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Dinuclear molybdenum complexes containing the novel $\mu,\eta^{1:3}$-$\mathrm{AsS_2}$ ligand: synthesis and molecular structure of $[\{\mathrm{Cp^*_2Mo_2(CO)_2As_2S_4}\}\cdot 2\mathrm{Cr(CO)_5}]\cdot 0.5\mathrm{CH_2Cl_2}$ ($\mathrm{Cp^*} = \mathrm{C_5Me_5}$)

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Abstract

The reaction of $[\mathrm{Cp^*Mo(CO)_3Cl}]$ ($\mathrm{Cp^*} = \mathrm{C_5Me_5}$) with $\mathrm{K_3AsS_3}$ has been investigated under different conditions. At 56°C, the already known compounds $[\mathrm{Cp^*_2Mo_2S_4}]$ (**2**), $[\mathrm{Cp^*_2Mo_2As_2S_3}]$ (**3**), and $[\mathrm{Cp^*_2Mo_2S_4H_2}]$ (**4**) are formed along with $[\mathrm{Cp^*_2Mo_2(CO)_2As_2S_4}]$ (**5**). Reaction at 120°C only gives **2** and **3**. Complex **5** was characterized by means of its bisadduct $[\{\mathrm{Cp^*_2Mo_2(CO)_2As_2S_4}\}\cdot 2\mathrm{Cr(CO)_5}]$ (**6**). An X-ray crystallographic study of **6** reveals the presence of two novel $\mathrm{AsS_2}$ ligands, bridging in a pseudoallylic manner two Mo atoms. The $\mathrm{Cr(CO)_5}$ fragments are coordinated to both the outer sulfur atoms. Thus, each $\mathrm{AsS_2}$ ligand in **6** acts as a seven-electron ligand. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Molybdenum; Mixed ligands; Arsenic; Sulfur; Structure

1. Introduction

Compounds built-up from the elements As and S range from simple salts to neutral or anionic cage molecules [1]. Their ability to coordinate metal ions either leads to extended solid-state structures [2] or molecular mixed main-group-transition-metal clusters [1]. In coordination chemistry, the formation of extended structures may be suppressed by the introduction of sterically demanding groups at the metal, i.e. cyclopentadienyl (Cp) [3] or tris(diphenylphosphinomethyl)ethane (triphos) [4]. One may suppose the $[\mathrm{AsS_3}]^{3-}$ anion as the simplest negatively charged mixed ligand from As and S, but up to now there is only one report concerning its incorporation into an organometallic complex [5]. In order to evaluate the behavior of the $[\mathrm{AsS_3}]^{3-}$ species towards other reactive organometallic fragments, we investigated the reaction of $[\mathrm{Cp^*Mo(CO)_3Cl}]$ with $\mathrm{K_3AsS_3}$. Originally, one would expect the formation of $[\{\mathrm{Cp^*Mo(CO)_3}\}_3\mathrm{AsS_3}]$ (**1**) by means of elimination of KCl. However, the reaction turned out to be strongly temperature dependent, leading to products that incorporate fragments of the $\mathrm{AsS_3}$ unit of varying size. In this regard, there are obvious parallels with the reaction of $[\mathrm{Cp^*_2Mo_2(CO)_4}]$ with realgar, $\mathrm{As_4S_4}$ [6].

2. Results and discussion

The reaction of $[\mathrm{Cp^*Mo(CO)_3Cl}]$ with $\mathrm{K_3AsS_3}$ has been carried out in acetone and DMF. The different solvents and also different stoichiometries do not considerably influence the nature of the products obtained. This has also been observed when using $[\mathrm{Cp^*Mo(CO)_3I}]$ instead of $[\mathrm{Cp^*Mo(CO)_3Cl}]$. However, we found a strong temperature dependency [7]. For these reasons, we describe in the following text the reactions of $[\mathrm{Cp^*Mo(CO)_3Cl}]$ with 0.5 equivalents of $\mathrm{K_3AsS_3}$ at 56°C in acetone and DMF and at 120°C in DMF.

