Electrochemical Synthesis and Structural Characterisation of Cadmium and Mercury Complexes Containing Pyrimidine-2-thionate Ligands

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Dedicated to Professor V. I. Minkin on the occasion of his 70th birthday

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The electrochemical oxidation of anodic metal (cadmium or mercury) in a cell containing an acetonitrile solution of the appropriate pyrimidine-2-thione (RpymSH) affords complexes [M(RpymS)$_2$] (M = Cd, Hg; R = 4-CF$_3$, 4,6-CF$_3$,Me and 4,6-CF$_3$,Ph). When 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen) was added to the electrolytic cell, adducts of cadmium and compounds with these coligands were obtained. All the compounds have been characterised by microanalysis, IR spectroscopy and, in the case of the compounds that were sufficiently soluble, by ^{1}H, ^{13}C and ^{199}Hg NMR spectroscopy. The compounds [Cd(4-CF$_3$pymS)$_2$] (**1**), [Cd(4,6-CF$_3$MepymS)$_2$(bipy)] (**4**), [Cd(4,6-CF$_3$PhpymS)$_2$-(phen)] (**6**) and [Hg(4,6-CF$_3$MepymS)$_2$] (**8**) were also characterised by X-ray diffraction. Compound **1** presents a polymeric structure with the polymer chains interconnected by intermolecular C–H···N interactions. Compounds **4** and **6** adopt mononuclear structures, with weak inter- and intramolecular C–H···π interactions, as well as π–π stacking interactions for compound **6**. Compound **8** also presents a mononuclear structure with intermolecular π–π interactions between the pyrimidine rings and additional weak Hg···Hg contacts (3.484 Å).

Introduction

The chemistry of metal–sulfur complexes has attracted much interest over the past decade because of the potential relevance of such compounds to active sites in metalloenzymes and also for their ability to adopt geometries of variable nuclearity and great structural complexity.[1–7] These latter features are the result of the tendency of thiolate ligands to bridge metal centres to yield oligomeric or polymeric species, a situation that makes it difficult to obtain and isolate crystals suitable for X-ray diffraction studies. It has been shown[8–10] that the degree of association depends intimately on both the reaction conditions and the nature of the thiolate ligands. Moreover, these association phenomena may be limited by incorporating steric constraints by appropriate ligand design or introducing coligands to block a number of coordination sites around the metal. Recently, a great deal of effort has been made[11–17] to modify the thiolate ligand by introducing a solubilizing group or a bulky substituent that might modify the aggregation process.

However, in comparison with the coordination chemistry of transition metals, the chemistry of the main-group metals with sulfur ligands remains much less developed.[18–22] In many cases, the interaction of toxic metals with biological systems involves bonding of the metal to the sulfydryl groups present in enzymes. Hence, an insight into the chemistry of main-group thiolate compounds is important in terms of understanding the aforementioned interaction and for the design of detoxifying agents.[23,24] The generally poor solubility of group 12 metal thiolate compounds makes it difficult to structurally characterise these systems.

As part of our continuing interest in the chemistry of sterically hindered thiolates,[25] we report here the electrochemical synthesis and characterisation of Cd and Hg complexes with a number of substituted pyrimidine-2-thiones (Scheme 1). This type of ligand, besides having solubilising and bulky groups that might modify the degree of aggregation as a result of steric constraints, is one of the most versatile sulfur ligands. These ligands can act as follows: (a) a neutral monodentate ligand coordinated through the sulfur atom,[26] through one of the nitrogen atoms,[27] and as a bridging ligand through sulfur[28] or as an N,S-chelating ligand,[29,30] and (b) as an anionic ligand, in which case it can be monodentate through the sulfur atom,[31] as an N,S-chelating ligand,[32] as a binuclear bridging ligand through

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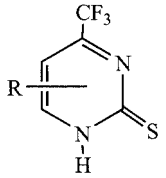
nitrogen and sulfur,[33] or sulfur only,[34] as a binuclear triply bridging ligand through sulfur and one of the nitrogens[35] or the two nitrogen and sulfur atoms,[36,37] and as a trinuclear triply bridging system.[38]



R = 4-CF_3, 4,6-CF_3, Me, 4,6-CF_3, Ph

Scheme 1.

In addition, and in order to reduce the nuclearity of the homoleptic cadmium(II) complexes, didentate N,N′-donor coligands, such as 2,2′-bipyridine or 1,10-phenanthroline, were added to the electrochemical cell. This modification results in the preparation of monomeric mixed cadmium(II) complexes in one step.

Results and Discussion

Cadmium and mercury complexes of general formula $[M(RpymS)_2]$ (M = Cd and Hg; R = 4-CF_3, 4,6-CF_3,Me and 4,6-CF_3,Ph) were easily prepared in reasonable yields by a simple, one-step electrochemical method. Mixed complexes of cadmium with 2,2′-bipyridine or 1,10-phenanthroline were also obtained by addition of the corresponding coligand to the cell. The compounds are air-stable and moderately soluble in organic non-polar solvents, but soluble in dimethyl sulfoxide or *N*,*N*′-dimethylformamide.

The values of the electrochemical efficiency, defined as the amount of metal dissolved per unit of charge, were close to 0.5 mol F^{-1} regardless of the presence or absence of additional ligand. This observation, along with the evolution of hydrogen at the cathode, is compatible with the following mechanism:

Cathode: 2 RpymSH + 2 $e^- \rightarrow$ 2 $RpymS^-$ + H_2

Anode: M + 2 $RpymS^- \rightarrow [M(RpymS)_2]$ + 2 e^-

(M = Cd, Hg)

or

M + 2 $RpymS^-$ + L $\rightarrow [M(RpymS)_2L]$ + 2 e^-

(M = Cd; L = bipy, phen)

Crystallographic Studies

Crystal and Molecular Structure of [Cd(4-CF_3pymS)$_2$] (1)

Figure 1 shows a perspective view of compound **1** along with the atomic labelling scheme used. A selection of bond lengths and angles (with estimated standard deviations) are given in Table 1.

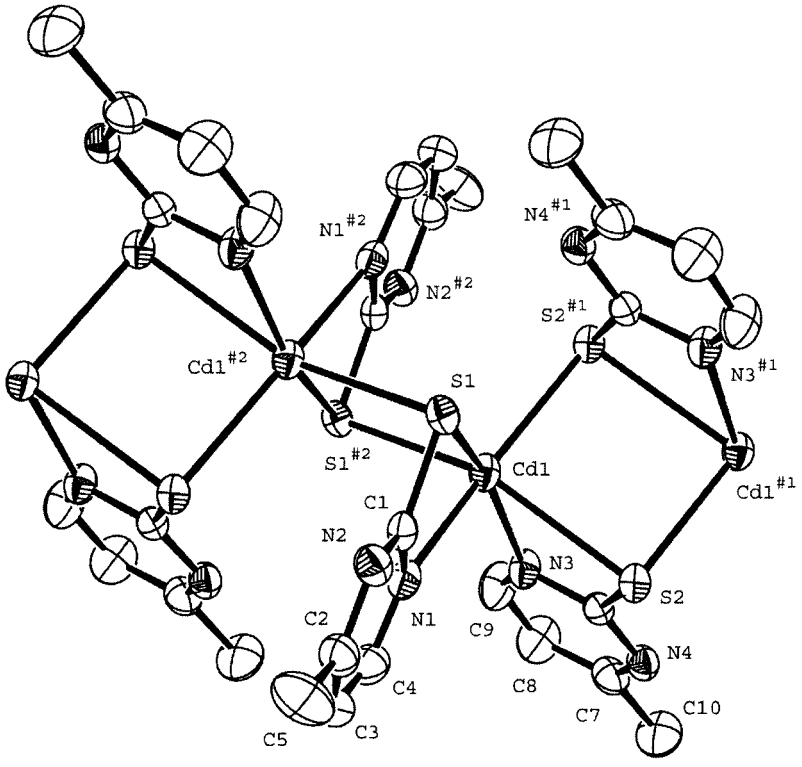


Figure 1. ORTEP diagram of the structure of $[Cd(4\text{-}CF_3pymS)_2]_x$ (**1**), showing 40% thermal ellipsoid probability. The hydrogen atoms and the CF_3 groups on C(5) and C(10) have been omitted for clarity. Symmetry codes: #1 = $-x + 2$, $-y$, $-z + 1$; #2 = $-x + 1$, $-y$, $-z + 1$.

Table 1. Selected bond lengths [Å] and angles [°] for [Cd(4-CF_3pymS)$_2$] (**1**).[a]

Cd(1)–N(3)	2.336(4)	Cd(1)–N(1)	2.457(4)
Cd(1)–S(2)#1	2.6347(12)	Cd(1)–S(1)#2	2.6733(11)
Cd(1)–S(1)	2.6777(12)	Cd(1)–S(2)	2.8011(11)
S(2)–C(6)	1.745(4)	S(1)–C(1)	1.755(5)
N(3)–Cd(1)–S(2)#1	96.89(11)	N(1)–Cd(1)–S(2)#1	158.73(10)
N(3)–Cd(1)–S(1)#2	97.31(9)	N(1)–Cd(1)–S(1)#2	92.70(8)
S(2)#1-Cd(1)–S(1)#2	99.56(3)	N(3)–Cd(1)–S(1)	156.88(11)
N(1)–Cd(1)–S(1)	61.71(9)	S(2)#1-Cd(1)–S(1)	99.54(4)
S(1)#2-Cd(1)–S(1)	95.89(3)	N(3)–Cd(1)–S(2)	60.63(9)
N(1)–Cd(1)–S(2)	85.41(8)	S(2)#1-Cd(1)–S(2)	89.76(4)
S(1)#2-Cd(1)–S(2)	157.13(4)	S(1)–Cd(1)–S(2)	103.15(3)

[a] Symmetry codes: #1 = $-x + 2, -y, -z + 1$; #2 = $-x + 1, -y, -z + 1$.

