.249(1)	2.263(4)
Cp–Co[b]	1.652	1.681	1.667	1.680	1.682	1.680	1.676	1.680	1.686		1.678	1.688
Bond angle												
S(1)–Co–S(2)	92.22(6)	91.77(3)	90.94(8)	90.71(4)	89.73(5)	90.15(5)	91.02(7)	90.82(3)	90.86(4)	90.1(1)	90.87(4)	86.8(1)
X–Co–S(1)[a]			92.68(9)	91.36(7)	93.68(8)	93.03(6)	92.78(7)	92.70(3)	92.26(3)	93.5(1)	92.10(4)	94.5(1)
X–Co–S(2)[a]			85.60(8)	91.59(6)	92.96(8)	97.22(5)	87.33(7)	86.84(2)	87.75(3)	97.40(9)	96.00(4)	92.1(1)
Co–S(2)–C(7)	105.0(2)	103.29(8)	112.2(3)	107.6(1)	110.3(1)	109.2(2)	111.7(3)[e]	110.2(1)[e]	110.0(2)[e]	111.6(3)[e]	114.4(2)[e]	109.6(4)[f]
Dihedral angle												
Cp/dithiolene	87.54	82.09	120.07	130.35	134.48	129.76	123.58	121.46	120.15		126.97	129.18

a) X = halogen or oxygen; b) Distance between Co and the center of pentagonal Cp; c) In this case, the bond distance of S(2)–C(5) which correspond to S(2)–C(7). It comes from the technical reason of the labelling of the atoms. d) In this case, the bond distance of S(2)–C(15); e) In this case, the bond angle of Co–S(2)–C(5). f) In this case, the bond angle of Co–S(2)–C(15).

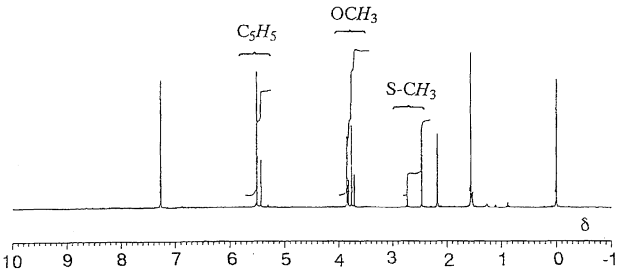


Fig. 2. ^{1}H NMR spectra of **3aBr** in a $CDCl_3$ solution.

stereoisomers can crystallize in separate forms under the conditions of usual crystal formation under rapid cooling. In order to answer this question, we measured the ^{13}C NMR of **3aFA** (single component case) and **3aI** (dual component case) in the powder state, which were prepared by rapid crystallization.

The ^{13}C NMR spectra in the powder state (Fig. 3) show that the single-component adduct **3aFA** gives a single signal at δ = 21.21 for S–CH_3, while the dual component adduct **3aI** gives dual signals for SCH_3 (at δ = 33.09 and 36.05) which agree with those in $CDCl_3$ solution (at δ = 33.26 and 36.05).

This fact suggests that each stereoisomer can form its own crystals individually under the usual conditions for recrystallization. However, we obtained only one kind of single crystals for X-ray structural analysis. This can be explained as follows. Crystallization by rapid cooling leads to the formation of two kinds of crystals, each of which is composed of one isomer. This is the case of the samples used for measuring the ^{13}C NMR in the powder state. Under the conditions for preparation of a single crystal for X-ray structural analysis, continuous equilibration for a long time causes the dissolution of less stable crystals and the growth of the more-stable crystals.

Ligand Exchange and Isomerization. The coordinated anions of the three-component-adducts are labile and are eas-