2.1. Reaction temperature 56°C

In acetone at 56°C red–violet $[\mathrm{Cp^*_2Mo_2As_2S_3}]$ (**3**) [6], red $[\mathrm{Cp^*_2Mo_2S_4H_2}]$ (**4**) [8] and bright red $[\mathrm{Cp^*_2Mo_2(CO)_2As_2S_4}]$ (**5**) complexes (Scheme 1) were

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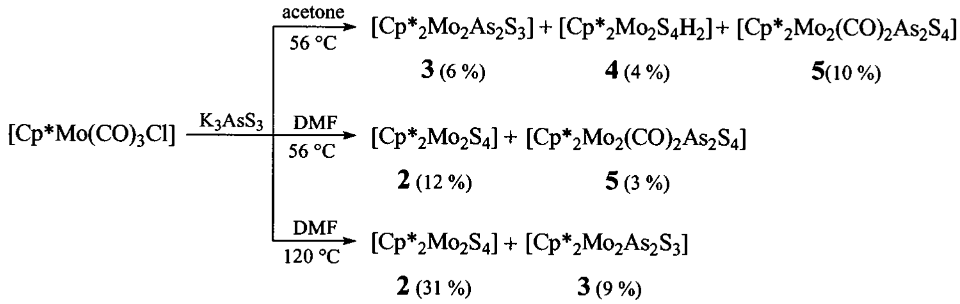
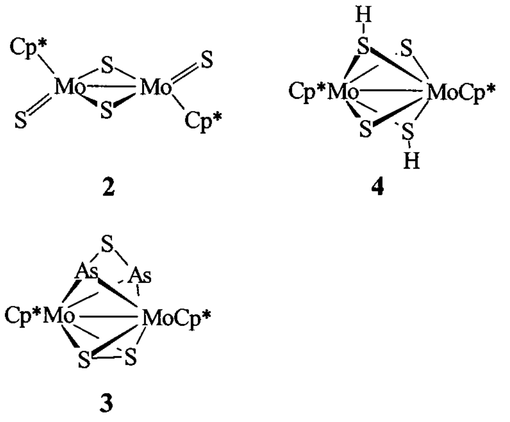


Scheme 1.



Scheme 2. Structures of the already known complexes **2** [9], **3** [6], and **4** [8].

formed after 16 h. In DMF, under similar conditions, [$Cp^*_2Mo_2(CO)_2As_2S_4$] (**5**) has been found along with brown [*anti*-$Cp^*_2Mo_2S_4$] (**2**) [9]. The yield for each complex was between 4 and 12%. In addition to the well-defined compounds **2–5**, a green–brown mixture of several compounds was obtained. According to ^{1}H-NMR spectra, up to 15 different Cp* signals of varying intensity were observed.

The colors and the spectroscopic data of the CO free compounds **2–4** are identical with those of already known complexes (Scheme 2). The composition of **5** follows from analytical data and the FD mass spectrum. The IR spectrum of **5** contains an absorption at 1915 cm^{-1} characteristic of equivalent terminal CO groups. The ^{1}H-NMR spectrum reveals only one sharp signal ($\delta = 1.85$) for the CH_3 groups. As the crystallization of **5** was extremely poor, its characterization has been achieved via the $Cr(CO)_5$ bisadduct **6** (see below).

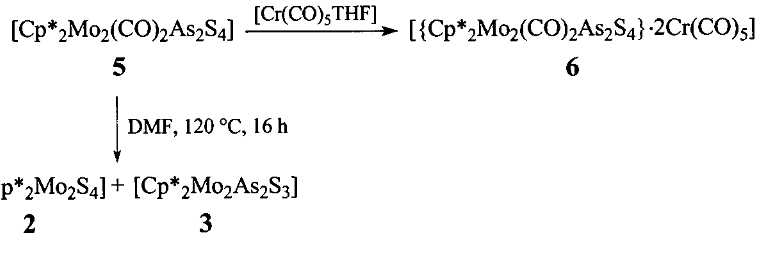
The reaction at 20°C (16 h) may be mentioned briefly. Several products were obtained which decomposed slowly in solution. The IR spectra of these compounds showed absorptions at 2005 and 1960 cm^{-1}, with patterns resembling that of the $Cp^*Mo(CO)_3$ moiety. One may speculate that one of these compounds could be the hypothetical [$\{Cp^*Mo(CO)_3\}_3AsS_3$] (**1**). Unfortunately, the thermal lability prevents further characterization. After 7 days, the CO containing compounds have disappeared and instead **2**, **5**, [*syn*-$Cp^*_2Mo_2S_4$] [10] and a brown–green mixture formed, the latter being closely related to that observed in the 56°C reaction.

