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Indium(III) thiolate-bridged molybdenocene complexes: crystal structure of $[InCl_2\{MoCp_2(\mu\text{-}SEt)_2\}_2][BPh_4]\cdot(CH_3)_2CO$

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Abstract

The reaction of $[MoCp_2(SR)_2]$ (R=CH_3, C_2H_5, n-$C_{14}H_{29}$ or C_6H_5) with $InCl_3$ in ethanol affords new compounds which, after treatment with NH_4PF_6, were fully characterized as the hexafluorophosphate salts $[In\{MoCp_2(\mu\text{-}SR)_2\}_3]\,[PF_6]_3$.

A new monocation $[InCl_2\{MoCp_2(\mu\text{-}SR)_2\}_2]^+$ was isolated as a tetraphenylborate salt and structurally characterized by a single-crystal X-ray diffraction study. The molybdenum atoms exhibit the usual bent metallocene structure with a distorted tetrahedron around each metal atom. The coordination around the indium atom is *cis*-octahedral. The InS_4Cl_2 core has a pseudo two-fold symmetry axis through the In atom bisecting the midpoint of the Cl–Cl edge of the coordination polyhedron. This pseudosymmetry extends to the Mo atoms and to some extent to the Cp ligands. The In–Mo distances, 4.0401(5) and 4.0703(5) Å, and the large In–S–Mo angles indicate no interaction between the two different metal centres.

Key words: Molybdenum; Indium; Metallocenes; Thiolate; Crystal structure

1. Introduction

The current interest in organotransition-metal complexes containing heavy metal atoms such as gallium, indium and thallium has been stimulated by the potential for novel catalytic systems and precursors for new materials relevant to the technology of semiconductors [1].

Although a significant number of indium complexes have been reported [2–9], heterometallic indium–transition metal compounds are less well known. The earliest studies describing the catalytic ability of this family of compounds, refers to compound $[In\{Co(CO)_4\}_3]$ [10] in the dimerization of norbornadiene [11]. Most of the compounds studied are manganese and rhenium carbonyl derivatives possessing metal–metal bonds [12,13], and some such as $[Re_4(CO)_{12}\{\mu_3\text{-}InRe(CO)_5\}_4]$ [14] and $[Fe_2(CO)_8\{\mu\text{-}InMn(CO)_5\}_2]$ [15] have had their structures determined by X-ray diffraction. However, there are only few examples of complexes with indium and Group 6 transition metals [16–18].

As an extension of our previous synthetic work on the chelation of metalloligands, $[MCp_2(SR)_2]$ (M = Mo^{IV} or W^{IV}) [19], and with the objective of preparing In–Mo complexes, we studied the reaction of $InCl_3$ with some molybdocene bisthiolate derivatives. The versatility of bisthiolate complexes $[MCp_2(SR)_2]$ (M = Mo, W, Ti, Nb, Ta or Zr) for the synthesis of thiolato-bridged complexes is well documented and a variety of heteronuclear bimetallic compounds has been characterized over the past 30 years [20]. To our knowledge we now report the synthesis and characterization of the first biscyclopentadienylmolybdenumindium complexes, and the molecular structure of $[InCl_2\{MoCp_2(\mu\text{-}SEt)_2\}][B(C_6H_5)_4]$.

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2. Results and discussion

2.1. Chemical studies

The product of the reaction between complexes $[MoCp_2(SR)_2]$ (R = alkyl or aryl) and $InCl_3$ depends on the bulk of the substituent R on the thiolate. It was found that, when R is a straight chain such as CH_3, C_2H_5 or n-$C_{14}H_{29}$, a metathesis reaction occurs, affording the compounds $[In\{MoCp_2(\mu\text{-}SR)_2\}_3]Cl_3$. However, when R is bulkier, such as s-C_3H_7, t-C_4H_9 or C_6H_5, insoluble products are obtained.

The knowledge that compounds of Group 13 form numerous adducts with Lewis bases [21] together with published results on phosphidoindium compounds showing the influence of the bulk of the ligands on the final monomeric or dimeric indium compound [4] led us to suggest the formula $(InCl_3\{MoCp_2(\mu\text{-}SR)_2\})_x$ for the insoluble products. This is consistent with the elementary analysis and IR spectroscopy studies of the crude products. However, no further characterization was reported.