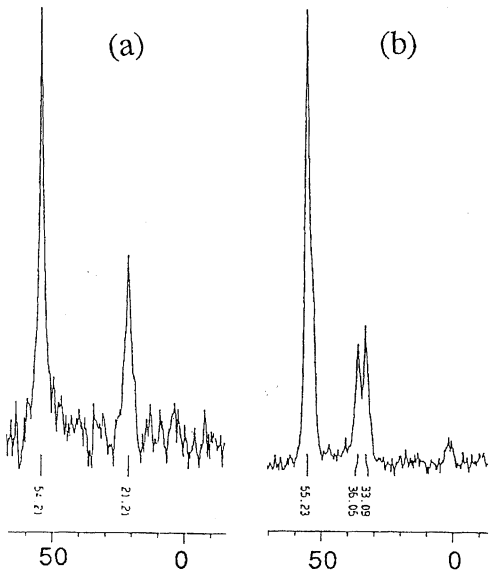
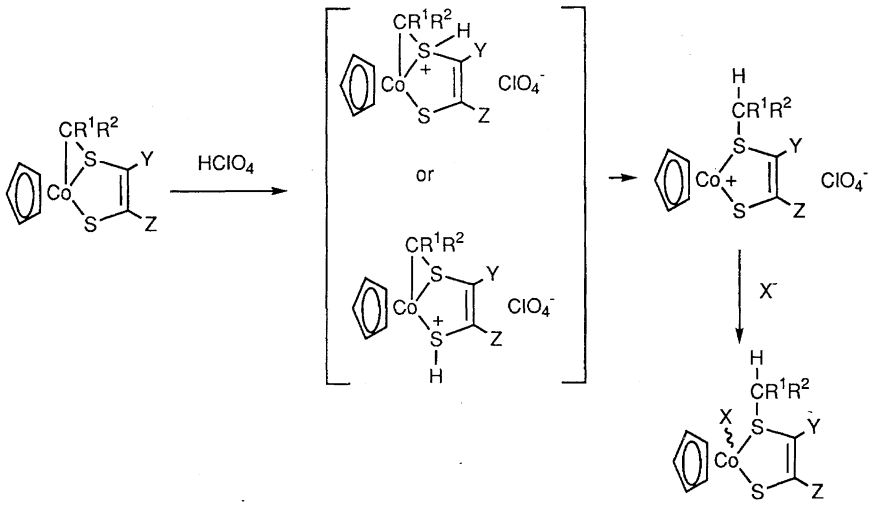


Fig. 3. ^{13}C NMR of **3aFA** (a) and **3aI** (b) in the powdered state.



Scheme 3.

ily substituted by other anions. When the stereoisomeric 4 : 1 mixture of **3aCl** (chloro complex) was treated with excess aqueous potassium bromide, a stereoisomeric 2 : 1 mixture of the bromo-complex **3aBr** was formed. On the other hand, when a stereoisomeric 2 : 1 mixture of the bromo-complex **3aBr** was treated with excess aqueous potassium chloride, a stereoisomeric 4 : 1 mixture of the chloro-complex **3aCl** was formed. The ratios of the stereoisomers formed by ligand exchange agree with the ratios of the stereoisomers obtained by the ring opening of the alkylidene-bridged complex with hydrogen halide. This shows the rapid exchange and rapid equilibrization of halide-coordinated complexes.

The chloro-complex **3aCl** was treated with an equal amount of potassium bromide to give a mixture of chloro-complex **3aCl** and bromo-complex **3aBr**. The ratio of the chloro-complex to the bromo-complex was 1 : 2. When the bromo-complex was treated with equimolar aqueous potassium chloride, the ratio of the chloro- to bromo-complexes was also 1 : 2. From these results, we can say that the softer bromide ion bonds to a cobalt atom more strongly than the harder chloride ion.

Reaction Mechanism for Ring Opening. Hydrogen halide causes the cleavage of the Co–C bonds of the three-membered cobaltathiirane ring, while potassium halide can not cleave the bond. This means that the attack of halide anions to the cobalt atom in neutral complexes can not cause the Co–C bond cleavage and the proton is important for the reaction.

When a dichloromethane solution of a methylene-adduct **2a** was shaken with an aqueous solution of perchloric acid, the brown color of the dichloromethane layer disappeared and the aqueous layer became red-brown. To the separated aqueous layer, aqueous sodium chloride was added and then the product was extracted with dichloromethane. The product moved to the dichloromethane layer. We identified the chloro-complex, **3aCl**. When acetonitrile or triphenylphosphine was added to the aqueous solution, the product was also extracted to the dichloromethane layer. These facts suggest that the reaction of **2a** with perchloric acid gives an cationic ring-opening product without coordination of the anion, because perchlorate is a very weak donor (Scheme 3). The donors such as chloride anion, acetonitrile, and triphenylphosphine, are bonded to the cation to form dichloromethane-soluble adducts.

Thus, a mechanism via the ring opening of the protonated alkylidene-bridged cobaltadithiolene and the succeeding coordination of anioic donors is plausible. Although the direct attack of a proton to the bridging carbon atom can not be excluded, the attack of a proton to the electron-rich sulfur atom may be plausible as the initial process. Then, the proton migrates to the methylene carbon and causes the ring opening.

