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Main Group Metal Halide Complexes with Sterically Hindered Thioureas XI. Complexes of Antimony(III) and Bismuth(III) Chlorides with a New Bidentate Thiourea — 1,1′-Methylenebis(3-methyl-2H-imidazole-2-thione)

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Abstract

A new bidentate ligand, mbit, [mbit = 1,1′-methylenebis(3-methyl-2H-imidazole-2-thione)] was synthesized and characterized along with two new pnictogen complexes — $SbCl_3mbit$ and $BiCl_3mbit$. A single crystal X-ray structure of $SbCl_3mbit$ gave the following cell parameters: space group $P2_1/c$, $a = 11.812(9)$, $b = 7.699(4)$, $c = 18.100(9)$ Å, $\beta = 101.29(5)°$, $Z = 4$, $V = 1614.2$ Å^3, $D_o = 1.92$ g/cm^3, $D_c = 1.927$ g/cm^3 ($\lambda = 0.71069$ Å). The structure refined to a conventional $R = 0.042$. The local geometry around the antimony atom was distorted octahedral with bridging sulfur atoms creating long zigzag chains of octahedra sharing vertices *cis* to each other. Two chlorine atoms are *trans* to each other, and the third chlorine is *trans* to the bridging sulfur. The Sb--S bridges are 3.41 Å in length. There is no strong evidence for a stereoactive lone pair in the coordination sphere of antimony. The ligand forms an eight-membered ring with the antimony atom included. Solid state IR data showed little change in ligand vibrational modes normally sensitive to coordination, and solution state proton NMR gave evidence for a high degree of association.

Introduction

A number of interesting structural features have been observed in complexes containing the sterically hindered heterocyclic aromatic thiourea 1,3-dimethyl-2(3H)-imidazolethione (dmit). One such study involved the molecular structure of $BiCl_3(dmit)_2$ which is best described as a dimer pair of octahedra sharing a common edge through chlorine bridging and the dmit molecules bonded through the sulfur *trans* to each other and perpendicular to the plane made up of chlorine atoms [1]. The methyl groups not only made the *trans* isomer energetically more favorable, but also hindered further polymerization through Bi–Cl bridges as seen in the structure of the very close analog $BiCl_3(etu)_2$ (etu = ethylenethiourea or 2H-imidazole-2-thione) reported by Battaglia *et al.* [2]. In this complex the ligands are *cis* to each other, and the structure consists of distorted octahedra linked in a long zigzag chain by single bridging chlorine atoms sharing common vertices *cis* to each other. This dramatic difference between two very similar complexes led to the question of what type of structural features would be observed if sterically hindered thioureas could be forced *cis* to each other as in $BiCl_3(etu)_2$. To accomplish this, we have synthesized a new bidentate analog of dmit shown in Fig. 1, and we have also synthesized two new pnictogen halide complexes with this ligand for structural studies.

This paper reports the synthesis and characterization of 1,1′-methylenebis(3-methyl-2H-imidazole-2-

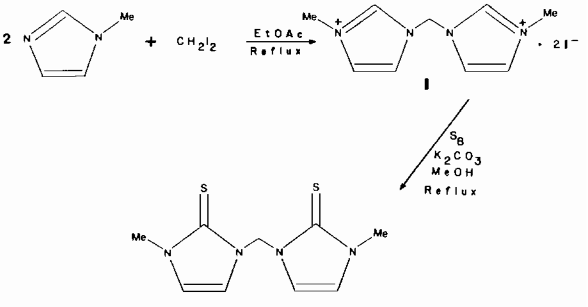

Fig. 1. Synthesis of I and II.

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thione) (mbit), $SbCl_3$mbit and $BiCl_3$mbit and also reports the crystal and molecular structure of the antimony complex.

Experimental

Chemicals

All chemicals were reagent grade and used as commercially obtained without further purification. Spectroscopic grade CD_3CN (Aldrich) was used as a solvent to obtain the proton NMR data.

Analytical

Elemental analysis was done by Atlanta Microlabs, Inc. Bismuth analysis was obtained with the aid of a Varian 1475 atomic absorption spectrophotometer using an acetylene/air flame.

Spectra

Infrared spectra were recorded as mineral oil (Nujol) mulls between AgCl plates from 4000 to 400 cm^{-1} on a Perkin-Elmer Model 1430 spectrophotometer. Values are reported in cm^{-1} (± 5): w = weak, m = medium, s = strong, br = broad, sh = shoulder.