In order to obtain suitable crystals for X-ray structural characterization of the compounds $[In\{MoCp_2(\mu\text{-}SR)_2\}_3]Cl_3$, various recrystallizations were carried out with the aim of replacing Cl^- by larger anions such as PF_6^- and $[B(C_6H_5)_4]^-$. Surprisingly a new monocationic complex was obtained in the last case, and the product was identified as $[InCl_2\{MoCp_2(\mu\text{-}SEt)_2\}_2]$-$[B(C_6H_5)_4]$. However, substitution of Cl^- by PF_6^- should have been straightforward, since this recrystallization is more rapid. The crystallographic structure revealed two *cis* Cl^- ligands (see below) as would be expected from substitution of one pair of thiolates in solution. The driving force on the initial reaction of $[MCp_2(SR)_2]$ with $InCl_3$ seems to be the insolubility of one of the compounds produced, $[In\{MCp_2(\mu\text{-}SR)_2\}_3]Cl_3$, and changes in the experimental conditions would eventually lead to other species such as $[InCl_2\{MCp_2(\mu\text{-}SR)_2\}_2Cl$. Nevertheless, no further experiments have been done to test this hypothesis.

Although this result is surprising, it can be understood on the basis of the Lewis acidity and chlorophilicity of indium compounds. This behaviour has also been reported recently by others who found that the reaction of indium(I) chloride with $[Mo_2(CO)_6(\eta^5\text{-}C_5H_5)_2]$ [17] or $InCl_3$ with two equivalents of $Na[Mo(CO)_3(\eta^5\text{-}C_5H_5)_2]$ [18] gives the same In(III) final product $[Na(THF)_2][InCl_2\{Mo(CO)_3(\eta^5\text{-}C_5H_5)\}_2]$.

2.2. Crystallographic studies

The crystal structure of the title complex contains discrete $[InCl_2\{MoCp_2(SEt_2)_2\}_2]^+$ cations, $[B(C_6H_5)_4]^-$ anions and a molecule of acetone.

The molecular structure of the cation is represented in Fig. 1. Selected bond lengths, bond angles and torsion angles are listed in Table 1.

The molybdenum atoms exhibit the usual bent metallocene structure formed by a distorted tetrahedron around each metal. The coordination sphere comprises two π-bonded cyclopentadienyl rings and two ethanothiolates, which bridge the two different metal centres.

The coordination of the indium atom can be discussed as proposed by Kepert [8] for six-coordinated

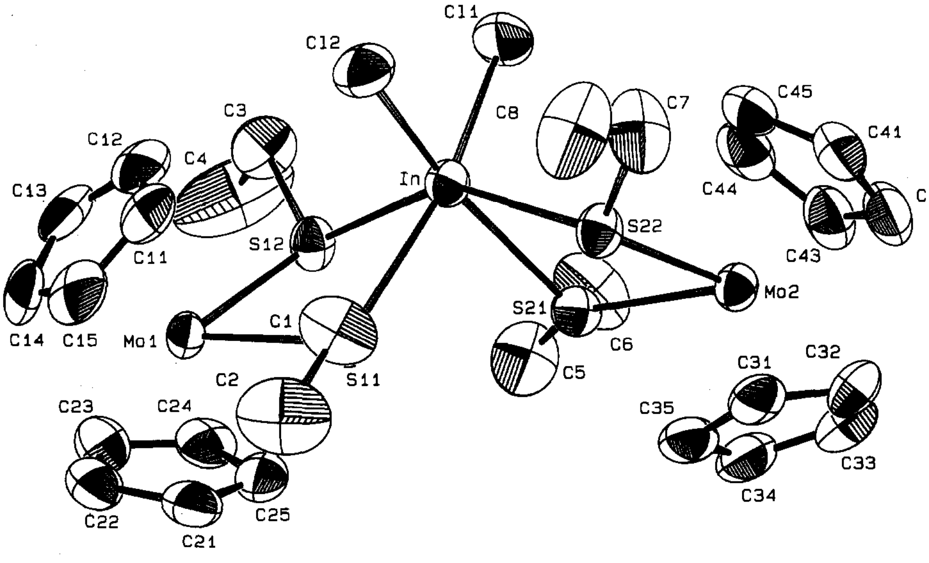

Fig. 1. ORTEP [4] drawing of the $[\{Cp_2Mo(SEt_2)_2\}_2InCl_2]^+$ cation, showing the atomic notation. The thermal ellipsoids are drawn at the 50% probability level.