The compound consists of polymeric chains along the *a* axis with the cadmium atom hexacoordinated by two nitrogen atoms from two different thionate ligands and four bridging sulfur atoms. Each ligand chelates one cadmium metal and bridges an adjacent cadmium atom through the exocyclic sulfur. A second ligand is almost perpendicular to the first one and also chelates this cadmium atom and bridges to the next cadmium atom in the chain. Each thionate ligand acts as a binuclear triply bridging μ_2-S,N(η^2-S;η^1-N) five-electron-donor ligand: each atom of cadmium is in a highly distorted [CdN_2S_4] octahedral environment with the nitrogen atoms in *cis* positions. The bond angles between the metal and the donor atoms that are in a *trans* disposition are in the range 151.6(3)–167.1(3)°, far from the ideal value of 180°. The values for the angles described by the donors in the *cis* positions are much lower than those expected for a regular octahedron, with values for the S–Cd–N angles of 61.1(3)° and 61.3(3)°.

Three of the four Cd–S bond lengths are very similar and are in the range 2.6347(12)–2.6777(12) Å. The other Cd–S distance is longer at 2.8011(11) Å. These values are within the range observed for other complexes containing CdN_2S_4 units with μ_2-S,N(η^2-S;η^1-N) bridging ligands; for example 2.638(6)–2.761(8) Å in the hexanuclear complex [{Cd(4,6-Me_2pymS)$_2$}$_6$][35] and 2.647–2.777 Å in other hexacoordinate thionate complexes.[39,40] However, the range for these distances in the complex [Cd(pyS)$_2$],[41] which has a similar chain structure, is much wider [2.543(5)–3.038(4) Å].

The Cd–N bond lengths of 2.336(4) and 2.457(4) Å are also close to the values found in other octahedral complexes of cadmium containing heterocyclic thionates as ligands; for example 2.42(2) and 2.53(2) Å in [Cd(pymS)$_2$(phen)],[42] [Cd(4,6-CF_3MepymS)$_2$(bipy)] and [Cd(4,6-CF_3PhpymS)$_2$-(phen)] (see below).

The S–C bond lengths of 1.755(5) and 1.745(4) Å are intermediate between the value found in free 4,6-dimethylpyrimidine-2-thione[30] [1.686(4) Å] and 1-phenyl-4,6-dimethylpyrimidine-2-thione[29] [1.676(2) Å], which exist in the thione form in the solid state, and the values of 1.781(2) Å and 1.782(3) Å found in bis(2-pyrimidyl) disulfide[43] and bis(4,6-dimethyl-2-pyrimidyl) disulfide,[44] both of which possess a simple C–S bond. This observation suggests that the ligand is coordinated in a way that is closer to the thionato form than to the thione form of the free ligand.

The packing structure of **1** (Figure 2) shows that every polymeric chain interacts with two parallel chains in the *b* direction through non-classical C–H···N hydrogen bonds. These interactions link the polymeric chains through weak C(8)–H···N(2) hydrogen bonds. The hydrogen bonds involve the uncoordinated pyrimidine nitrogen atoms, N(2), on alternate ligands in one chain that are parallel to one another and also parallel to the chain with the pyrimidyl protons bond at C(8) atom on ligands in the adjacent chains, which are again parallel between themselves but almost perpendicular to the first ones. The bond lengths and angles in this system are as follows: C···N = 3.422(7) Å, N···H = 2.58 Å and C–H···N = 150.3°.

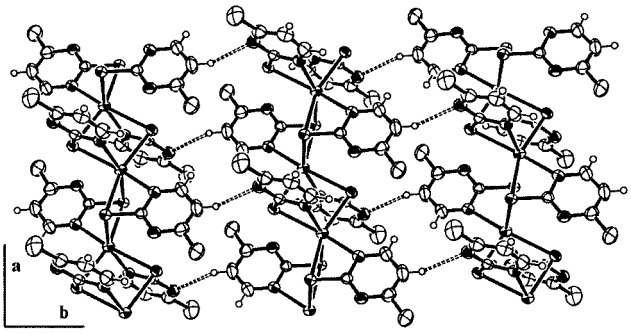


Figure 2. The crystal packing of **1** viewed along the *c* axis. Dashed lines show the C–H···N interactions.

These interactions result in the formation of layers parallel to the crystallographic *ab* plane that stack along the *c* axis.

A comparison of the structures of cadmium complexes with different pyridine and pyrimidine-2-thiones clearly demonstrates that the degree of aggregation depends to a large extent on the steric effects created by the ligand substituents. Thus, while the complex with pyridine-2-thione consists of [Cd(pyS)$_2$]$_x$,[41] a polymeric chain structure, the increased steric constraints introduced by the methyl groups in the case of 4,6-dimethylpyrimidine-2-thione reduce the tendency for polymerisation and the complex obtained is hexanuclear [Cd(4,6-Me_2pymS)$_2$]$_6$.[35] The metal atom in the latter complex is hexacoordinate as in [Cd(pyS)$_2$]$_x$.[41] A higher degree of steric hindrance, such as in 3-trimethylsilylpyridine-2-thione, produces a dimer [Cd(3-Me_3Sipyt)$_2$]$_2$,[45] with each cadmium atom in a five-coordinate environment. In the case of 4-trifluoromethylpyrimidine-2-thione, the presence of a CF_3 group in the 4-position produces greater steric hindrance than in pyridine-2-thione, but less hindrance than in 4,6-dimethylpyrimidine-2-thione. However, the steric hindrance introduced by the CF_3 group is not sufficient to reduce the aggregation level and the complex is also polymeric as in [Cd(pyS)$_2$]$_x$.[41] Naturally, other factors such as reaction conditions, kinetic factors, nature of the solvent, etc., can also play a role in the aggregation process.[25,45]

Molecular Structures of [Cd(4,6-CF_3MepymS)$_2$(bipy)] (4) and [Cd(4,6-CF_3PhpymS)$_2$(phen)] (6)

Figure 3 and Figure 4 show perspective views of compounds **4** and **6**, respectively, together with the atomic labelling schemes used. A selection of bond lengths and angles (with estimated standard deviations) are given in Table 2 and Table 3, respectively.

The cadmium atoms in both **4** and **6** are located on a twofold rotation axis; accordingly, their asymmetric units contain one half of the bipyridine (**4**) or phenanthroline (**6**) ligand, one pyrimidine-2-thionate ligand and one half of the cadmium atom.

Table 2. Selected bond lengths [Å] and angles [°] for [Cd(4,6-CF_3MepymS)$_2$bipy] (**4**).[a]

Cd–N(3)	2.38(3)	N(2)–C(2)	1.35(4)
N(3)–C(7)	1.25(4)	Cd–S	2.523(10)
N(3)–C(11)	1.38(5)	Cd–N(l)	2.56(2)
S–C(l)	1.68(3)		
N(3)–Cd–N(3)#l	69.9(14)	N(3)–Cd–S	150.9(7)
N(3)#l-Cd–S	94.2(8)	N(3)–Cd–S#l	94.2(8)
S–Cd–S#l	109.4(6)	N(3)–Cd–N(l)#l	86.8(9)
S–Cd–N(l)#l	118.5(6)	N(3)–Cd–N(l)	90.6(10)
N(3)#l-Cd–N(l)	86.8(9)	S–Cd–N(l)	63.5(7)
S#l-Cd–N(l)	118.5(6)	N(l)#l-Cd–N(l)	176.9(14)

[a] Symmetry code: #1 = –*x*, –*y*, *z*.

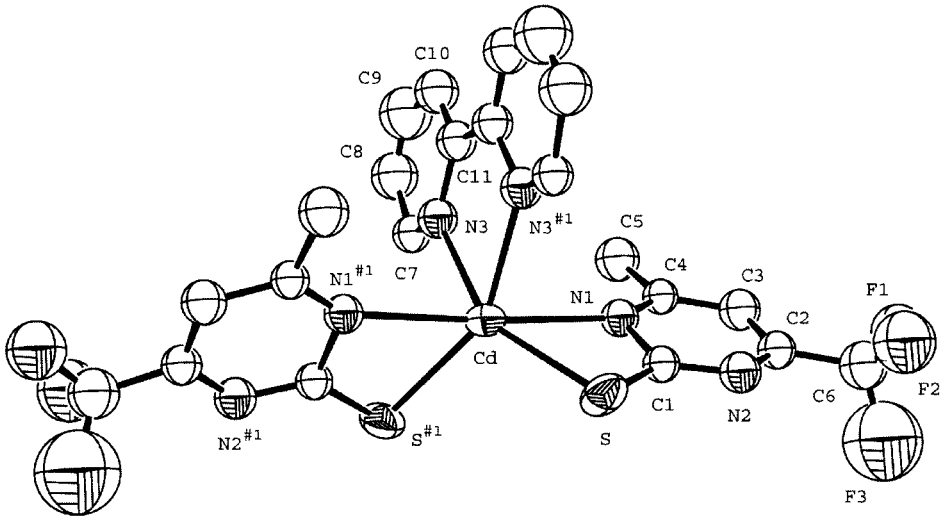


Figure 3. ORTEP diagram of the molecular structure of [Cd(4,6-CF_3MepymS)$_2$(bipy)] (**4**), with 40% thermal ellipsoid probability. The hydrogen atoms have been omitted for clarity. Symmetry code: #1 = –*x*, –*y*, *z*.