Proton NMR were recorded in CD_3CN on a 300 MHz GE Model QE-300 FT-NMR spectrometer. Chemical shifts are reported in ppm (δ) relative to external tetramethylsilane: s = singlet, d = doublet.

Synthesis

Melting points (uncorrected) were obtained on a Fisher-Johns stage-type apparatus and reported in degrees Celsius. The synthetic pathway for the formation of mbit is shown in Fig. 1.

1,1′-Methylenebis(3-methylimidazolium) diiodide (I)

In a 100 ml round-bottomed flask fitted with a reflux condenser were placed 16.0 g (0.200 mol) of 1-methylimidazole (Aldrich), 26.0 g (0.100 mol) of diiodomethane (Eastman), and 30 ml ethyl acetate (Fisher) as solvent. After 12 h reflux, the white solid which had separated was filtered and washed with a few small portions of diethyl ether. Yield of **I**: 24.5 g (crude, 70%). Recrystallization from hot ethanol produced fine white needles, melting point (m.p.) 283–285d. *Anal.* Calc. for $C_9H_{14}I_2N_4$: C, 25.01; H, 3.26; N, 12.96; I, 58.76%. Found: C, 25.10; H, 3.28; N, 12.92; I, 58.66%.

1.1′-Methylenebis(3-methyl-2H-imidazole-2-thione) (II, mbit)

In a 500 ml round-bottomed flask fitted with reflux condenser were placed 20.0 g (46.3 mmol) of **I**, 3.0 g S (94 mmol), 10.3 g K_2CO_3 and 200 ml methanol as solvent. The mixture was allowed to reflux for 24 h after which the methanol was removed with a rotary evaporator. The remaining solid was shaken with 200 ml $CHCl_3$ which was then filtered and rotary evaporated. Yield of **II**: 9.0 g (crude, 81%). **II** was redissolved in 300 ml hot H_2O, treated with a few mg of decolorizing carbon (Norit-A), hot-filtered, and the filtrate boiled down to half-volume. Long, flat needles separated upon cooling, m.p. 202–203. *Anal.* Calc. for $C_9H_{12}N_4S_2$: C, 44.99; H, 5.04; N, 23.30. Found: C, 44.91; H, 5.08; N, 23.27%. IR (cm^{-1}): 1580m, 1560w,sh, 1310w, 1280w, 1240m, 1230w,sh, 1175m, 1160w,sh, 1105m, 1075w,sh, 1020w, 985m, 850w, 840s, 810m, 785s, 725s, 695s, 620w, 535s, 490m. ^1H NMR (δ): 3.48 (s, 3, methyl), 6.19 (s, 1, methylene), 6.79 (d, 1, $J_{AB} = 3$ Hz, ethylenic), 7.44 (d, 1, $J_{AB} = 3$ Hz, ethylenic).

Trichloro[1,1′-methylenebis(3-methyl-2H-imidazole-2-thione)]antimony(III)

Equal molar quantities of both the antimony trihalide (0.58 g, 2.54 mmol) and mbit (**II**, 0.60 g, 2.50 mmol) were dissolved in CH_2Cl_2, mixed, and the resultant yellow crystalline precipitate filtered and recrystallized in hot CH_3CN. Yield: 0.85 g (73%), m.p. 212–215 (sublimes). *Anal.* Calc. for $C_9H_{12}Cl_3N_4S_2Sb$: C, 23.08; H, 2.58; N, 11.96; Cl, 22.71. Found: C, 23.15; H, 2.61; N, 11.89; Cl, 22.79%. IR (cm^{-1}): 1580w, 1255m, 1225w, 1190w, 1170w,sh, 985w,br, 780s, 770m,sh, 755s, 735s. ^1H NMR (δ): 3.59 (s, 3, methyl), 6.31 (s, 1, methylene), 6.95 (d, 1, $J_{AB} = 3$ Hz, ethylenic), 7.45 (d, 1, $J_{AB} = 3$ Hz, ethylenic).