TABLE 1. Selected bond lengths (Å), bond angles (°) and torsion angles (°) for $[\text{InCl}_2(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}(\mu\text{-SEt})_2\}_2][\text{BPh}_4]\cdot(\text{CH}_3)_2\text{CO}$

Bond lengths			
Cation			
In–S(11)	2.6776(12)	In–S(21)	2.7196(13)
In–S(12)	2.5868(12)	In–S(22)	2.6058(13)
In–Cl(1)	2.4740(14)	In–Cl(2)	2.4978(13)
Mo(1)–S(11)	2.5051(12)	Mo(1)–S(12)	2.4648(12)
Mo(2)–S(21)	2.4811(12)	Mo(2)–S(22)	2.4852(12)
Mo(1)–Cp(11–15) [a]	1.973(16)	Mo(1)–Cp(21–25) [b]	1.984(14)
Mo(2)–Cp(31–35) [c]	1.990(9)	Mo(2)–Cp(41–45) [d]	1.977(10)
S(11)–C(1)	1.824(7)	S(12)–C(3)	1.829(6)
S(21)–C(5)	1.850(8)	S(22)–C(7)	1.817(6)
Anion			
B(1)–C(51)	1.628(7)	B(1)–C(61)	1.665(7)
B(1)–C(71)	1.654(7)	B(1)–C(81)	1.651(7)
Ranges of C–C bond lengths in cation and anion			
C(1–8)	1.479(13)–1.535(9)		
C(11–15)	1.356(11)–1.413(11)	C(21–25)	1.380(8)–1.402(8)
C(31–35)	1.374(9)–1.411(8)	C(41–45)	1.389(9)–1.421(9)
C(51–56)	1.356(9)–1.393(7)	C(61–66)	1.357(8)–1.394(8)
C(71–76)	1.351(10)–1.408(7)	C(81–86)	1.348(9)–1.396(7)
Bond angles			
Cation			
S(11)–In–S(12)	69.62(5)	S(11)–In–S(21)	89.27(4)
S(11)–In–S(22)	88.45(5)	S(12)–In–S(21)	85.76(4)
S(12)–In–S(22)	147.24(7)	S(21)–In–S(22)	69.40(5)
Cl(1)–In–Cl(2)	91.56(6)		
In–S(11)–Mo(1)	101.85(3)	In–S(12)–Mo(1)	105.31(3)
In–S(21)–Mo(2)	101.79(3)	In–S(22)–Mo(2)	104.95(3)
S(11)–Mo(1)–S(12)	74.44(5)	S(21)–Mo(2)–S(22)	75.29(5)
Cp–Mo(1)–Cp [e]	133.0(2)	Cp–Mo(2)–Cp [e]	133.5(2)
S(11)–C(1)–C(2)	114.0(4)	S(12)–C(3)–C(4)	111.4(5)
S(21)–C(5)–C(6)	112.3(4)	S(22)–C(7)–C(8)	113.8(4)
Anion			
C(51)–B(1)–C(61)	107.0(4)	C(51)–B(1)–C(71)	110.5(4)
C(51)–B(1)–C(81)	108.8(4)	C(61)–B(1)–C(71)	110.0(4)
C(61)–B(1)–C(81)	111.5(4)	C(71)–B(1)–C(81)	109.1(3)
Ranges of C–C–C bond angles in cation and anion			
C(11–15)	106.9(7)–110.3(7)	C(21–25)	106.4(5)–109.2(6)
C(31–35)	106.9(5)–108.8(6)	C(41–45)	105.7(5)–109.7(6)
C(51–56)	114.7(5)–123.0(5)	C(61–66)	114.1(5)–123.6(6)
C(71–76)	114.3(5)–123.0(6)	C(81–86)	114.1(5)–123.5(6)
Torsion angles			
Cation			
In–S(11)–C(1)–C(2)	−179.8(5)	In–S(12)–C(3)–C(4)	150.9(5)
In–S(21)–C(5)–C(6)	−94.2(3)	In–S(22)–C(7)–C(8)	82.6(4)
Anion			
C(51)–B(1)–C(61)–C(62)	169.9(7)	C(51)–B(1)–C(71)–C(72)	134.6(9)
C(51)–B(1)–C(81)–C(82)	68.2(6)	C(61)–B(1)–C(71)–C(72)	16.7(7)
C(61)–B(1)–C(81)–C(82)	−174.0(8)	C(71)–B(1)–C(81)–C(82)	−52.4(7)