Experimental

General Consideration. NMR spectra were normally measured with an NMR spectrometer (JEOL Model GX-270) of Nihon Denshi Co. For measurement the solid state NMR, a Model JNM-LAMDA 500 of Nihon Denshi Co. was employed. MS, IR, and UV-visible spectra were recorded on JMS-SX102A of Nihon Denshi Co., Hitachi IR spectrometer Model 260-50, and Hitachi UV-visible spectrometer Model 288, respectively.

Materials. The syntheses of the cobaltadithiolene complexes and their methylene or substituted methylene-bridged complexes **2a**, **2b**, **2c**, **2d**, **2f**, and **2g** were described in Ref. 6b. The complex **2e** was synthesized according to the method in Ref. 14.

Reaction with Protic Acid. To a dichloromethane solution (50 cm^3) of the cobaltadithiolene complex, **2** (ca. 0.3 mmol), 2 or 3 drops of concentrated hydrochloric, hydrobromic, or hydroiodic acid were added, and the suspension was stirred for 30 min at room temperature. The color of the solution changed from brown to deep blue-violet.

The reaction mixture was washed with water and dried with anhydrous sodium sulfate. The crude crystals obtained by evaporation of the solvent were recrystallized from a mixed solvent of hexane and dichloromethane. The reaction with CF_3COOH was performed in a similar way.

Identification of Three-Component-Adducts. 3aCl: Blue-violet crystals; mp 160—162 °C; IR (KBr disk) 1731 and 1685 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, 270 MHz) were obtained as two sets of signals, and these spectra were assigned to major and minor

component according to the intensities. Major component, δ = 2.30 (3H, s, CH_3), 3.77 (3H, s, OCH_3), 3.86 (3H, s, OCH_3), and 5.54 (5H, s, Cp); minor component, δ = 2.74 (3H, s, CH_3), 3.71 (3H, s, OCH_3), 3.82 (3H, s, OCH_3), and 5.47 (5H, s, Cp); MS (EI, 70 eV) *m/z* (rel intensity) 380 (M^+; 5), 345 (M^+-Cl; 63), 330 ($M^+-Cl-CH_3$; 81), 188 ($CpCoS_2^+$; 100), and 124 ($CpCo^+$; 25). Found: C, 37.65; H, 3.71%. Calcd for $C_{12}H_{14}ClCoO_4S_2$: C, 37.85; H, 3.71%;

3aBr: Blue-violet crystals; mp 180—181 °C; IR (KBr disk) 1746 and 1698 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, 270 MHz) were obtained as two sets of signals, and these spectra were assigned to major and minor component according to the intensities. Major component δ = 2.46 (3H, s, CH_3), 3.82 (3H, s, OCH_3), 3.85 (3H, s, OCH_3), and 5.51 (5H, s, Cp); minor component δ = 2.73 (3H, s, CH_3), 3.71 (3H, s, OCH_3), 3.76 (3H, s, OCH_3), and 5.43 (5H, s, Cp); MS (EI, 70 eV) *m/z* (rel intensity) 345 (M^+-Br; 10), 330 ($M^+-Br-CH_3$; 89), 188 ($CpCoS_2^+$; 100), and 124 ($CpCo^+$; 35). Found: C, 33.85; H, 3.15%. Calcd for $C_{12}H_{14}BrCoO_4S_2$: C, 33.90; H, 3.32%.

3aI: Blue-violet crystals; mp 184—187 °C; IR (KBr disk) 1732 and 1686 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, 270 MHz) were obtained as two sets of signals. In this case the assignment to each component was difficult because of the similarity of the intensities. Thus, we describe the corresponding signals in parallel. δ = 2.69 and 2.72 (3H, s, CH_3), 3.72, 3.75, 3.84, and 3.81 (3H, s, OCH_3), 5.43 and 5.47 (5H, s, Cp); ^{13}C NMR ($CDCl_3$, 270 MHz) δ = 31.01, 33.26 (CH_3), 52.61, 52.63, 53.24, 53.30 (OCH_3), 85.28, 86.31 (Cp), 117.12, 117.84 (ring C), 161.78, 165.82, 165.82, 166.11 (C=O), 173.19, 174.46 (ring C); Solid state ^{13}C NMR (500 MHz) δ = 33.09, 36.05 (CH_3), 55.23 (OCH_3), 87.57 (Cp), 115.99, 118.62 (ring C), 161.69, 163.53, 166.16, 167.84 (C=O), 173.76, 179.72 (ring C); FAB MS 472 (M^++1), 471 (M^+), 346 (M^+-I+1), and 345 (M^+-I). Found: C, 30.40; H, 2.98%. Calcd for $C_{12}H_{14}CoIO_4S_2$: C, 30.52; H, 2.99%.