Trichloro[1,1′-methylenebis(3-methyl-2H-imidazole-2-thione)]bismuth(III)

A procedure similar to that described for $SbCl_3$mbit was used for the synthesis of $BiCl_3$mbit. The solvent used was CH_3CN, and after mixing the solution was brought to a boil. From a mixture of 0.48 g (2.0 mmol) of $BiCl_3$ and 0.66 g (2.8 mmol) mbit was obtained upon cooling 0.64 g (yield 56%) of a yellow solid. $BiCl_3$mbit proved too insoluble for recrystallization in most non-aqueous polar solvents. Analytically pure crytals of $BiCl_3$mbit were obtained from adding an equal volume of $CHCl_3$ to the reaction mixture filtrate and cooling to 5 °C overnight, m.p. 214–216d. *Anal.* Calc. for $C_9H_{12}BiCl_3N_4S_2$: C, 19.46; H, 2.18; N, 10.18; Cl, 19.14; Bi, 37.6. Found: C, 19.39; H, 2.20; N, 10.04; Cl, 19.08; Bi, 38.6. IR (cm^{-1}): 1585m, 1355m, 1325m, 1285m, 1270w,sh, 1105w, 1085w, 1060w, 1035w, 800m, 755s,br, 720w,sh, 680w. Too insoluble ^1H NMR study in CD_3CN.

X-ray Crystallographic Data

Suitable crystals of $SbCl_3$mbit grown from CH_3CN were mounted on a glass fiber using epoxy cement such that the longest crystal dimension was approximately parallel to the fiber axis. Unit cell parameters were determined on a Syntex P2$_1$ four circle diffractometer equipped with a graphite monochrometer (Bragg 2θ angle = 12.2°) using Mo Kα ($\lambda = 0.71069$ Å) radiation at a takeoff angle of 6.75°. Fifteen reflections were machine centered and used in a least-squares refinement of the lattice parameters. Omega scans of several low 2θ angle reflections gave peak widths at half-height of less than 0.24 Å indicating a satisfactory mosaic spread for the crystal examined.

Axial photographs were used to determine the space group with zero and upper level intensity data being examined for systematic absences in the usual fashion.

Intensity data were collected using ω scans with X-ray source and monochromator settings identical to those used for determination of the unit cell parameters. A variable scan rate of 3.91 to 29.3° min^{-1} was used, and a scan width of 1.0° was sufficient to collect all the peak intensity. Stationary background counts were measured at the beginning and at the end of each scan with a total background-to-scan time ratio of 1.0. No significant fluctuations were observed in the intensities of three standard reflections (008, 900, 040) measured every 100 reflections. Intensities were calculated from the total scan count and background counts by the usual relationship.

The intensities were assigned standard deviations in the usual manner, and from a total of 3270 reflections collected in a complete quadrant ($\pm h + k + l$) of data out to $2\theta = 50°$, 2819 were accepted as statistically above background on the basis of that F was greater than $3\sigma(F)$. Lorentz and polarization corrections were made in the usual way. Absorption corrections were not applied.

Solution and Refinement of the Structure

Computations were performed using the standard programs [3], and were carried out on the CDC Cyber 74 System. For structure factor calculations, the scattering factors were taken from the International Tables for X-ray Crystallography [4]. The agreement factors are defined in the conventional way. In all least-squares refinements, the quantity minimized has been previously defined [5]. The weighting scheme based on counting statistics are also as previously defined for the calculation of R_w and in least-squares refinement [5].

TABLE 1. Crystallographic data for SbCl$_3$mbit with e.s.d.s in parentheses

Chemical formula	C$_9$H$_{12}$Cl$_3$N$_4$S$_2$Sb
Space group	$P2_1/c$
Cell parameters	$a = 11.812(9)$ A
	$b = 7.699(4)$ A
	$c = 18.100(9)$ A
	$\beta = 101.29(5)°$
	$Z = 4$
	$V = 1614.2$ A^3
	$D_o = 1.92$ g cm^{-1}
	$D_c = 1.927$ g cm^{-1}
	$\lambda = 0.71069$ A

TABLE 2. Final positional parameters for non-hydrogen atoms with e.s.d.s in parentheses