[a] Denotes ring normal to C(11)–C(15).
[b] Denotes ring normal to C(21)–C(25).
[c] Denotes ring normal to C(31)–C(35).
[d] Denotes ring normal to C(41)–C(45).
[e] Denotes angle between ring normals.

TABLE 2. Kepert spherical coordinates of the chelating atoms with respect to the central indium atom

Chelating atom (Kepert notation)	r (Å)	ϕ (°)	θ (°)
S11(A)	2.677	45.70	292.33
S12(B)	2.587	73.19	10.02
S22(C)	2.606	73.19	188.50
S21(D)	2.720	43.58	111.85
Cl1(E)	2.474	133.93	90.00
Cl2(F)	2.497	134.49	270.00

r, ϕ and θ are spherical coordinates.

The regular *cis*-octahedral coordination is characterized by the following relationships for the various binding atoms A to F: $\phi_A = \phi_D$, $\phi_B = \phi_C$ and $\phi_E = \phi_F$; $\theta_C = 180 + \theta_B$, $\theta_D = 180 + \theta_A$, $\theta_E = 90°$ and $\theta_F = 270°$.

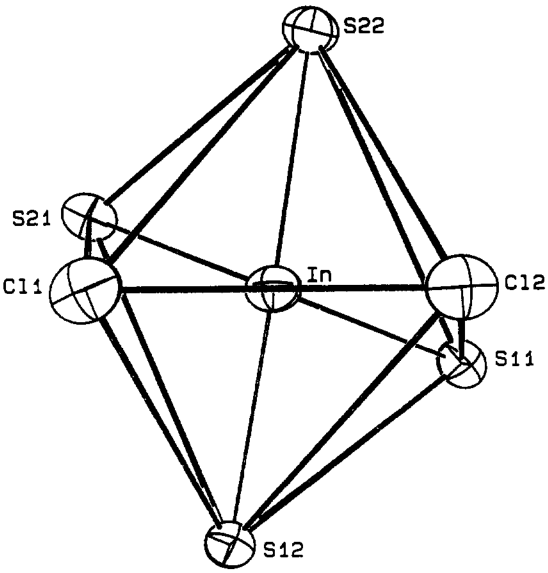

Fig. 2. ORTEP [4] drawing of the $InCl_2S_4$ core of the $[\{Cp_2Mo(SEt_2)_2\}_2InCl_2]^+$ cation, viewed down the pseudo two-fold axis. The thermal ellipsoids are drawn at the 50% probability level.

$[M(bidentate)_2(monodentate)_2]$ complexes. Each $MoCp_2(SEt)_2$ moiety can be regarded as bidentate, while the chlorides are monodentate. Table 2 lists the spherical coordinates of the chelating sulfur and chloride atoms with respect to the central metal atom. These data are consistent with a *cis*-octahedral coordination about the In atom. Kepert also used the normalized bite, defined as the distance between the two donor atoms of each bidentate ligand divided by the average metal–ligand bond length, to characterize the different stereochemical isomers observed in $[M(bidentate)_2(monodentate)_2]$ complexes. Values between 0.95 and 1.25 were obtained for complexes where the *cis*-octahedral structure was found to be significantly more stable than the other possible isomers, *trans*-octahedral, pentagonal pyramid or trigonal prism. The values calculated for the title complex, 1.13 and 1.14, are consistent with *cis*-octahedral geometry. Figure 2 clearly shows that the InS_4Cl_2 core has a pseudo two-fold symmetry axis through the In atom which bisects the midpoint of the Cl–Cl edge of the coordination polyhedron. This pseudosymmetry extends to the Mo atoms and to some extent to the Cp ligands, but not to the ethyl groups bonded to the sulfur atoms.