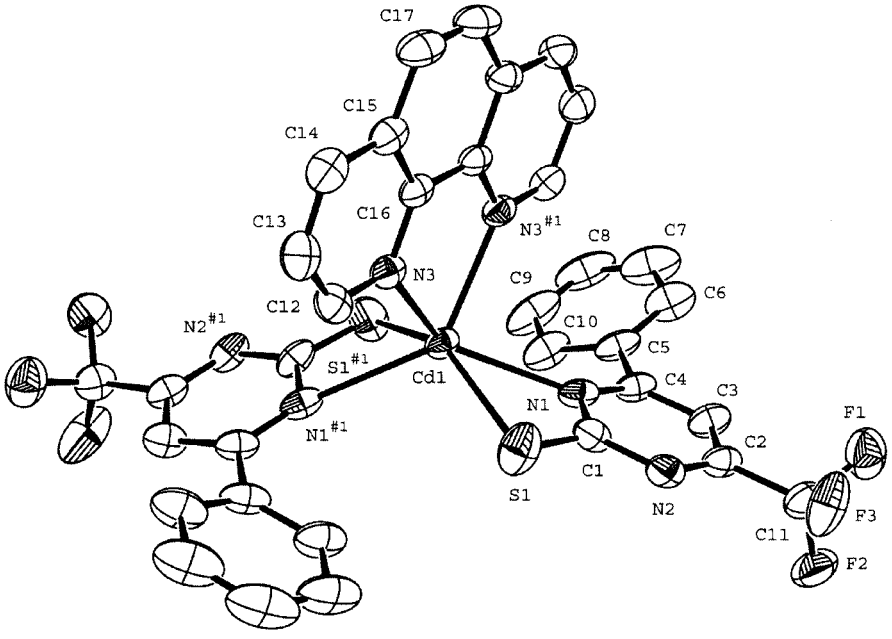


Figure 4. ORTEP diagram of the molecular structure of [Cd(4,6-CF_3PhpymS)$_2$(phen)] (**6**), with 30% thermal ellipsoid probability. The hydrogen atoms have been omitted for clarity. Symmetry code: #1 = –*x* + 2, *y*, –*z* + 1/2.

Table 3. Selected bond lengths [Å] and angles [°] for [Cd(4,6-CF_3PhpymS)$_2$phen] (**6**).[a]

Cd(1)–N(3)#1	2.378(4)	Cd(1)–N(3)	2.378(4)
Cd(1)–S(1)	2.4758(17)	Cd(1)–S(1)#1	2.4758(17)
Cd(1)–N(1)	2.570(4)	Cd(1)–N(1)#1	2.570(4)
S(1)–C(1)	1.533(6)		
N(3)#1-Cd(1)–N(3)	70.62(19)	N(3)#1-Cd(1)–S(1)	113.99(10)
N(3)–Cd(1)–S(1)	94.92(10)	N(3)–Cd(1)–S(1)#1	113.99(10)
S(1)–Cd(1)–S(1)#1	144.89(11)	N(3)#1-Cd(1)–N(1)	87.86(12)
N(3)–Cd(1)–N(1)	136.46(11)	S(1)–Cd(1)–N(1)	59.18(8)
S(1)#1-Cd(1)–N(1)	104.96(9)	N(3)–Cd(1)–N(1)#1	87.86(12)
S(1)–Cd(1)–N(1)#1	104.96(9)	N(1)–Cd(1)–N(1)#1	130.17(16)

[a] Symmetry code: #1 = $-x + 2$, y, $-z + 1/2$.

In both cases the molecular structure consists of discrete molecular species, which shows that the presence of an additional didentate coligand inhibits the polymerisation of the complexes. In both compounds the cadmium atom is hexacoordinated by the chelating nitrogen donors of the coligand (bipy or phen) and two anionic pyrimidine-2-thionate ligands, which also act in a didentate chelating (S,N) manner.

The cadmium atom in compound **4** is in a distorted [CdS_2N_4] octahedral environment. The disposition of the ligands in **4** is such that the sulfur atoms occupy *cis* positions. The equatorial plane of the molecule can be considered as being formed by the two nitrogen atoms from the 2,2′-bipyridine molecule and two sulfur atoms from pyrimidine-2-thionato ligands; these four atoms are not exactly coplanar. In terms of the best plane that includes these four donor atoms and the cadmium centre, the atoms N(3) and S, which occupy *trans* positions, are both below this plane (by –0.514 and –0.318 Å respectively), while the atoms N(3#1) and S(#1) are located above this plane (by +0.514 and +0.318 Å respectively). The cadmium atom, however, is in the plane defined above.

These deviations produce N(3)–Cd–S and N(3#1)–Cd–S(#1) bond angles of 150.9(7)°, which differ from the ideal value of 180°. In addition, the small angles of the chelate rings, together with the elongation in the axial direction, cause the S–Cd–S′ and S–Cd–N(3#1) angles to deviate significantly from 90° [109.4(6) and 94.2(8)°, respectively].

In complex **6** the disposition of the 4-trifluoromethyl-6-phenylpyrimidine-2-thionate ligands differs from that found in [Cd(4,6-CF_3MepymS)$_2$(bipy)] (**4**). As in compound (**4**), the cadmium atom in **6** is also in a [CdS_2N_4] environment, although in this case the geometry is best described as distorted trigonal prismatic. This can clearly be seen by inspection of the twist angle between the two parallel faces of the coordination polyhedron, as shown in Figure 5. These values are 14.2° for N(3) and N(3#1), 10.5° for N(1) and S(1) and 10.5° for N(1#1) and S(1#1). The expected values are 0° for a regular trigonal-prismatic geometry and 60° for an octahedral one.

In the structure, the three didentate ligands (two pyrimidine-2-thionates and one phenanthroline) link the two triangular faces of the trigonal prism. The higher value of 14.2° for the twist angle involving the phenanthroline ligand

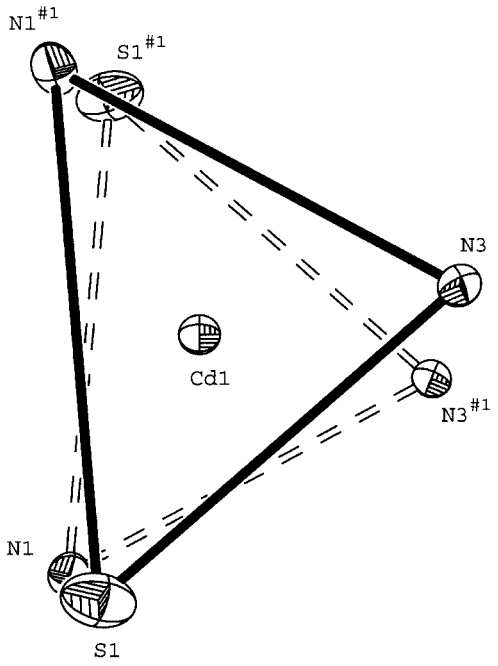


Figure 5. Distorted trigonal-prismatic environment for [Cd(4,6-CF_3PhpymS)$_2$(phen)] (**6**).

[N(3) and N(3#1)] can be explained by the formation of a rigid five-membered chelating ring, while the pyrimidine-2-thionate ligands form four-membered rings.

The Cd–S bond lengths [2.523(10) for **4** and 2.4578(17) Å for **6**] are similar to those found in other octahedral compounds of cadmium(II) with heterocyclic thionate ligands [2.588–2.5331 Å].[42,46] The Cd–N_{pymS} bond lengths [2.56(2) Å and 2.570(4) Å for **4** and **6**, respectively] are clearly longer than those involving the metal and the nitrogen atoms of the bipyridine in **4** or phenanthroline in **6** [Cd–N_{bipy} = 2.38(3) Å and Cd–N_{phen} = 2.378(4) Å]. This situation is probably due to the fact that the chelate coordination of the thionate ligand gives rise to a four-membered ring, which causes an elongation of the C–N bond as the interaction with sulfur is more favourable and the thionate ligand is rigid. However, these Cd–N_{bipy} and Cd–N_{phen} bond lengths [2.38(3) Å] do not differ significantly from those found in other octahedral cadmium(II) 2,2′-bipyridine and 1,10-phenanthroline complexes.[42,46]

The thionate ring is nearly planar and the exocyclic sulfur atom is also in the same plane. Other structural characteristics of the thionate ligand and the 2,2′-bipyridine or 1,10-phenanthroline unit are as one would expect and do not warrant further discussion.