2.2. Reaction temperature 120°C

The reaction of [$Cp^*Mo(CO)_3Cl$] with K_3AsS_3 at 120°C in DMF gave [*anti*-$Cp^*_2Mo_2S_4$] (**2**) (31% yield) and [$Cp^*_2Mo_2As_2S_3$] (**3**) (9%) (Scheme 1). The CO-containing complex **5** was not observed any more. In order to check whether **5** behaves as a thermally labile intermediate product a solution of **5** in DMF was heated at 120°C for 16 h. After chromatographic work up, the CO-free products **2** and **3** were obtained in 16 and 28% yield, respectively (Scheme 3).

2.3. Reaction of [$Cp^*_2Mo_2(CO)_2As_2S_4$] (5) with [$Cr(CO)_5THF$]

As the crystallization tendencies of [$Cp^*_2Mo_2(CO)_2As_2S_4$] (**5**) in different solvents were strikingly



Scheme 3.

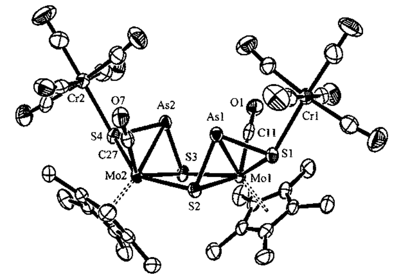


Fig. 1. Molecular structure of **6** (ORTEP plot with 50% probability). The solvent (0.5 CH_2Cl_2 per molecule) is not shown.

Table 1
Selected distances (Å) and angles (°) of **6**

Mo(1)–As(1)	2.617(1)	Mo(2)–As(2)	2.605(1)
Mo(1)–S(1)	2.538(2)	Mo(2)–S(2)	2.541(2)
Mo(1)–S(2)	2.551(2)	Mo(2)–S(3)	2.544(2)
Mo(1)–S(3)	2.539(2)	Mo(2)–S(4)	2.540(2)
Mo(1)–C(11)	1.946(7)	Mo(2)–C(27)	1.966(7)
O(1)–C(11)	1.168(9)	O(7)–C(27)	1.150(9)
As(1)–S(1)	2.206(2)	As(2)–S(3)	2.211(2)
As(1)–S(2)	2.208(2)	As(2)–S(4)	2.205(2)
Cr(1)–S(1)	2.495(2)	Cr(2)–S(4)	2.490(2)
Mo(1)···Mo(2)	4.021	As(1)···As(2)	3.177
Mo(1)–S(2)–Mo(2)	104.3(1)	Mo(1)–S(3)–Mo(2)	104.6(1)
S(1)–As(1)–S(2)	91.5(1)	S(3)–As(2)–S(4)	91.2(1)
S(1)–Mo(1)–S(2)	76.8(1)	S(3)–Mo(2)–S(4)	76.7(1)
As(1)–Mo(1)–S(1)	50.7(1)	As(2)–Mo(2)–S(3)	50.9(1)
As(1)–Mo(1)–S(2)	50.6(1)	As(2)–Mo(2)–S(4)	50.7(1)
As(1)–Mo(1)–S(3)	90.6(1)	As(2)–Mo(2)–S(2)	90.6(1)
S(1)–Mo(1)–C(11)	89.7(2)	S(2)–Mo(2)–C(27)	87.0(2)
S(3)–Mo(1)–C(11)	86.9(2)	S(4)–Mo(2)–C(27)	88.9(2)
Mo(1)–C(11)–O(1)	175.9(6)	Mo(2)–C(27)–O(7)	176.5(5)
As(1)–S(1)–Cr(1)	99.9(1)	As(2)–S(4)–Cr(2)	102.2(2)
Mo(1)–S(1)–Cr(1)	127.3(1)	Mo(2)–S(4)–Cr(2)	127.3(1)

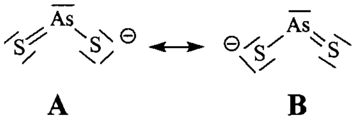
poor, we tried to improve these properties by the coordination of $Cr(CO)_5$ groups. Indeed, reaction of a THF solution of **5** with two equivalents of [$Cr(CO)_5$-THF] gave the bisadduct [{$Cp^*_2Mo_2(CO)_2As_2S_4$}·$2Cr(CO)_5$] (**6**) in 70% yield (Scheme 3). Additional products **7** and **8** have been identified by means of FD mass spectra as [$Cp^*_2Mo_2S_6O{\cdot}Cr(CO)_5$] (**7**) and [$Cp^*_2Mo_2S_6{\cdot}Cr(CO)_5$] (**8**), respectively. The presence of $Cr(CO)_5$ groups in **7** and **8** is supported by IR spectra. ^{1}H-NMR spectra indicate equivalent Cp* ligands. A structural assignment is not yet possible because of the lack of analytical data and single crystals. It should be noted that for sulfur-rich dimolybdenum compounds there are numerous isomerism possibilities [11].