The In–Cl bond lengths, 2.474(1) and 2.498(1) Å, are comparable with the values in other indium(III) six-coordinated species [22] with chloride ligands only (average In–Cl distance of 2.52 Å) or in complexes also containing oxygen donor ligands, where the mean value for the In–Cl length *trans* to O is 2.46 Å. Five- and four-coordinated species [22], such as $[InCl_5]^{2-}$ and $[InCl_4]^-$ have, on average, In–Cl lengths shorter by 0.09 Å and 0.17 Å respectively.

A comparison of structural parameters of six-coordinated indium species with thio and oxygen ligands is presented in Table 3. In the majority of the cases, complete coordination is achieved with a tris-bidentate ligand. Thus symmetry in the metal is often referred to

TABLE 3. Structural data for six-coordinated indium complexes

Compound	Bond length range (Å)		Chelate angle range (°)		Reference
	In–S	In–O	S–In–S	O–In–O	
Title compound	2.587(1)–2.720(1)		69.40(5)–69.62(5)		This work
$[In(S_2COEt)_3]$ [a]	2.574(1)–2.622(1)	2.193(3)–2.221(3)	69.77(4)	83.9(1)–84.9(2)	[23]
$[In[(SC(C_6H_5)CHC(C_6H_5)O)]_3]$ [b]	2.525(2)–2.530(2)				[24]
$[In(dtp)_3]$ [a]	2.591(11)–2.633(9)		77.1(2)–79.1(2)		[25]
$[In(S_2C_2(CN)_2)_3]^{3-}$ [b]	2.585(8)–2.626(8)		80.6(3)–83.1(3)		[26]
$[In(pmtc)_3]$ [a]	2.582(3)–2.593(3)		69.3(1)–69.6(1)		[27]
$[In(S_2CNEt_2)_3]$ [a]	2.582(2)–2.611(2)		69.40(7)–69.75(5)		[28]
$[In_2(dto)_5]^{4-}$ [a]		2.334(7)		74.0(2)	[29]

[a] Complexes with four-membered chelating rings.

[b] Complexes with five-membered chelating rings.

as intermediate between D_3 and O_h. The last example in Table 3 is a dinuclear complex with one of the dithiooxalates bridging two $In(S_2C_2O_2)_2$ units.

The In–S distances observed in the title complex range from 2.587(1) to 2.720(1) Å and are comparable with similar bond lengths listed in Table 3. However, the S–In–S chelating angles are a result of the steric requirements imposed by the restrictive bite of the bidentate ligands; the values observed in complexes with four-membered rings are lower than those in complexes having five-membered chelating rings. In the case of the title complex, the two thiolate bridges form with an Mo atom a four-membered ring on each side of the In atom, and the observed S–In–S angles of 69.62(5) and 69.40(5)° lie on the lower end of the usual range. This is not surprising, since the opposed S–Mo–S angles, 74.44(5)° and 75.29(5)°, are also restricted by the coordination geometry around the molybdenum atoms, as has been observed [30] in similar complexes with significant steric strain in the chelate rings.

Other biscyclopentadienyl complexes with a central MoS_2M core have comparable Mo–S lengths and S–Mo–S bond angles, namely $[FeCl_2\{MoCp_2(\mu\text{-}S^nBu)_2\}]$ [31] with 2.463 Å and 72.62°, $[Ni\{MoCp_2(\mu\text{-}SCH_3)_2\}_2]^{2+}$ [32] with 2.435 Å and 70.29° and $[Ni(C_5H_5)\{MoCp_2(\mu\text{-}S^tBu)_2\}]$ [33] with 2.510 Å and 68.67°.

The presence or absence of a metal–metal interaction in this type of heterobimetallic complex can be determined from the value of the distances between the metal positions when compared with the sum of the corresponding covalent radii, and also by the angles at the sulphur bridging atoms [34]. Metal–metal interactions are characterized by short distances and acute angles, while no interactions correspond to long distances and angles close to 100° [34].

The In–Mo distances of 4.0401(5) and 4.0703(5) Å and the In–S–Mo angles listed in Table 2 indicate that no In–Mo interactions are present. Comparable values have been determined for these parameters in similar transition metals complexes [31,35]. In contrast, distortions to the central core on some early–late heterobimetallic complexes [34] indicate some metal–metal bonding.