Compound **6** shows a wide variety of intra- and intermolecular interactions that involve the π clouds of the aromatic rings.

A view of the crystal packing of this compound is shown in Figure 6. Each molecule in the crystal lattice interacts with four neighbouring molecules: two through the phenanthroline groups and two through the pyrimidine rings. Only the interactions between the phenanthroline rings are

shown in the figure (upper part of Figure 6). The crystal packing is such that the phenanthroline rings are opposite one another and π–π stacking occurs between the outer rings of each phenanthroline unit (distance between centroids = 3.597 Å). The rings of the phenanthroline groups involved in the π interactions are arranged in such a way that the six atoms of the ring do not completely eclipse those of the other ring, meaning that the interaction is not "perfect face alignment" but "offset or slipped stacking" (distances between the corresponding atoms of the two rings of 3.587, 3.588 and 3.616 Å). Figure 7 shows a view perpendicular to the planes of the phenanthroline groups.

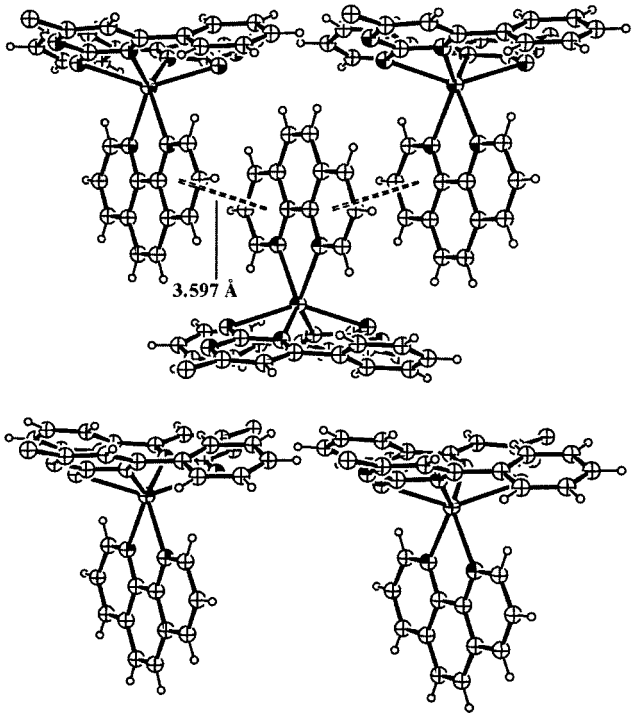


Figure 6. Crystal packing diagram of **6**; intermolecular π–π stacking interactions between phenanthroline rings are represented by dashed lines.

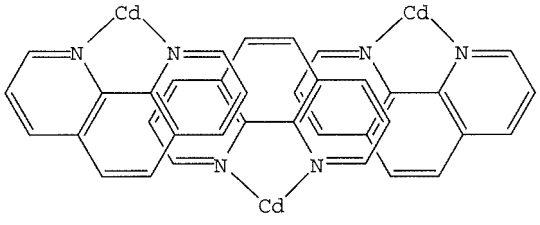


Figure 7. Overlapping between phenanthroline rings of three neighbouring molecules in **6**.

A view of the interactions between one molecule in the crystal lattice and neighbouring molecules through the pyrimidine rings is shown in Figure 8 (see also lower part of Figure 6).

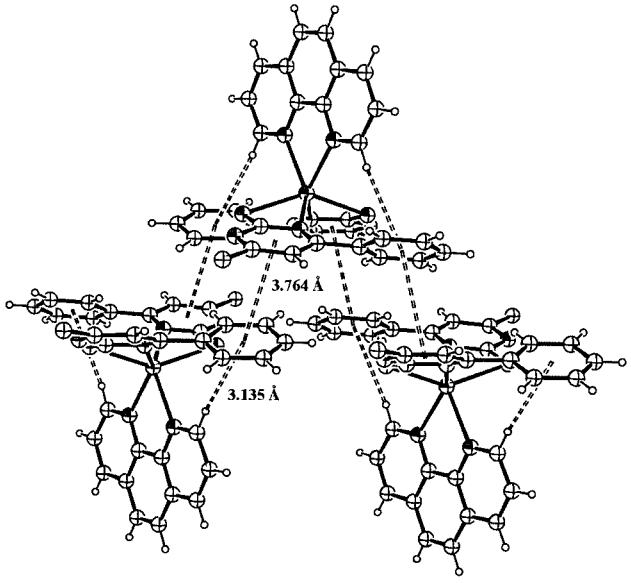


Figure 8. A view of complex **6** showing intramolecular C–H···π bonds and intermolecular π–π interactions between phenyl rings.

It can be seen from Figure 8 that, besides the π–π stacking interactions discussed above, each molecule in the crystal lattice is involved in two other interactions through the π clouds of the aromatic rings of the heterocyclic thione: one of these interactions is intramolecular and the other is intermolecular. The intramolecular interaction is of the C–H···π type and occurs between the protons *ortho* to the phenanthroline nitrogen (the most acidic protons in this unit) and the phenyl groups in the 6-position of the pyrimidine rings (H–centroid distance = 3.135 Å; C–centroid distance = 4.060 Å; C–H–centroid angle = 173.70°). It is interesting to note the high level of directionality of this interaction. In this situation each molecule is involved in two identical interactions of this type due to the presence of two pyrimidine units in each molecule.

As far as the intermolecular interaction is concerned, each pyrimidine ring takes part in a π–π stacking interaction with a phenyl ring in the 6-position of a pyrimidine ring in a neighbouring molecule. This π–π stacking interaction is of the most common offset or slipped-stacking type. This type of interaction is characterised by a distance between the centroids of the rings in question of about 3.8 Å. In the case under discussion here the distance between the centroids is 3.764 Å (the distances between the corresponding atoms ranges between 3.637 and 3.899 Å).

The compounds [Cd(4,6-CF_3MepymS)$_2$(bipy)] (**4**) and [Cd(4,6-CF_3PhpymS)$_2$(phen)] (**6**) (Figure 9) have different groups in the 6-position of the pyrimidine rings and, consequently, the disposition of the pyrimidine ligands in the two complexes is very different. These differences are clear when one considers the dihedral angles R–C–C′–R′, where R or R′ is the group in the 6-position (Me or Ph) and C or C′ is the carbon atom in the 6-position of the ring to which the substituent is attached. These angles have values of 110.0° when R = Me and 175.8° when R = Ph.

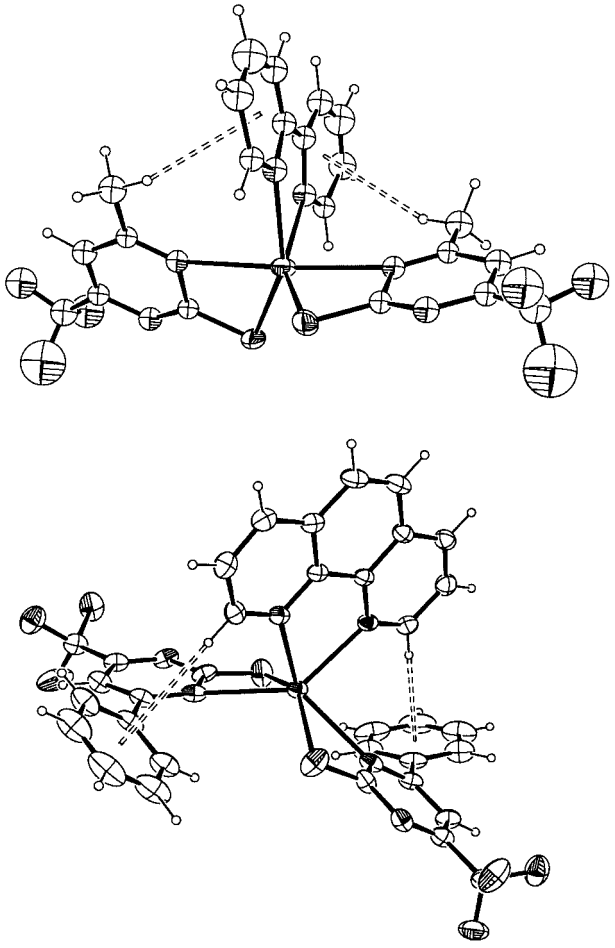


Figure 9. Views of complexes **4** (top) and **6** (bottom) illustrating the disposition of the pyrimidine rings.

Molecular structure of [Hg(4,6-CF_3MepymS)$_2$] (8)

Figure 10 shows a view of compound **8** together with the atomic numbering scheme. Selected bond lengths and angles (with estimated deviations) are given in Table 4.

Table 4. Selected bond lengths [Å] and angles [°] [Hg(4,6-CF_3MepymS)$_2$] (**8**).[a]

Hg–S#l	2.330(2)	N(1)–C(4)	1.325(9)
Hg–S	2.330(2)	Hg–N(1)	2.773(6)
N(2)–C(2)	1.320(9)	Hg–Hg#2	3.4845(5)
N(2)–C(1)	1.325(7)	Hg–Hg#3	3.4845(5)
S–C(l)	1.752(6)	N(1)–C(1)	1.333(9)
S#l-Hg–S	180.0	N(2)–C(2)–C(6)	114.3(8)
S#l-Hg–Hg#2	90.0	C(3)–C(2)–C(6)	120.6(6)
S–Hg–Hg#2	90.0	C(2)–C(3)–C(4)	115.1(6)
S#l-Hg–Hg#3	90.0	N(1)–C(4)–C(3)	122.3(6)
S–Hg–Hg#3	90.0	N(1)–C(4)–C(5)	115.2(7)
Hg#2-Hg–Hg#3	180.0	C(3)–C(4)–C(5)	122.6(7)
C(l)-S–Hg	94.2(2)		

[a] Symmetry codes: #1 = $-x + 1, -y + 1, -z + 1$; #2 = $-x + 1, y, -z + 1/2$; #3 = $-x + 1, y, -z + 3/2$.