The IR spectrum of **6** exhibits CO absorptions at 2060, 1985, and 1930 cm^{-1}, being typical for the $Cr(CO)_5$ fragment, and a shoulder at 1910 cm^{-1}. The latter may be attributed to the Mo(CO) fragments. The ^{1}H-NMR spectrum of **6** resembles that of **5**, there is only a slight shift of the singlet of the methyl resonances.

Single crystals of **6** were obtained from CH_2Cl_2 and studied by an X-ray diffraction analysis. The molecular structure of **6** (Fig. 1) contains a planar Mo_2S_2 four-membered ring as the central feature. Two CO and two Cp* ligands are attached to this ring at the same side. The coordination sphere around each of the Mo atoms is completed by a η^3-AsS_2 ligand. Each of the non-bridging wingtips of this ligand bears a $Cr(CO)_5$ fragment. The molecule contains a (non-crystallographic) C_2 axis perpendicular to the four-membered ring, which is in agreement with the spectroscopic data.

The AsS_2 ligands behave as five-electron ligands with respect to both Mo atoms and as seven-electron ligands with respect to all metal centers. Together with the electronic contribution of the other ligands, the metal atoms achieve noble gas configuration. In agreement with this is the Mo–Mo distance of 4.021 Å, which excludes a metal–metal bond. The interligand distance As(1)···As(2) (3.177(2) Å) is beyond that of direct bonding interactions [12].

Of particular interest is the novel AsS_2 ligand. This ligand may be described by the two resonance formulas **A** and **B**, which illustrate an analogy with the NO_2^- ion. The only other related mixed Group 15/16 ligand belonging to this structural type is the terminal PSe_2 ligand in [$W(=Se)(PSe_4)(PSe_2)$]$^{2-}$ [13]. The pseudoallylic character of the ligand is also supported by the observation that both As–S distances within one and the same ligand are practically identical. The relatively short As–S distances (average 2.208(2) Å) may indicate (Table 1) some p(π) contribution by the main-group ligands [12].



In conclusion, the reaction of [$Cp^*Mo(CO)_3Cl$] with K_3AsS_3 proceeds in a rather unselective manner. The temperature dependence leads to final products that are made exclusively of sulfur ligands (**2**) or contain a mixed Group 15/16 ligand (**3**). Complex **5** forms as an intermediate product at lower temperature. This complex is distinguished by two novel pseudoallylic $\mu,\eta^{1:3}$-AsS_2 ligands. At higher temperatures the formal elimination of sulfur from this mixed ligand seems to be likely, for **5** decomposes thermally under the release of sulfur, which may be incorporated in **2**. The other product from this thermal degradation is $Cp^*_2Mo_2As_2S_3$ (**3**). This complex, which has a triple-decker-like structure is one of the final products in the reaction of [$Cp^*_2Mo_2(CO)_4$] with realgar [6]. Thus, the fragmentation of the AsS_3 building block seems to parallel to that of the As_4S_4 cradle in the presence of the reactive Cp*Mo fragments.

3. Experimental

Experimental and spectroscopic techniques have been reported in Ref. [14]. K_3AsS_3 was prepared from K, S_8, and As_2S_3 in liquid NH_3 [15]. $[\mathrm{Cp^*Mo(CO)_3Cl}]$ was synthesized as described in Ref. [16].