Atom	x	y	z
Sb	0.28247(3)	0.08119(5)	0.22595(2)
Cl1	0.2693(1)	0.0835(2)	0.08160(9)
Cl2	0.1165(2)	0.2869(3)	0.2035(1)
Cl3	0.2712(2)	0.0277(3)	0.3669(1)
S1	0.1626(1)	−0.1910(2)	0.22249(9)
S2	0.4786(1)	−0.1597(2)	0.24030(9)
N1	0.0346(4)	−0.2069(7)	0.0796(3)
N2	0.1999(4)	−0.3399(7)	0.0909(3)
N3	0.4056(4)	−0.3138(7)	0.1016(3)
N4	0.5463(4)	−0.1325(7)	0.1054(3)
C1	0.1330(5)	−0.2434(9)	0.1283(3)
C2	0.1408(7)	−0.358(1)	0.0161(4)
C3	0.0395(6)	−0.277(1)	0.0100(4)
C4	0.3118(6)	−0.4151(9)	0.1218(4)
C5	0.4761(5)	−0.2020(8)	0.1478(3)
C6	0.5213(6)	−0.200(1)	0.0334(4)
C7	0.4347(6)	−0.313(1)	0.0310(4)
C8	−0.0637(6)	−0.113(1)	0.1001(5)
C9	0.6384(6)	−0.007(1)	0.1324(4)

TABLE 3. Interatomic angles (°) with e.s.d.s in parentheses

Angles (σ)			
Cl2–Sb–Cl1	86.6(0.1)	Cl3–Sb–Cl1	169.3(0.1)
Cl3–Sb–Cl2	94.1(0.1)	S1–Sb–Cl1	93.3(0.1)
S1–Sb–Cl2	96.0(0.1)	S1–Sb–Cl3	76.0(0.1)
S2–Sb–Cl1	89.1(0.1)	S2–Sb–Cl2	175.7(0.1)
S2–Sb–Cl3	90.2(0.1)	S2–Sb–S1	84.7(0.1)
C1–S1–Sb	102.9(0.2)	C5–S2–Sb	99.9(0.2)
C3–N1–C1	109.2(0.6)	C8–N1–C1	124.1(0.6)
C8–N1–C3	126.6(0.6)	C2–N2–C1	107.9(0.5)
C4–N2–C1	127.0(0.5)	C4–N2–C2	125.1(0.6)
C5–N3–C4	126.0(0.5)	C7–N3–C4	124.7(0.5)
C7–N3–C5	109.3(0.5)	C6–N4–C5	110.2(0.5)
C9–N4–C5	124.9(0.5)	C9–N4–C6	124.8(0.6)
N1–C1–S1	125.6(0.5)	N2–C1–S1	126.7(0.5)
N2–C1–N1	107.6(0.5)	C3–C2–N2	107.6(0.6)
C2–C3–N1	107.7(0.6)	N3–C4–N2	111.7(0.5)
N3–C5–S2	127.9(0.5)	N4–C5–S2	126.2(0.5)
N4–C5–N3	105.8(0.5)	C7–C6–N4	107.3(0.6)
C6–C7–N3	107.3(0.6)		

The structure was solved using a Patterson map. Hydrogen atoms were not added. Final calculated values were $R = 0.042$ and $R_w = 0.041$. Table 1 summarizes crystallographic data for SbCl$_3$mbit while Table 2 lists final positional parameters for

TABLE 4. Interatomic distances (A) with e.s.d.s in parentheses

Interatomic distances (σ)			
Sb-Cl1	2.587(0.002)	Sb-Cl2	2.491(0.002)
Sb-Cl3	2.613(0.002)	Sb-S1	2.523(0.002)
Sb-S2	2.939(0.002)	S1-C1	1.721(0.006)
S2-C5	1.701(0.006)	N1-C1	1.343(0.008)
N1-C3	1.383(0.009)	N1-C8	1.476(0.009)
N2-C1	1.357(0.008)	N2-C2	1.403(0.008)
N2-C4	1.452(0.008)	N3-C4	1.458(0.008)
N3-C5	1.364(0.008)	N3-C7	1.387(0.008)
N4-C5	1.346(0.008)	N4-C6	1.381(0.008)
N4-C9	1.466(0.009)	C2-C3	1.333(0.011)
C6-C7	1.338(0.010)		

the non-hydrogen atoms. Interatomic angles and distances are listed in Tables 3 and 4 respectively. See also 'Supplementary Material'.

Results and Discussion

The novel bidentate ligand, mbit (**II**), is synthesized in a fashion similar to that reported for dmit. Furthermore, when reacted in 1:1 molar stoichiometry with either antimony(III) or bismuth(III) chloride, air-stable yellow solids with chemical compositions corresponding to 1:1 adducts are produced.