3. Experimental details

All manipulations were performed under dinitrogen or argon by use of standard Schlenk techniques. The solvents were dried by published methods [36] and distilled just before use under dinitrogen. The starting materials $[MoCp_2X_2]$ (X = H, Cl or SR) were prepared by reported methods [37]. Commercial hydrated indium trichloride was dehydrated *in vacuo* at 150°C and used without further purification. Elemental analyses were performed in our laboratories with a Perkin–Elmer 240 B microanalyser. IR spectra were recorded on a Perkin–Elmer 457 spectrophotometer in KBr pellets. ^1H nuclear-magnetic resonance (NMR) spectra were recorded on a Bruker CXP 300 spectrometer at probe temperature with tetramethylsilane as internal reference. Specific conductivities were determined in 10^{-3} M solutions in nitromethane, on a Radiometer CDM 3 conductivity meter instrument, calibrated with a KCl solution. The values were compared with those for standard electrolytes [38].

3.1. Preparation of $[In\{MoCp_2(\mu\text{-}SR)_2\}_3][PF_6]_3$

3.1.1. General procedure

To a filtered solution of $[MoCp_2(SR)_2]$ (R = CH_3, C_2H_5, n-$C_{14}H_{29}$ or C_6H_5) (about 1.0 mmol) in 30 ml of ethanol was added dropwise a solution of $InCl_3$ in the same solvent at room temperature until no more precipitate was formed. The stirring was mantained for a few minutes. After filtration, the orange precipitate was washed several times with ethanol to remove the excess of $InCl_3$ and dissolved in distilled water. The compound was recovered as a PF_6^- salt, by addition of a saturated solution of NH_4PF_6 in degassed water. After filtration, the orange precipitate was washed several times with water and recrystallized in acetone–ethyl ether (yield, about 70%).

$[In\{MoCp_2(\mu\text{-}SCH_3)_2\}_3][PF_6]_3$: molar conductivity, 230 Ω^{-1} cm^2 mol^{-1}. ^1H NMR ($(CD_3)_2CO$): 5.94 (s, 10H, C_5H_5); 2.54 (s, 6H, SCH_3) ppm. Anal. Found: C, 29.3; H, 3.7. $C_{36}H_{48}F_{18}InMo_3P_3S_6$ calc.: C, 28.7; H, 3.2%.

$[In\{MoCp_2(\mu\text{-}SC_2H_5\}_3][PF_6]_3$: molar conductivity, 203 Ω^{-1} cm^2 mol^{-1}. ^1H NMR ($(CD_3)_2CO$): 5 (s, 10H, C_5H_5); 3.06 (m, 4H, CH_2); 1.35 (m, 6H, CH_3) ppm.

$[In\{MoCp_2(\mu\text{-}SCH_{14}H_{29})_2\}_3][PF_6]_3$: molar conductivity, 223 Ω^{-1} cm^2 mol^{-1}. ^1H NMR ($(CD_3)_2CO$): 5.68 (s, 10H, C_5H_5); 1.76 (m, 4H, SCH_2); 1.34 (m, 4H, CH_2); 0.91 (t, 6H, CH_3) ppm. Anal. Found: C, 53.2; H, 7.3. $C_{114}H_{204}F_{18}InMo_3P_3S_6$ calc.: C, 52.6; H, 7.9%.

3.2. Preparation of $[InCl_2\{MoCp_2(\mu\text{-}SC_2H_5)_2\}_2]$-$[B(C_6H_5)_4]\cdot(CH_3)_2CO$

The procedure described above was followed for the synthesis. However, for recrystallization a solution of $NaB(C_6H_5)_4$ was used instead of an NH_4PF_6 solution. The orange precipitate was washed several times with distilled water and recrystallized from acetone–ethyl ether (molar conductivity, 73 Ω^{-1} cm^2 mol^{-1}). ^1H NMR ($(CD_3)_2CO$): 5.71 (s, 20H, C_5H_5); 2.86 (q, 8H,

TABLE 4. Fractional atomic coordinates [a] and thermal motion parameters for $[InCl_2\{(\eta^5\text{-}C_5H_5)_2Mo(\mu\text{-}SEt)_2\}_2][BPh_4]\cdot(CH_3)_2CO$