3.1. Reaction of K_3AsS_3 with $[\mathrm{Cp^*Mo(CO)_3Cl}]$

56°C/acetone. A mixture of 0.28 g (0.97 mmol) of K_3AsS_3, 0.68 g (1.94 mmol) of $[\mathrm{Cp^*Mo(CO)_3Cl}]$ and 50 ml of acetone was stirred for 16 h at 56°C. After the evaporation of the solvent the brown residue was suspended in toluene, filtered and washed several times with toluene. Then the combined filtrates were concentrated to 20 ml. Chromatography on SiO_2 (column 15 cm, ∅ 3 cm) gave upon elution with toluene an orange band, containing small amounts of starting material and $[\mathrm{Cp^*_2Mo_2(CO)_6}]$ [17], followed by a red band containing $[\mathrm{Cp^*_2Mo_2As_2S_3}]$ (**3**) in 6% yield and another red band containing $[\mathrm{Cp^*_2Mo_2S_4H_2}]$ (**4**) in 4% yield. Elution with acetone gave 245 mg of a complex green–brown mixture that could not be separated by chromatography. The brown residue from the filtration was dissolved in CH_2Cl_2 and chromatographed on SiO_2 (column 7 cm, ∅ 3 cm). Elution with CH_2Cl_2 gave, after a bright red impurity, a red band containing $[\mathrm{Cp^*_2Mo_2(CO)_2As_2S_4}]$ (**5**) in 10% yield.

56°C/DMF. The suspension of 0.28 g (0.97 mmol) of K_3AsS_3 and 0.68 g (1.94 mmol) of $[\mathrm{Cp^*Mo(CO)_3Cl}]$ in 50 ml of DMF was stirred for 16 h at 56°C. After vacuum distillation of the solvent the brown residue was suspended in toluene, filtered and washed with toluene. The combined filtrates were concentrated to 20 ml and then chromatographed on SiO_2 (column 15 cm, ∅ 3 cm). Elution with toluene gave a red band containing small amounts of yet unidentified compounds followed by a brown band containing [*anti*-$\mathrm{Cp^*_2Mo_2S_4}$] (**2**) in 12% yield. Elution with acetone gave 215 mg of a complex green–brown mixture as already described above. The red–brown residue from the filtration was dissolved in CH_2Cl_2 and chromatographed on SiO_2 (column 7 cm, ∅ 3 cm). Elution with CH_2Cl_2 gave a red band containing $[\mathrm{Cp^*_2Mo_2(CO)_2As_2S_4}]$ (**5**) in 3% yield.

Complex **2** [9]: $C_{20}H_{30}Mo_2S_4$ (590.6). ^{1}H-NMR ($CHCl_3$-*d*): 2.07 (s, 30) ppm. FDMS (toluene): 590.0.

Complex **3** [6]: $C_{20}H_{30}As_2Mo_2S_3$ (708.4). ^{1}H-NMR ($CHCl_3$-*d*): 2.15 (s, 30) ppm. FDMS (toluene): 708.0.

Complex **4** [8]: $C_{20}H_{32}Mo_2S_4$ (592.6). ^{1}H-NMR ($CDCl_3$-*d*): -1.95 (s, 1), -2.02 (s, 1), 2.24 (s, 30). FDMS (toluene): 592.0.

Complex **5**: Anal. Found: C, 32.58; H, 3.83. Calc. for $C_{22}H_{30}As_2Mo_2O_2S_4$ (MW 796.5): C, 33.18; H, 3.80%. ^{1}H-NMR ($CHCl_3$-*d*): 1.85 (s, 30) ppm. IR (KBr): $\tilde{\nu}$(CO) 1915 cm^{-1}. FDMS (CH_2Cl_2): 795.8.

120°C/DMF. A suspension of 0.28 g (0.97 mmol) of K_3AsS_3 and 0.68 g (1.94 mmol) of $[\mathrm{Cp^*Mo(CO)_3Cl}]$ in 50 ml of DMF was stirred for 16 h at 120°C. After removal of the solvent in vacuo the brown residue was suspended in toluene, filtered, and washed with toluene. After concentration of the filtrates to 15 ml the solution was chromatographed on SiO_2 (column 15 cm, ∅ 3 cm). Elution with toluene gave a red band containing a mixture of brown [*anti*-$\mathrm{Cp^*_2Mo_2S_4}$] (**2**) and red $[\mathrm{Cp^*_2Mo_2As_2S_3}]$ (**3**). The yields were 9% for **2** and 31% for **3** as determined by ^{1}H-NMR spectroscopy. Elution with acetone gave 180 mg of a green–brown mixture (see Section 2.1).

3.2. Thermolysis of $[\mathrm{Cp^*_2Mo_2(CO)_2As_2S_4}]$ (5)

A solution of 0.12 g (0.14 mmol) of $[\mathrm{Cp^*_2Mo_2(CO)_2As_2S_4}]$ (**5**) in 50 ml of DMF was stirred for 16 h at 120°C. After removal of the solvent in vacuo, the brown residue was dissolved in toluene and chromatographed on SiO_2 (column 15 cm, ∅ 3 cm). Elution with toluene gave red $[\mathrm{Cp^*_2Mo_2As_2S_3}]$ (**3**) in 28% yield and [*anti*-$\mathrm{Cp^*_2Mo_2S_4}$] (**2**) in 16% yield as determined by ^{1}H-NMR spectroscopy.