3aFA: Blue-violet crystals; mp 142 °C; IR (KBr disk) 1729 and 1692 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, 270 MHz) δ = 2.14 (3H, s, CH_3), 3.79 (3H, s, OCH_3), 3.87 (3H, s, OCH_3), and 5.70 (5H, s, Cp); ^{13}C NMR ($CDCl_3$, 270 MHz) 19.25 (CH_3), 52.81 (OCH_3), 53.39 (OCH_3), 86.32 (Cp), 115.85 (ring C), 117.95 (CF_3), 161.38 (C=O), 165.59 (C=O), and 175.38 (ring C); Solid state ^{13}C NMR (500 MHz) 21.21 (CH_3), 54.21 (OCH_3), 88.55 (Cp), 117.64 (ring C), 132.80 (CF_3), 162.67 (C=O), 167.15 (C=O), and 174.09 (ring C); MS (EI, 70 eV) *m/z* (rel intensity) 458 (M^+; 3), 345 (M^+-CF_3COO; 73), 330 ($M^+-CF_3COO-CH_3$; 67), 188 ($CpCoS_2^+$; 100), and 124 ($CpCo^+$; 39). Found: C, 36.72; H, 3.06%. Calcd for $C_{14}H_{14}CoF_3O_6S_2$: C, 36.69; H, 3.08%.

3bFA: Blue-violet crystals; mp 145—150 °C; IR (KBr disk) 1738 and 1710 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, 270 MHz) δ = 0.27 (9H, s, $Si(CH_3)_3$), 1.41 (1H, d, J = 3.43 Hz, CH_2), 2.17 (1H, d, J = 3.43 Hz, CH_2), 3.78 (3H, s, OCH_3), 3.86 (3H, s, OCH_3), and 5.65 (5H, s, Cp); MS (EI, 70 eV) *m/z* (rel intensity) 530 (M^+; 0.16), 417 (M^+-CF_3COO; 67), 330 ($M^+-CF_3COO-CH_2SiMe_3$; 40), 188 ($CpCoS_2^+$; 100), and 124 ($CpCo^+$; 47). Found: C, 38.52; H, 4.11%. Calcd for $C_{17}H_{22}CoF_3O_6S_2Si$: C, 38.49; H, 4.18%.

3dCl: Blue-violet crystals; mp 137—138 °C; IR (KBr disk) 1685 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, 270 MHz) were obtained as two sets of signals and these spectra were assigned to major and minor component according to the intensities. Major component δ = 2.33 (3H, s, CH_3), 3.75 (3H, s, OCH_3), 5.49 (5H, s, Cp), and 7.79 (1H, s, ring H); minor component δ = 2.68 (3H, s, CH_3), 3.71 (3H, s, OCH_3), 5.41 (5H, s, Cp), and 7.81 (1H, s, ring H); MS (EI, 70 eV) *m/z* (rel intensity) 322 (M^+; 4), 287 (M^+-Cl; 81), 272 ($M^+-Cl-CH_3$; 98), 188 ($CpCoS_2^+$; 100), and 124 ($CpCo^+$; 38). Found: C, 36.69; H, 3.64%. Calcd for $C_{10}H_{12}ClCoO_2S_2$: C, 37.22; H, 3.75%.

3dBr: Blue-violet crystals; mp 165—167 °C; IR (KBr disk) 1686 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, 270 MHz) were obtained as two sets of signals and these spectra were assigned to major and minor component according to the intensities. Major component δ = 2.49 (3H, s, CH_3), 3.74 (3H, s, OCH_3), 5.46 (5H, s, Cp), and 7.37 (1H, s, ring H); minor component δ = 2.67 (3H, s, CH_3), 3.71 (3H, s, OCH_3), 5.41 (5H, s, Cp), and 7.81 (1H, s, ring H); ^{13}C NMR ($CDCl_3$, 270 MHz) major component δ = 25.55 (CH_3), 52.22 (OCH_3), 86.52 (Cp), 119.26 (ring C), 162.86 (C=O), and 169.43 (ring C); minor component δ = 29.11 (CH_3), 52.22 (OCH_3), 85.72 (Cp), 119.26 (ring C), 162.86 (C=O), and 170.28 (ring C); MS (EI, 70 eV) *m/z* (rel intensity) 368 (M^+; 6.19), 366 (M^+; 5.91), 287 (M^+-Br; 100), 272 ($M^+-Br-CH_3$; 42), 188 ($CpCoS_2^+$; 61), and 124 ($CpCo^+$; 38). Found: C, 32.86; H, 3.26%. Calcd for $C_{10}H_{12}BrCoO_2S_2$: C, 32.71; H, 3.29%.