In compound **8** the whole molecule, except F(2), lies on a mirror plane (symmetry code #4) and the mercury atom is located on a centre of symmetry (symmetry code #1); accordingly, the asymmetric unit contains one pyrimidine-2-thionate ligand (apart from one of the fluorine atoms of the CF_3 group) and one half of the mercury atom. In the molecule, the mercury atom is bonded to two sulfur atoms in a linear disposition. The Hg–S bond length [2.330(2) Å] is very similar to those found in other thionatomercury complexes with a linear geometry.[11,47–49]

In the complex the two ligands are on different sides of the line defined by the S–Hg–S bonds, and the pyrimidine rings are in a staggered conformation. The ligands are oriented in such a way that the N(1) atom is close to the mercury atom (distance of 2.773 Å). This value is larger than those observed in other mercury complexes containing heterocyclic donor nitrogen ligands, such as [Hg(pyS)(OAc)][50] (2.210 Å) or [HgMepy](NO_3)[51] [2.12(2) Å], but shorter than the sum of the van der Waals radii (3.23 Å),[52] and comparable to the distances in other mercury thiolate complexes characterised by weak intramolecular Hg···N interactions (2.798–2.980 Å).[46,53–55]

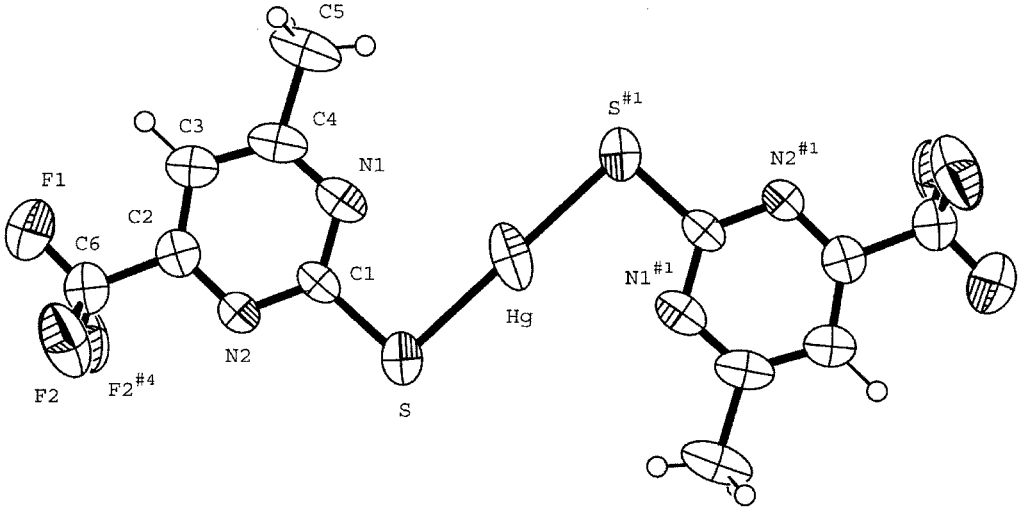
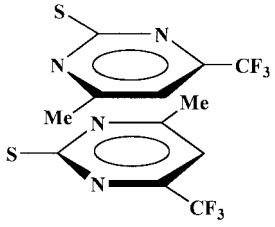


Figure 10. ORTEP diagram of the molecular structure of [Hg(4,6-CF_3MepymS)$_2$] (**8**), with 50% thermal ellipsoid probability. Symmetry codes: #1 = $-x + 1, -y + 1, -z + 1$; #4 = $x, y, -z + 1$.

The Hg···Hg distance [3.4845(5) Å] is much longer than those found in elemental mercury[56] (3.02 Å), in mercury clusters with mercury in an oxidation state of zero or in dinuclear mercury(I) complexes (Hg_2^{2+}, 2.5 Å).[57] However, the distance is close to or shorter than the sum of the van der Waals radii (1.7–2.0 Å)[58] and even shorter than that observed in most other mercury(II) complexes (3.848–3.578 Å).[59–63] It is also similar to the shortest Hg···Hg distance found in the case of tris(1,3-dimethyluracil-5-yl)mercurioxonium salt, which dimerises in two different ways through weak Hg···Hg contacts [Hg···Hg distances in the range 3.4552(6) to 3.5974(5) Å].[64]

The pyrimidine rings are planar and the sulfur atoms are located in the same plane as the corresponding ring and the Hg atom. The S–C bond length (1.752 Å) is close to those found in many other complexes containing thionate ligands.

Each [Hg(4,6-CF_3MepymS)$_2$] unit is essentially planar given that the pyrimidine ring is planar and both rings in each unit are related by an inversion centre located on the mercury atom. The pyrimidine rings of each unit are parallel to the crystallographic *ab* plane. In the crystal packing of the complex these units are arranged parallel to one another (Figure 11). The units are not superimposable but are related through a rotation of 180° around an axis that passes through the Hg centres and is parallel to the *b* axis, followed by a translation about the *c* axis (1 – *x*, *y*, *z* + 0.5). In this arrangement the molecules are stacked in the direction of the crystallographic *c* axis. Two types of intermolecular interaction are responsible for the packing arrangement. On the one hand, an Hg–Hg interaction exists between two units and this results in the Hg atoms being in a linear arrangement parallel to the *c* axis (Hg–Hg distance = 3.484 Å). On the other hand, a π–π stacking interaction exists between the pyrimidine rings of the contiguous [Hg(4,6-CF_3MepymS)$_2$] units (distance between the centroids = 3.512 Å). In this case the π–π stacking interaction gives rise to "perfect facial alignment", as shown by the angle formed by the centroids of the three consecutive rings (165.56°). This angle is very close to the 180° that one would expect for a complete interaction. It should also be noted that, for each interaction of this type, each ring is rotated with respect to the adjacent ring, meaning that the groups present on one ring do not eclipse those on other rings. This situation can clearly be seen in the diagram below (Scheme 2), which shows a view perpendicular to the plane of the pyrimidine rings (along the crystallographic *c* axis).



Scheme 2.

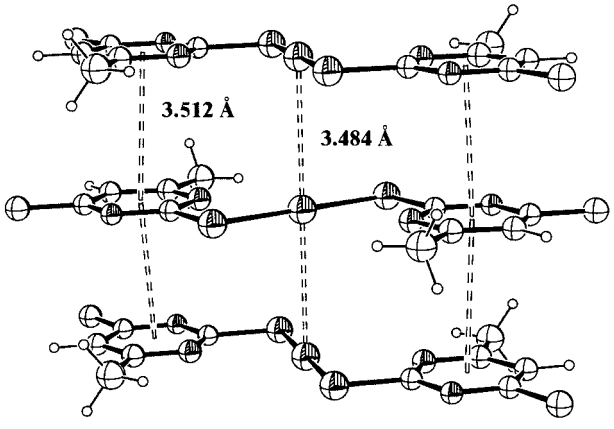


Figure 11. Partial packing diagram of **8** showing intermolecular π–π interactions and weak Hg···Hg contacts.

Spectroscopic Data

IR Spectra

The IR spectra of the complexes do not show bands due to ν(N–H), which in the free ligands appear between 3200 and 3050 cm^{-1}. This shows that deprotonation of the NH group has occurred during the synthesis and, therefore, that the ligand is coordinated in the thionato form. This conclusion is supported by the shift to smaller wavenumbers of the strong bands for ν(C=C) and ν(C=N), which appear at 1600–1550 and 1570–1525 cm^{-1}, respectively, in the free ligands, on going from the free ligands to the complexes. In addition, bands attributable to the ring breathing vibration at ca. 1000 and 630 cm^{-1} are observed. These shifts provide evidence that the nitrogen atom is bound to the metal atom.[65,66] In addition, the mixed complexes show bands typical for coordinated 2,2′-bypyridine[67] (770 and 730 cm^{-1}) and 1,10-phenanthroline[67,68] (1530–1505, 840 and 720 cm^{-1}).

NMR Spectra

The ^{1}H NMR spectra of the complexes do not contain a signal for the NH proton of the free ligand, which shows that the ligands are deprotonated in the complexes. The signals of all the protons of the pyrimidine ring and phenyl or methyl groups in the complexes are slightly shifted with respect to those of the free ligands. The NMR spectra of mixed complexes show additional signals for 2,2′-bipyridine and 1,10-phenanthroline at around δ = 7.6–9.2 ppm. These signals are slightly shifted to lower field in comparison to the corresponding signals in the free ligands. These changes again provide evidence of coordination of the ligands to the metal atom through the nitrogen atoms.[69–71] The ^{13}C NMR spectra of the free ligands 4,6-CF_3MepymSH and 4,6-CF_3PhpymSH show double the expected number of signals for C(2), C(6), CF_3 and CH_3, as the free ligands exist in two tautomeric forms. This doubling in the number of signals is not observed in the ^{13}C NMR spectra of the metal complexes. This situation provides evidence that, in solu-

tion, the ligand is coordinated to the metal in the thionate form only.