Infrared spectra in the 4000 to 400 cm^{-1} region reveal very little change in the vibrational data of mbit in going from the free state to the combined state. Of particular interest in this region are the N–C–N asymmetric stretching mode and the C=S stretch which shift upon coordination as discussed in Part IX of this series [6]. For the free ligand, the peak observed at 1580 cm^{-1} and the two peaks observed at 1175 and 1160 cm^{-1} are assigned as ν(N–C–N)$_{asym}$ and ν(C=S) respectively based on reported values for analogous modes in dmit [6]. In SbCl$_3$mbit, these modes are observed at 1580 cm^{-1} and as two peaks at 1190 and 1170 cm^{-1}. For BiCl$_3$-mbit, only the N–C–N stretch is observed at 1585 cm^{-1}. As can be seen from the above data, there is no significant shift for the N–C–N asymmetric stretch in going from free to coordinated state unlike other thioureas such as tetramethylthiourea for which this mode has been observed to increase up to 90 cm^{-1} upon bonding [6]. This lack of change is, however, very similar that which has been noted for dmit [6] thus leading to speculation that there is little structural difference between the free and combined forms of mbit. We are currently determining the crystal structure of pure mbit to substantiate this. The C=S stretch is, however, significantly altered, and the observation of two peaks can be best understood from the crystal structure of the antimony complex reported below. The direction of the shift is enigmatic, however, in that a decrease in frequency is usually observed upon coordination [6]. Again, a comparative crystal structural study between the complex and free ligand would be instructive.

Proton NMR of the ligand compared to that of the complex shows distinct downfield shifts for the methyl protons (3.48 to 3.59 ppm), the methylene protons (6.19 to 6.31 ppm), and for the ethylenic protons on the carbon adjacent to the methyl-substituted nitrogen (6.79 to 6.95 ppm). The only shift not significantly affected is the one observed for the ethylenic protons adjacent to the methylene-substituted nitrogen (7.44 versus 7.45 ppm). The downfield shifts are consistent with those noted for other thiourea complexes, and are an indicator of significant association of the complex in the solution state [7, 8].

Figure 2 shows the structure of SbCl$_3$mbit as determined by the X-ray crystallographic study. As can be seen, the ligand forms an eight-membered ring with the metal included. In the coordination sphere of antimony, it looks as though the structure were a distorted square pyramid with the base being made up of three chlorine atoms and one of the sulfur atoms (S2). The other sulfur atom, S1, makes up the apex of the square pyramid. Upon inspection of intermolecular contacts, however, as can be seen in Fig. 3, instead of a lone pair of electrons occupying the space below the basal plane of the square pyramid, there is a sulfur atom (S2′ in Fig. 3) from a neighboring molecule bridging to the antimony at a distance of 3.41 Å – well within the sum of the van der Waal's radii of 4.0 Å [9]. Thus the structure better described as a polymeric zig-zag chain of distorted octahedra linked via long sulfur bridges *cis* to each other as seen in the unit cell stereo drawing in Fig. 4. Notably, this is analogous to the BiCl$_3$(etu)$_2$ structure mentioned earlier.

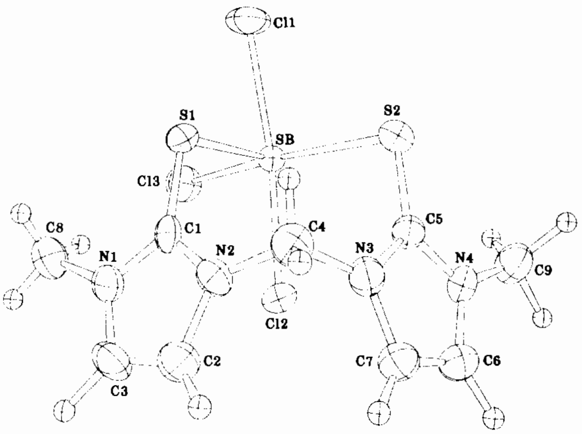

Fig. 2. Molecular structure of SbCl$_3$mbit with thermal ellipsoids drawn at the 50% probability level.

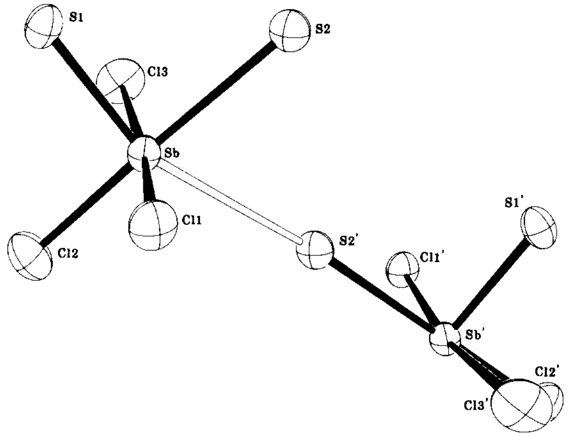

Fig. 3. Coordination sphere around Sb including intermolecular contacts between neighboring molecules.