3dI: Blue-violet crystals; mp 177—183 °C; IR (KBr disk) 1686 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, 270 MHz) were obtained as two sets of signals. In this case the assignment to each component was difficult because of the similarity of the intensities. Thus we describe the corresponding signals in parallel. δ = 2.63, 2.74 (3H, s, CH_3), 3.71, 3.73 (3H, s, OCH_3), 5.37, 5.41 (5H, s, Cp), 7.60, 7.71 (1H, s, ring H); MS (EI, 70 eV) *m/z* (rel intensity) 414 (M^+; 2), 287 (M^+-I; 100), 272 ($M^+-Br-CH_3$; 38), 188 ($CpCoS_2^+$; 82), and 124 ($CpCo^+$; 33). Found: C, 29.07; H, 2.85%. Calcd for $C_{10}H_{12}CoIO_2S_2$: C, 29.00; H, 2.92%.

3eCl: The data for identification was described in the Ref. 14.

3fCl: Blue-violet crystals; IR (KBr disk) 2230, 2195, 1501, 1418, 1159, and 860 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ = 2.18 (3H, s, CH_3) and 5.66 (5H, s, Cp); MS (EI, 70 eV) *m/z* (rel intensity) 279 (M^+-Cl; 14), 264 ($M^+-Cl-CH_3$; 83), 188 ($CpCoS_2^+$; 100), and 124 ($CpCo^+$; 35). Found: C, 37.97; H, 2.50; N, 8.91%. Calcd for $C_{10}H_8ClCoN_2S_2$: C, 38.17; H, 2.56; N, 8.90%.

3gCl: Blue-violet crystals; mp 183—184 °C; ^1H NMR ($CDCl_3$, 270 MHz) δ = 2.23 (3H, s, CH_3), 5.46 (5H, s, Cp), and 7.0—7.3 (10H, m, Ph); MS (EI, 70 eV) *m/z* (rel intensity) 415 (M^+; 2), 380 (M^+-Cl; 57), 366 ($M^+-Cl-CH_3$; 82), 188 ($CpCoS_2^+$; 100), and 124 ($CpCo^+$; 47). The structure of the complex was determined by X-ray analysis but the satisfactory elemental analysis was not obtained.

Exchane of Anionic Ligand in a Suspension. To a dichloromethane solution (30 cm^3) of a three-component adduct (0.1—0.5 mmol), a small amount of aqueous solution of the salt of another anion was added. The suspension was stirred vigorously for 30 min at room temperature. After the reaction, the dichloromethane was removed. The composition of the three-component-adducts were determined by ^1H NMR.

X-Ray Crystallographic Studies. Crystals for X-ray analyses were obtained as described in the preparations. All of the measuremnts were made on a Rigaku AFC5S diffractometer with graphite monochomated Mo $K\alpha$ radiation (λ = 0.71069 Å).

The structure was solved by direct methods or the Patterson method and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Idealized positions were used for the hydrogen atoms, but their positions were not refined; the B values were refined.

All of the calculations were performed using the teXsan crystallographic software pakage of Molecular Structure Corporation. Table 3 presents crystal data, data collection parameters, and least-squares refinement parameters. Full crystal data, H-atom coordinates, thermal parameters, F_o-F_c tablers, and bond lengths and

Table 3. Crystal Data for Complexes **3aCl**, **3aFA**, **3bFA**, **3cCl**, **3dCl**, **3dBr**, **3dI**, **3fCl**, and **3gCl**.