The mercury complexes have $\delta(^{199}Hg)$ values in the δ = –1180 to –1213 ppm range. These values are similar to those found in other mercury(II) thionates in which a weak interaction between the metal atom and the heterocyclic nitrogen is observed.[11,49]

Mass Spectra

The cadmium and mercury complexes were also characterised by mass spectrometry using the positive-ion FAB technique in 3-nitrobenzyl alcohol (NBA) as matrix. The FAB spectra of $[Cd(RpymS)_2(bipy)]$ and $[Cd(RpymS)_2(phen)]$ show the molecular ion with the appropriate isotope distribution, as well as peaks due to the fragments produced by the loss of one and two thionate ligands. In the case of $[Cd(4,6\text{-}CF_3MepymS)_2(phen)]$ the peak due to the loss of the 1,10-phenanthroline is also observed at m/z = 294.

The FAB mass spectra of both of the mercury compounds, $[Hg(RpymS)_2]$, show the molecular ion peak at m/z = 561 (R = CF_3) and 589 (R = 4,6-CF_3,Me) along with peaks at m/z = 381 and 386, respectively, which are associated with [Hg(RpymS)] formed by loss of one thionate ligand.

Conclusions

In this report we have described the electrochemical synthesis of a series of homoleptic and heteroleptic neutral cadmium(II) complexes and homoleptic mercury complexes with pyrimidine-2-thione derivatives. The ligands differ in the nature, position and number of substituents in the heterocyclic ring.

In the case of $[Cd(4\text{-}CF_3pymS)_2]$ (**1**), the presence of the trifluoromethyl substituent is not sufficient to prevent the association process and, as a consequence, the compound is a polymer, with the metal atom in an $[S_4N_2]$ octahedral environment. However, the presence of coligands, such as 1,10-phenanthroline and 2,2′-bipyridine, in the coordination sphere of cadmium modifies the aggregation process and the complexes $[Cd(4,6\text{-}CF_3MepymS)_2bipy]$ (**4**) and $[Cd(4,6\text{-}CF_3PhpymS)_2bipy]$ (**6**) are monomers with the metal atom in a different $[S_2N_4]$ hexacoordinate environment for both compounds − distorted octahedral for **4** and distorted trigonal prismatic for **6**. The crystal packing of compound **6** shows the presence of C–H···π and π–π stacking interactions. The groups involved in the C–H···π interactions are in the 6-position of the pyrimidine rings.

Experimental Section

General Considerations: 4-Trifluoromethylpyrimidine-2-thione, 1,1,1-trifluoroacetone, 1,1,1-trifluoro-2,4-pentanedione, thiourea, benzaldehyde, 1,10-phenanthroline and 2,2′-bipyridine are all commercial products and were used as supplied. Cadmium (Aldrich) was used as 2 × 2 cm plates. Mercury metal, a commercial product, was washed with nitric acid and water prior to use.

Elemental analysis was performed with a Carlo–Erba EA microanalyser. IR spectra were recorded as KBr mulls on a Bruker IFS-66V spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker AMX 300 MHz instrument with $CDCl_3$ or $[D_6]$DMSO as solvent. Chemical shifts are given relative to TMS as the internal standard. ^{119}Hg NMR spectra were recorded on a Bruker AMX500 spectrometer with $CDCl_3$ as solvent. The mass spectra (FAB) were recorded on a Micromass Autospec spectrometer, with 3-nitrobenzyl alcohol as the matrix material.

[4,6-CF_3MepymSH]: This compound was obtained by direct reaction between thiourea (2.428 g, 32 mmol) and 1,1,1-trifluoro-2,4-pentanedione (5 g, 32 mmol) in ethanol in the presence of concentrated hydrochloric acid (1 mL) as a catalyst. The mixture was heated under reflux for 2 h and the resulting dusty yellow solid was filtered off. $C_6H_5F_3N_2S$ (194.17): calcd. C 37.11, H 2.60, N 14.43, S 16.51; found C 36.89, H 2.60, N 14.26, S 16.08. IR (KBr): $\tilde{\nu}$ = 3100–3200 (m, br), 1615 (vs), 1590 (vs), 1440 (m), 1350 (vs), 1320 (w), 1200(s, br), 1130 (m), 1100 (m), 1030 (w), 970 (s), 920 (m), 860 (w), 850 (m), 705 (w), 660 (w), 595 (w), 570 (w), 530 (m), 510 (w), 470 (m), 450 (m), 370 (w) cm^{-1}. ^1H NMR (300 MHz, $[D_6]$DMSO, 25°): δ = 14.40 (s, 1 H, NH), 7.19 (s, 1 H, H^5), 2.39 (s, 3 H, CH_3) ppm. ^{13}C NMR (300 MHz, $[D_6]$DMSO): δ = 181.00 and 172.13 (s, C^2), 155.86 and 153.72 (q $^2J_{^{13}C\text{-}^{19}F}$ = 35 Hz, C^4), 104.89 (s, C^5), 163.61 (s, C^6), 119.27 and 119.67 (q, $^1J_{^{13}C\text{-}^{19}F}$ = 275 Hz, CF_3), 23.45 and 18.46 (s, CH_3) ppm. MS (FAB): m/z = 194 (4,6-CF_3MepymSH).

[4,6-CF_3PhpymSH]: The precursor 1,1,1-trifluoro-4-phenyl-3-buten-2-one was prepared previously. Benzaldehyde (5.22 g, 49 mmol) and 1,1,1-trifluoroacetone (5.21 g, 49 mmol) were added to a solution of NaOH (9.93 g, 0.25 mol) in cold water (200 mL). The mixture was allowed to reach room temperature, stirred for 6 h and finally heated to 65 °C for 12 h. The organic compounds were extracted with CH_2Cl_2, dried ($MgSO_4$) and the solvent removed by vacuum distillation to give a colourless liquid. (yield: 3.81 g, 39%). ^1H NMR (300 MHz, $CDCl_3$): δ = 6.8 (d, olefinic protons), 6.9 (d, olefinic protons), 7.3 (m, Ph) ppm. ^{13}C NMR (300 MHz, $[D_6]$-DMSO): δ = 180.53 (q, CF_3), 150.44 (CO), 115–130 (C, phenyl ring), 34.42 and 38.42 (C, olefinic) ppm.

Dry ethanol (40 mL) was placed in a flame-dried round-bottomed flask purged with argon, and sodium (0.45 g, 19.9 mmol) was added at 0 °C. When effervescence had ceased, a solution of thiourea (0.38 g, 4.99 mmol) in dry ethanol (30 mL) was added by cannula and the mixture was stirred for 15 min at room temperature. A solution of the previously prepared 1,1,1-trifluoro-4-phenyl-3-buten-2-one (1 g, 5 mmol) in dry ethanol was added to the reaction mixture by cannula. The mixture was heated under reflux under argon for 24 h. When the reaction was complete, the solvent was removed and the resultant solid was added to water (50 mL). The suspension was filtered and the alkaline solution was acidified to pH 6 with AcOH. The resulting dusty yellow solid was filtered off and washed with water until the washings were neutral. The solid was dried under vacuum to give 1.1 g of a dusty orange solid. The product was recrystallized from ethanol to give an orange solid. Yield: 0.652 g (51%). $C_{11}H_7F_3N_2S$ (256.25): calcd. C 51.50, H 2.75, N 10.93, S 12.51; found C 51.40, H 2.81, N 11.02, S 12.39. IR (KBr): $\tilde{\nu}$ = 3100–3200 (m, br), 1645 (m), 1610 (s), 1570 (s), 1550 (m), 1530 (m), 1490 (m), 1460 (m), 1450 (w), 1390 (vs), 1350 (m), 1330 (m), 1310 (w), 1260 (s), 1190 (vs), 1140 (m), 1110 (m), 1000 (s), 970 (w), 900 (m), 870 (w), 830 (s), 720 (m), 710 (w), 690 (s), 630 (m), 580 (m), 470 (w), 410 (w) cm^{-1}. ^1H NMR (300 MHz, $[D_6]$-DMSO): δ = 13.0 (s, 1 H, NH), 7.8 (s, 1 H, H^5), 7.6 (m, Ph) ppm. ^{13}C NMR (300 MHz, $[D_6]$DMSO): δ = 169.30 (s, C^2), 167.31 (q,

C^4), 110.42 (s, C^5), 163.85 (s, C^6), 118.54 (q, CF_3), 122.98–135.32 (phenyl ring) ppm. MS: m/z = 257.2 [M^+], 511 [M_2^+].

Electrochemical Synthesis: All complexes were obtained by an electrochemical procedure.[25] The cell was a 100-mL, tall-form beaker fitted with a rubber bung. An acetonitrile solution of the thione containing tetraethylammonium perchlorate (10 mg) was electrolysed using a platinum wire as the cathode and a cadmium plate as a sacrificial anode suspended from another platinum wire. For the synthesis of mercury compounds, the anode, which was in the bottom of the vessel, was also connected through a platinum wire. For the synthesis of mixed complexes, the corresponding co-ligand was added to the solution phase. In all cases, hydrogen was evolved at the cathode. The cells can be summarised as $M_{(+)}/CH_3CN$ + RpymSH + L′/$Pt_{(-)}$. During the electrolysis the yellow colour of the solution faded and, at the end of the reaction, the solids were isolated by filtration.