Atom	x	y	z	U_{eq} [b] ($Å^2$)
In	20280(3)	15232(3)	17539(2)	334(1)
Mo(1)	4419(4)	−7428(3)	25133(2)	296(1)
Mo(2)	53817(4)	29905(3)	23806(2)	313(1)
Cl(1)	24122(16)	17506(12)	3825(8)	555(5)
Cl(2)	−1200(14)	20620(11)	16949(9)	521(5)
S(11)	14518(12)	7998(9)	30569(7)	330(3)
S(12)	17854(12)	−2239(9)	14721(7)	342(4)
S(21)	45234(13)	13815(9)	20418(7)	340(4)
S(22)	30719(12)	29670(9)	26237(8)	353(4)
C(1)	520(8)	1542(5)	3684(4)	57(3)
C(2)	146(9)	1193(7)	4431(4)	86(3)
C(3)	1345(7)	−727(5)	473(4)	53(2)
C(4)	1850(11)	−1609(8)	278(6)	113(5)
C(5)	5389(9)	774(5)	1251(4)	63(3)
C(6)	5411(8)	−230(5)	1338(6)	68(3)
C(7)	2393(8)	3997(5)	2474(6)	71(3)
C(8)	1210(7)	4135(6)	29116(6)	82(3)
C(11)	−1305(5)	76(5)	2412(5)	53(2)
C(12)	−1074(5)	−311(6)	1682(4)	56(3)
C(13)	−1217(6)	−1239(6)	1667(4)	57(2)
C(14)	−1569(6)	−1414(6)	2423(5)	63(3)
C(15)	−1595(5)	−570(6)	2882(4)	55(2)
C(21)	1279(6)	−1124(4)	3627(3)	46(2)
C(22)	443(6)	−1863(5)	3319(4)	52(2)
C(23)	884(6)	−2235(4)	2606(4)	49(2)
C(24)	2018(6)	−1746(4)	2471(4)	44(2)
C(25)	2252(5)	−1046(4)	3090(4)	45(2)
C(31)	5427(6)	3489(4)	3708(3)	44(2)
C(32)	6546(6)	3866(5)	3431(4)	51(2)
C(33)	7242(6)	3157(5)	3145(4)	52(2)
C(34)	6560(6)	2352(5)	3246(4)	49(2)
C(35)	5415(6)	2539(4)	3582(3)	42(2)
C(41)	5459(6)	4249(4)	1744(4)	51(2)
C(42)	6664(6)	3953(5)	1758(4)	55(2)
C(43)	6634(6)	3081(5)	1328(4)	54(2)
C(44)	5417(7)	2853(5)	1008(3)	53(2)
C(45)	4687(6)	3557(5)	1263(4)	53(2)
B(1)	5439(5)	7150(4)	3457(3)	30(2)
C(51)	4366(4)	6752(4)	4025(3)	30(1)
C(52)	4261(5)	5860(4)	4183(3)	37(2)
C(53)	3238(6)	5486(4)	4569(3)	46(2)
C(54)	2296(5)	5995(5)	4818(3)	48(2)
C(55)	2361(5)	6870(5)	4687(3)	45(2)
C(56)	3392(5)	7242(4)	4306(3)	40(2)
C(61)	4828(4)	6948(3)	2553(3)	30(1)
C(62)	5399(5)	7315(4)	1928(3)	44(2)
C(63)	4914(7)	7142(5)	1172(3)	53(2)
C(64)	3813(7)	6589(5)	1008(4)	51(2)
C(65)	3211(6)	6214(4)	1593(4)	48(2)
C(66)	3704(5)	6395(4)	2355(3)	35(2)
C(71)	6744(5)	6641(3)	3509(3)	33(1)
C(72)	7432(5)	6313(4)	2861(3)	35(2)
C(73)	8576(6)	5948(4)	2943(4)	44(2)
C(74)	9091(6)	5899(4)	3652(4)	50(2)
C(75)	8438(6)	6188(4)	4304(4)	48(2)
C(76)	7291(5)	6545(4)	4231(3)	39(2)
C(81)	5780(4)	8244(3)	3740(3)	29(1)
C(82)	6410(6)	8570(4)	4449(3)	45(2)
C(83)	6614(6)	9486(5)	4731(4)	50(2)
C(84)	6215(6)	10120(4)	4329(4)	47(2)
C(85)	5586(6)	9825(4)	3619(4)	46(2)
C(86)	5382(5)	8912(4)	3344(4)	38(2)
C(91)	972(14)	3909(7)	9615(6)	107(5)
C(92)	2385(11)	4191(9)	9650(7)	121(5)
C(93)	270(12)	3844(9)	10348(7)	136(6)
O(1)	4243(10)	3762(8)	8987(6)	195(6)