3.3. Synthesis of $[\{\mathrm{Cp^*_2Mo_2(CO)_2As_2S_4}\}\cdot 2\mathrm{Cr(CO)_5}]$ (6)

An orange solution of 100 mg (0.125 mmol) of $[\mathrm{Cp^*_2Mo_2(CO)_2As_2S_4}]$ (**5**) and two equivalents of $[\mathrm{Cr(CO)_5THF}]$ (from 55 mg (0.25 mmol) of $[\mathrm{Cr(CO)_6}]$) in 80 ml of THF was stirred for 16 h at 20°C. After evaporation of the solvent the residue was dissolved in toluene. Chromatography on SiO_2 (column 20 cm, ∅ 3 cm) gave upon elution with toluene green–brown $[\mathrm{Cp^*_2Mo_2S_6O}\cdot\mathrm{Cr(CO)_5}]$ (**7**) (yield 15%), green–brown $[\mathrm{Cp^*_2Mo_2S_6}\cdot\mathrm{Cr(CO)_5}]$ (**8**) (yield 7%) and then red $[\{\mathrm{Cp^*_2Mo_2(CO)_2As_2S_4}\}\cdot 2\mathrm{Cr(CO)_5}]$ (**6**) (yield 70%). Single crystals of **6** have been obtained from CH_2Cl_2.

Complex **6**: Anal. Found: C, 33.41; H, 2.80. Calc. for $C_{32}H_{30}As_2Cr_2Mo_2O_{12}S_4$ (MW 1180.6): C, 32.56; H, 2.56%. ^{1}H-NMR ($CHCl_3$-*d*): 1.93 (s, 30) ppm. IR (KBr, cm^{-1}): $\tilde{\nu}$(CO) 2060m, 1985w, 1930vs(br), 1910sh. FDMS (toluene): 796.6 [Calc. mass 795.8 for $C_{22}H_{30}As_2Mo_2O_2S_4$ (**5**)].

Complex **7**: $C_{25}H_{30}CrMo_2O_6S_6$ (862.8): ^{1}H-NMR ($CHCl_3$-*d*): 1.85 (s, 30) ppm. IR (KBr, cm^{-1}): $\tilde{\nu}$(CO) 2050w, 1995s, 1960s, 1935s, 1880s. FDMS (toluene): 862.0.

Complex **8**: $C_{25}H_{30}CrMo_2O_5S_6$ (846.8): ^{1}H-NMR ($CDCl_3$-*d*): 1.78 (s, 30). IR (KBr, cm^{-1}): $\tilde{\nu}$(CO) 2050w, 2000s, 1965s, 1930s, 1875s. FDMS (toluene): 846.1.

3.4. Crystallographic data for $\mathbf{6}\cdot 0.5CH_2Cl_2$

Dark needles ($0.30 \times 0.26 \times 0.10$ mm^3), monoclinic $P2_1/n$; cell: *a*, 10.2679(6); *b*, 27.5940(19); *c*, 17.8065(11)

Å; β, 103.673(7)°; V, 4902.2 Å^3, $Z=4$; absorption correction: numerical. Transmission factor (min/max) 0.7835/0.4988, μ, 2.60 mm^{-1}. $F(000)$ 2520, d(calc) = 1.734 g cm^{-3}; Stoe-IPDS. Mo–K$_\alpha$ radiation, graphite monochromator, 36 539 collected reflections; 6446 unique reflections [$I > 2.0\sigma(I)$]. Structure solution by means of direct methods and Fourier synthesis. $R_1 = 0.0483$, $wR_2 = 0.1252$; residual electron density (max/min) 1.851/−0.606 e Å^{-3}, goodness-of-fit on $F^2 = 1.050$. During structural refinement, two holes have been detected containing two disordered solvent molecules. Refinement by difference Fourier analysis was not possible. Calculation by means of the program SQUEEZE [18] localized these gaps at −0.008, 0.0, 0.0, and 0.010, 0.50, 0.50, respectively. The approximate size of 503 Å^3 of each gap corresponds to 38 and 40 electrons, respectively, equal to two CH_2Cl_2 molecules.

4. Supplementary material

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Center, CCDC no. 153532 for compound **5**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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