	3aCl	**3aFA**	**3bFA**	**3cCl**	**3dCl**	**3dBr**	**3dI**	**3fCl**	**3gCl**
Formula	$C_{12}H_{14}O_4S_2ClCo$	$C_{14}H_{14}O_6S_2F_3Co$	$C_{14}H_{22}O_6SiF_3S_2Co$	$C_{15}H_{18}O_6S_2ClCo$	$C_{10}H_{12}O_2S_2ClCo$	$C_{10}H_{12}O_2S_2BrCo$	$C_{10}H_{12}O_2S_2ICo$	$C_{10}H_8N_2S_2ClCo$	$C_{20}H_{18}S_2ClCo$
Fw	380.75	458.31	520.41	452.81	322.71	367.16	414.16	314.69	416.87
Cryst. color, habit	Black, plate	Brown, cubic	Brown, cubic	Blue purple, needle	Black, cubic	Darkbrown, cubic	Darkbrown, prismatic	Black, cubic	Black, prismatic
Cryst. dimmens/nm	$0.07 \times 0.15 \times 0.30$	$0.23 \times 0.33 \times 0.37$	$0.37 \times 0.22 \times 0.27$	$0.17 \times 0.10 \times 0.33$	$0.20 \times 0.20 \times 0.25$	$0.17 \times 0.27 \times 0.27$	$0.13 \times 0.23 \times 0.27$	$0.15 \times 0.24 \times 0.27$	$0.13 \times 0.17 \times 0.30$
Cryst. system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic	Monoclinic
a/Å	14.451(2)	7.676(3)	9.277(5)	24.639(10)	8.021(2)	9.583(1)	9.640(2)	8.178(2)	30.623(4)
b/Å	7.284(2)	11.999(3)	13.140(7)	7.721(6)	15.092(1)	10.103(1)	10.260(1)	10.670(3)	5.968(1)
c/Å	15.951(2)	20.235(3)	19.240(3)	20.660(6)	10.3594(9)	7.270(1)	7.451(1)	7.402(2)	23.654(7)
α/deg						100.26(1)	98.75(1)	107.41(2)	
β/deg	113.75(1)	99.64(2)	102.82(2)	105.05(3)	94.26(1)	107.83(1)	108.40(1)	94.84(2)	122.606(7)
γ/deg						100.79(1)	102.53(1)	88.10(2)	
V/Å^3	1536.8(5)	1837.5(9)	2286(1)	3795(2)	1250.5(3)	637.0(2)	663.0(2)	614.1(3)	3642(4)
Space group	$P2_1/c$ (#14)	$P2_1/c$ (#14)	$P2_1/c$ (#14)	$C2_1/c$ (#15)	$P2_1/c$ (#14)	$P1$ (#2)	$P1$ (#2)	$P1$ (#2)	$C2/c$ (#15)
Z	4	4	4	8	4	2	2	2	8
d_{calc}/g cm^3	1.646	1.675	1.511	1.585	1.714	1.914	2.074	1.702	1.520
μ (Mo $K\alpha$)/cm^{-1}	15.69	12.18	10.38	12.92	19.00	48.02	39.20	19.25	13.17
No. of reflcns	Total: 3958	Total: 4746	Total: 5804	Total: 13692	Total: 3197	Total: 3108	Total: 3238	Total: 3201	Total: 4682
	Unique: 3814	Unique: 4425	Unique: 5477	Unique: 13351	Unique: 2994	Unique: 2935	Unique: 3057	Unique: 2822	Unique: 4595
	(R_{int} = 0.068)	(R_{int} = 0.015)	(R_{int} = 0.022)	(R_{int} = 0.056)	(R_{int} = 0.043)	(R_{int} = 0.011)	(R_{int} = 0.013)	(R_{int} = 0.009)	(R_{int} = 0.058)
Transm factors	0.8479—0.9890	0.8082—0.9997	0.8524—0.9989	0.8590—0.9997	0.8471—0.9999	0.5270—0.9979	0.7936—0.9997	0.5877—0.9964	0.6759—0.9945
No. observns with $I > \sigma(I)$	1317	3019	3159	3427	1579	2226	2651	2297	1669
No. variables	181	249	293	244	193	193	181	153	235
Reflcns/param	7.28	12.12	10.78	14.05	8.18	11.53	14.65	15.01	7.10
R; R_w	0.046; 0.032	0.038; 0.030	0.041; 0.031	0.047; 0.030	0.046; 0.034	0.025; 0.022	0.022; 0.025	0.037; 0.033	0.070; 0.054
Goodness of fit	1.36	2.54	2.11	1.72	1.78	1.76	3.69	3.61	2.62
Max peak (e Å^{-3}) infinal diff map	0.19	0.34	0.12	0.58	0.09	0.19	0.08	0.06	0.12

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