[Cd(4-CF_3pymS)$_2$] (1): Electrochemical oxidation of a cadmium anode in a solution of 4-(trifluoromethyl)pyrimidine-2-thione (4-CF_3pymSH; 0.150 g, 0.83 mmol) in acetonitrile (50 mL) at 14 V and 10 mA for 1.5 h caused 36 mg of cadmium to be dissolved (E_f = 0.52 mol F^{-1}). During the electrolysis hydrogen was evolved at the cathode and at the end of the experiment a crystalline solid, suitable for X-ray studies, had formed at the bottom of the vessel. The yellow solid was filtered off, washed with acetonitrile and diethyl ether and dried under vacuum. Yield: 0.102 g (52%). $C_{10}H_4CdF_6N_4S_2$ (470.69): calcd. C 25.5, H 0.9, N 11.9, S 13.6; found C 25.5, H 0.8, N 12.0, S 13.6. IR (KBr): $\tilde{\nu}$ = 1570 (s), 1550 (vs), 1420 (m), 1345 (s), 1325 (vs), 1200 (s), 1175 (m), 1145 (m), 1110 (s), 830 (vs), 780 (m), 730 (s), 670 (s), 470 (m), 440 (m) cm^{-1}. ^1H NMR (300 MHz, [D_6]DMSO): δ = 7.37 (d, 1 H, H^5), 8.53 (d, 1 H, H^6) ppm. ^{13}C NMR (300 MHz, [D_6]DMSO): δ = 183.34 (C^2), 168.68 (C^6), 154.17 (q, C^4), 114.95 (C^5), 120 (q, CF_3) ppm.

[Cd(4-CF_3pymS)$_2$(bipy)] (2): Electrolysis of an acetonitrile solution containing 4-CF_3pymSH (0.150 g, 0.83 mmol), 2,2′-bipyridine (0.065 g, 0.42 mmol) and a small amount of tetraethylammonium perchlorate (ca. 10 mg) at 10 mA and 16 V for 1.5 h dissolved 26 mg of cadmium (E_f = 0.44). At the end of the experiment the white solid was filtered off, washed with acetonitrile and dried in vacuo. The compound was characterised as [Cd(4-CF_3pymS)$_2$(bipy)] (**2**). Yield: 0.142 g (55%) $C_{20}H_{12}CdF_6N_6S_2$ (626.88): calcd. C 38.3, H 1.9, N 13.4, S 10.2; found C 38.0, H 1.9, N 13.5, S 10.2. IR (KBr): $\tilde{\nu}$ = 1585 (m), 1550 (vs), 1475 (w), 1460 (w), 1430 (m), 1415 (s), 1335 (vs), 1240 (w), 1200 (vs), 1165 (w), 1150 (w), 1130 (m), 1110 (m), 1010 (m), 970 (m), 830 (m), 820 (m), 760 (s), 730 (m), 670 (s), 645 (w), 620 (w) cm^{-1}. ^1H NMR (300 MHz, [D_6]DMSO): δ = 7.21 (d, 2 H, H^5), 8.51 (d, 2 H, H^6); bipy: 9.10 (d, 2 H, $H^6/H^{6'}$), 7.60 (dd, 2 H, $H^5/H^{5'}$), 8.10 (dd, 2 H, $H^4/H^{4'}$), 8.80 (d, 2 H, $H^3/H^{3'}$) ppm. ^{13}C NMR (300 MHz, [D_6]DMSO): δ = 168.67 (C^2), 162.10 (C^6), 154.45 (q, C^4), 121 (q, CF_3), 114.9 (C^5), 149.12 (bipy, $C^2/C^{2'}$); 139.16 (bipy, $C^5/C^{5'}$), 125.38 (bipy, $C^3/C^{3'}$), 118.55 (bipy, $C^4/C^{4'}$) ppm. MS (FAB): m/z = 448 [Cd(4-CF_3pymS)(bipy)], 627 [Cd(4-CF_3pymS)$_2$(bipy)].

[Cd(4-CF_3pymS)$_2$(phen)] (3): A similar experiment to that described above (12 V, 10 mA, 1.5 h) with 4-CF_3pymSH (0.150 g, 0.83 mmol) and phenanthroline (0.084 g, 0.467 mmol) in acetonitrile (50 mL) dissolved 27 mg of cadmium (E_f = 0.46). The solid was filtered off, washed with cold acetonitrile and diethyl ether, and dried under vacuum. Yield: 0.122 g (45%). $C_{22}H_{12}CdF_6N_6S_2$ (650.90): calcd. C 40.6, H 1.9, N 12.9, S 9.8; found C 40.6, H 1.8, N 12.9, S 9.9. IR (KBr): $\tilde{\nu}$ = 1610 (m), 1580 (m), 1550 (vs), 1525 (w), 1510 (w), 1500 (s), 1480 (m), 1415 (vs), 1335 (vs), 1320 (m), 1190 (s), 1160 (m), 1130 (w), 1110 (w), 1095 (w), 1070 (w), 1010 (m), 985 (m), 970 (w), 860 (m), 840 (s), 830 (s), 815 (s), 770 (m), 720 (vs), 665 (s), 635 (m), 460 (w), 430 (w), 415 (w), 350 (w), 310 (w) cm^{-1}. ^1H NMR (300 MHz, [D_6]DMSO): δ = 7.60 (d, 2 H, H^5), 8.60 (d, 2 H, H^6); phen: 8.87 (d, 2 H, H^2/H^9), 7.80 (dd, 2 H, H^3/H^8), 8.80 (d, 2 H, H^7/H^4), 8.00 (s, 2 H, H^6/H^5) ppm. ^{13}C NMR (300 MHz, [D_6]DMSO): δ = 170.12 (C^2), 162.11 (C^6), 154.21 (C^4), 114.96 (C^5), 127 (q, CF_3), 149.62 (phen, C^9/C^2), 139.80 (phen, C^{4b}/C^{6b}), 139.33 (C^4/C^7), 128.74 (phen, C^{4a}/C^{6a}), 127.05 (phen, C^5/C^6), 125.13 (phen, C^3/C^8) ppm. MS (FAB): m/z = 471 [Cd(4-CF_3pymS)(phen)], 650 [Cd(4-CF_3pymS)$_2$(phen)].

[Cd(4,6-CF_3MepymS)$_2$(bipy)] (4): Electrolysis of an acetonitrile solution containing 4,6-CF_3MepymSH (0.200 g, 1.03 mmol) and bipyridine (0.080 g, 0.51 mmol) at 10 mA and 32 V for 2.75 h dissolved 73 mg of cadmium (E_f = 0.56). At the end of the experiment the yellow solid was filtered off, washed with acetonitrile and diethyl ether, and dried in vacuo. The compound was characterised as [Cd(4,6-CF_3MepymS)$_2$(bipy)]. Yield: 0.128 g (38%). $C_{22}H_{16}CdF_6N_6S_2$ (654.93): calcd. C 40.3, H 2.5, N 12.8, S 9.8; found C 40.7, H 2.3, N 12.9, S 9.6. IR (KBr): $\tilde{\nu}$ = 1590 (m), 1565 (vs), 1540 (vs), 1465 (m), 1435 (s), 1380 (vs), 1360 (m), 1310 (m), 1270 (vs), 1255 (s), 1220 (m), 1190 (m), 1135 (s), 1100 (m), 1010 (m), 1000 (m), 970 (m), 910 (m), 845 (s), 760 (s), 730 (m), 705 (s), 645 (w), 540 (m), 460 (w), 405 (w) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.53 (s, 6 H, CH_3), 6.87 (s, 2 H, H^5); bipy: 8.91 (d, 2 H, $H^6/H^{6'}$), 7.82 (dd, 2 H, $H^5/H^{5'}$), 8.05 (dd, 2 H, $H^4/H^{4'}$), 8.23 (d, 2 H, $H^3/H^{3'}$) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 184.07 (C^2), 169.13 (C^6), 155.17 (q, C^4), 109.57 (s, C^5), 24.33 (s, CH_3), 122.49 (q, CF_3), 150.62 (bipy, $C^2/C^{2'}$), 150.03 (bipy, $C^6/C^{6'}$), 140.17 (bipy; $C^5/C^{5'}$), 126.4 (bipy, $C^3/C^{3'}$), 112.8 (bipy, $C^4/C^{4'}$) ppm. MS (FAB): m/z = 463 [Cd(4,6-CF_3MepymS)(bipy)], 499 [Cd(4,6-CF_3MepymS)$_2$], 655 [Cd(4,6-CF_3MepymS)$_2$(bipy)].

Crystals of [Cd(4,6-CF_3MepymS)$_2$(bipy)] (**4**) suitable for X-ray studies were obtained by recrystallisation of the initial product from *i*PrOH.