[a] Positional parameters multiplied by 10^5 for In, Mo, S and Cl atoms, and by 10^4 for other atoms.

[b] U_{eq} ($Å^2$) multiplied by 10^4 for In, Mo, S and Cl atoms, and by 10^3 for other atoms.

CH_2); 1.33 (t, 12H, CH_3); 6.78, 6,93, 7.34 (complex, 20 H, C_6H_5) 2.83 (s, 6H, $(CH_3)_2CO$) ppm. Anal. Found: C, 51.24; H5.52; S, 10.00. $C_{55}H_{66}BCl_2InMo_2OS_4$ calc.: C, 52.44; H, 5.28; S 10.18%.

3.3. Crystal data

$C_{54}H_{66}BCl_2InMo_2OS_4$; M_r = 1259.78; triclinic; space group, $P\bar{1}$; $a = 10.594(1)$ Å, $b = 14.997(4)$ Å, $c = 17.308(4)$ Å, $\alpha = 97.52(2)°$; $\beta = 90.66(1)°$ and $\gamma = 95.95(2)°$; $V = 2710.53$ Å^3; $Z = 2$; $D_{calc} = 1.54$ g cm^{-3}; μ(Mo Kα) = 10.83 cm^{-1}.

3.4. Data collection

X-ray measurements were made with an Enraf–Nonius CAD-4 diffractometer and graphite monochromated Mo Kα radiation (0.71069 Å). Cell dimensions were determined from the measured θ values for 25 intense reflections with $10° < \theta < 16°$. The intensities of 8423 independent reflections in the range $2.0° \leqslant \theta \leqslant 25.0°$ were measured by the ω–2θ scan mode. The data were corrected for Lorentz, polarization and absorption effects, with transmission factors ranging between 87.9 and 99.9%.

3.5. Structure determination and refinement

The 6873 reflections with $F > 3\sigma(F)$ were used in the structure solution and in the early stages of refinement. The In and Mo positions were located from a Patterson map with program SHELXS-86 [39], and the positions of the other non-hydrogen atoms were obtained from the subsequent difference Fourier maps with program SHELX-76 [40]. The non-hydrogen atoms were then refined anisotropically with unit weights to $R = 0.051$. At this stage, some hydrogen atomic positions could be seen in a difference Fourier map. However, because of problems with the stability of the freely refining hydrogen atomic coordinates, all hydrogen atoms were first placed in calculated positions assuming d(C–H) = 0.95 Å; the methyl and methylene hydrogen atoms were then refined as riding on the respective carbon atom while the cyclopentadienyl and phenyl hydrogens were refined with C–H bond lengths restrained to 0.95(2) Å. Group isotropic thermal parameters (one Biso for each Cp ring, Ph ring, all the methylene and all the methyl hydrogen atoms) were used, and no hydrogen atoms were included for the acetone molecule. The final refinement was carried out using the program UPALS [41], minimizing $\Sigma w(F_o - F_c)^2$ with $w = 1/[\sigma^2(F_o) + (0.02\ F_o)]^2$, and converged to $R(F) = 0.043$, $R_w(F) = 0.041$ and $S = 1.25$, for 7187 reflections with $F_o > \sigma(F_o)$ and 725 refined parameters.

Final atomic positional and thermal parameters for the non-hydrogen atoms are given in Table 4. Anisotropic thermal parameters, atomic positional and thermal parameters for hydrogen atoms and a list of observed and final calculated structure factors are available as suplementary material. Drawings were made with the program ORTEP [42]. Atomic scattering values were taken from the *International Tables of X-ray Crystallography* [43].

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