TABLE 5. Bond angles (°) and distances (Å) for SbCl$_3$dmit with e.s.d.s in parentheses [10]

Interatomic angles		Interatomic distances	
Cl1–Sb–S	91.3(1)	Sb–Cl1	2.535(2)
Cl2–Sb–S	94.1(1)	Sb–Cl2	2.431(1)
Cl3–Sb–S	76.2(1)	Sb–Cl3	2.636(1)
Cl2–Sb–Cl1	90.4(1)	Sb–S	2.511(1)
Cl3–Sb–Cl2	89.1(1)	Sb···Cl3'	2.98(1)
Cl1–Sb–Cl3	167.4(1)	Sb···S	3.76(1)

(···) denotes intermolecular contact.

Bond distances and angles in the coordination sphere of antimony compare favorably to those observed for SbCl$_3$dmit [10]. Table 5 lists bond angles and distances for the dmit complex for comparative purposes. SbCl$_3$dmit is also polymeric but linked through bridging chlorine atoms as well as bridging sulfur atoms. The sulfur–antimony bridges in the dmit complex are much longer (3.76 Å) than those observed in the mbit complex. The reason is not totally clear, but may merely be a packing phenomenon. Antimony–chlorine bond distances compare favorably as do the sulfur–antimony distances. The notable exception is the Sb–S2 bond which is considerably longer (2.939 Å) due to bridging interaction with the neighboring antimony. Bond angles also show similar distortions in the coordination sphere the largest deviation from ideality being observed in the mbit complex with the S1–Sb–Cl3 bond (76.0°). A deviation of similar magnitude was observed for the dmit complex with the Cl3–Sb–S bond (76.2°). While the reason for the deviation in the dmit complex was not totally clear other than perhaps a packing phenomenon or the involvement of Cl3 with bridging, inspection of Fig. 4 reveals a close approach of one of the neighboring mbit molecules to the Cl3 atom thus explaining the reduction of the angle below 90°. In neither complex was there any clear structural evidence for the nonbonded pair of electrons in the coordination sphere.

Bond distances and angles in mbit are also quite similar to analogous values for dmit. The only notable exceptions are observed in the C–S distances. In the mbit complex, both C–S distances are significantly shorter (1.721 and 1.701 Å in mbit versus 1.743 Å in dmit) and also significantly different from each other thus explaining the two observed C=S stretching frequencies in the IR spectrum mentioned earlier. Changes in distances and angles for mbit in the complex as compared to in the free state are, of course, still unknown since a crystallographic study of II has yet to be done.

Supplementary Material

Additional tables of structure factors, thermal parameters, intermolecular contacts, and calculated positions of hydrogen atoms are available from the author for correspondence on request.

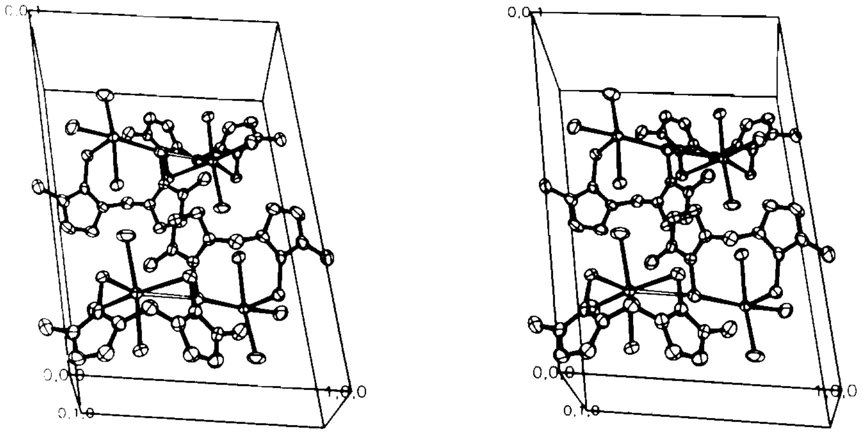

Fig. 4. Stereoview of unit cell with thermal ellipsoids drawn at the 50% probability level.

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