[Cd(4,6-CF_3MepymS)$_2$(phen)] (5): An acetonitrile solution of 4,6-CF_3MepymSH (0.200 g, 1.03 mmol) and phenanthroline (0.100 g, 0.55 mmol) was electrolysed at 10 mA during 2.75 h and 68 mg of cadmium was dissolved from the anode (E_f = 0.53). At the end of the electrolysis the solution was concentrated and the resulting green solid was filtered off, washed with cold acetonitrile and diethyl ether, dried under vacuum and identified as [Cd(4,6-CF_3MepymS)$_2$(phen)]. Yield: 0.269 g (79%). $C_{24}H_{16}CdF_6N_6S_2$ (678.95): calcd. C 42.3, H 2.4, N 12.4, S 9.4; found C 42.0, H 2.4, N 12.6, S 9.0. IR (KBr): $\tilde{\nu}$ = 1570 (s), 1540 (vs), 1525 (w), 1505 (m), 1420 (m), 1385 (vs), 1360 (s), 1300 (m), 1270 (vs), 1255 (vs), 1220 (m), 1175 (s), 1160 (m), 1005 (w), 970 (w), 915 (m), 840 (s), 770 (w), 725 (s), 705 (vs), 630 (w), 545 (m), 460 (m) cm^{-1}. ^1H NMR (300 MHz, [D_6]DMSO): δ = 7.09 (s, 2 H, H^5), 2.06 (s, 6 H, CH_3); phen: 9.22 (dd, 2 H, H^2/H^9), 8.80 (d, 2 H, H^4/H^7), 8.01 (dd, 2 H, H^8/H^3), 8.2 (s, 2 H, H^5/H^6) ppm. ^{13}C NMR (300 MHz, [D_6]DMSO): δ = 184.07 (C^2), 169.13(C^6), 155.42 (q, C^4), 122.50 (q, CF_3), 109.34 (C^5), 24.40 (CH_3), 150.15 (phen, C^9/C^2), 141.82 (phen, C^{4b}/C^{6b}), 139.29 (phen, C^4/C^7), 129.62 (phen, C^{4a}/C^{6a}), 127.50 (phen, C^5/C^6), 125.39(phen, C^3/C^8) ppm. MS (FAB): m/z = 180 [phen], 294 [Cdphen], 487 [Cd(4,6-CF_3MepymS)(phen)], 499 [Cd(4,6-CF_3MepymS)$_2$], 679 [Cd(4,6-CF_3MepymS)$_2$(phen)].

[Cd(4,6-CF_3PhpymS)$_2$(phen)] (6): A similar experiment (6 V, 10 mA, 1 h) with 4,6-CF_3PhpymSH (0.100 g, 0.55 mmol) and phen (0.035 g, 0.19 mmol) in acetonitrile (50 mL) dissolved 18 mg of cadmium (E_f = 0.48). Crystals suitable for X-ray studies were obtained directly from the cell. The solid was filtered off, washed with cool acetonitrile and diethyl ether, and dried under vacuum. Yield:

0.119 g (36%). $C_{34}H_{20}CdF_6N_6S_2$ (803.08): calcd. C 50.8, H 2.5, N 10.4, S 8.0; found C 50.4, H 2.3, N 10.4, S 7.9. IR (KBr): $\tilde{\nu}$ = 1615 (s), 1559 (m), 1540 (w), 1515 (w), 1500 (m), 1430 (w), 1400 (w), 1380 (vs), 1318 (s), 1300 (m), 1241 (m), 1180 (s), 1150 (s), 1135 (s), 1000 (s), 840 (m), 810 (w), 780 (s), 720 (w), 730 (m), 715 (w), 700 (m), 650 (w), 640 (m) cm^{-1}. ^1H NMR (300 MHz, [D$_6$]DMSO): δ = 8.41 (s, 2 H, H^5); phen: 9.07 (dd, 2 H, H^2/H^9), 8.79 (d, 2 H, H^4/H^7), 8.00 (dd, 2 H, H^3/H^8), 8.20 (s, 2 H, H^5/H^6) ppm; signals at δ = 7.39–7.84 ppm were assigned to the phenyl group.

[Hg(4-CF$_3$pymS)$_2$] (7): A solution of acetonitrile (50 mL) containing 4-CF$_3$pymSH (0.150 g, 0.83 mmol) was electrolysed at 10 mA during 2 h. No precipitation occurred initially, but within several hours a white solid had formed and this was filtered off, washed with acetonitrile, dried and identified by elemental analysis. Yield: 0.096 g (41%). $C_{10}H_4F_6HgN_4S_2$ (558.87): calcd. C 21.5, H 0.7, N 10.0, S 11.5; found C 22.0, H 0.6, N 10.3, S 11.2. IR (KBr): $\tilde{\nu}$ = 1550 (vs), 1420 (s), 1350 (vs), 1330 (vs), 1280 (w), 1200 (s), 1175 (w), 1110 (s), 1005 (w), 975 (s), 845 (m), 830 (m), 750 (w), 730 (m), 670 (s), 630 (w), 455 (w), 365 (w) cm^{-1}. ^1H NMR (300 MHz, [D$_6$]DMSO): δ = 7.43 (d, 2 H, H^5), 8.61 (d, 2 H, H^6) ppm. ^{13}C NMR (300 MHz, [D$_6$]DMSO): δ = 176.95 (C^2), 160.45 (C^6), 153.85 (q, C^4), 111.98 (C^5), 121.49 (q, CF_3) ppm. ^{119}Hg NMR (500 MHz $CDCl_3$): δ = –1213 ppm. MS (FAB): m/z = 560 [Hg(4-CF$_3$pymS)$_2$], 381 [Hg(4-CF$_3$pymS)].

[Hg(4,6-CF$_3$MepymS)$_2$] (8): A similar procedure was used to that described for [Hg(4-CF$_3$pymS)$_2$]. 4,6-CF$_3$MepymSH (0.200 g, 1.03 mmol) was electrolysed at 10 mA during 2 h. At the end of the experiment a microcrystalline white solid had formed and this was filtered off, washed with acetonitrile, dried and identified by elemental analysis. Yield: 0.114 g (38%). $C_{12}H_8F_6HgN_4S_2$ (587.94): calcd. C 24.6, H 1.4, N 9.6, S 11.0; found C 24.6, H 1.2, N 9.5, S 11.1. IR (KBr): $\tilde{\nu}$ = 1580 (vs), 1535 (s), 1385 (vs), 1310 (w), 1270 (s), 1255 (m), 1220 (m), 1170 (m), 1140 (m), 1110 (m), 1025 (w), 975 (m), 920 (w), 865 (s), 845 (s), 780 (w), 750 (w), 710 (vs), 680 (w), 635 (w), 565 (w), 550 (m), 485 (w), 450 (w), 370 (w) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.18 (s, 2 H, H^5), 2.47 (s, 6 H, CH_3) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 177.13 (s, C^2), 170.80 (s, C^6), 155.60 (q, C^4), 118.70 (CF_3), 112.58 (s, C^5), 24.40 (s, CH_3) ppm. ^{119}Hg NMR (500 MHz, $CDCl_3$): δ = –1207 ppm. MS (FAB): m/z = 386 [Hg(4,6-CF$_3$MepymS)], 588 [Hg(4,6-CF$_3$MepymS)$_2$], 386 [Hg(4,6-CF$_3$MepymS)].

Crystallisation from ethanol/acetone gave monocrystals suitable for X-ray studies.

X-ray Crystal Structure Determinations: X-ray data were collected on a Bruker Smart CCD 1000 diffractometer for **1** and **6**, and on an Enraf–Nonius CAD4 diffractometer in the cases of **4** and **8**, with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The data were collected at 293 K for all structures. The ω-scan technique was employed to measure intensities for all crystals. Decomposition of the crystals did not occur during data collection. Absorption effects in compounds **1** and **6** were corrected with SADABS.[72] Absorption in **4** and **8** was corrected by semi-empirical Ψ scans. All the structures were solved by direct methods and refined[73] by full-matrix least-squares based on F^2. For all the complexes, hydrogen atoms were also included in idealised positions and refined with isotropic displacement parameters. All non-hydrogen atoms in the structures were refined anisotropically with the exception of compound **4**, in which only the heavy atoms (mercury and sulfur) were refined anisotropically due to the poor quality of the high-angle data. The CF_3 groups of compounds **1** and **6** are disordered over two positions with occupancies 51:49 and 57:43 for the groups on C(5) and C(10) in compound **1** and 63:37 for the CF_3 group in compound **6**. Atomic scattering factors and anomalous dispersion corrections for all atoms were taken from the International Tables for X-ray Crystallography.[74] The crystal data and summary of data collection and structure refinement for these compounds are given in Table 5. The structures were visualised with ORTEP3.[75]

CCDC-240151–240154 (for **1**, **4**, **6** and **8**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 5. Crystal data and structure refinement for **1**, **4**, **6** and **8**.

	1	**4**	**6**	**8**
Empirical formula	$C_{10}H_4CdF_6N_4S_2$	$C_{22}H_{16}CdF_6N_6S_2$	$C_{17}H_{10}Cd_{0.50}F_3N_3S$	$C_{12}H_8F_6HgN_4S_2$
Formula mass	470.69	654.93	401.54	587.94
Crystal System	triclinic	orthorhombic	monoclinic	orthorhombic
Space group	$P\bar{1}$	*Aba*2	*C*2/*c*	*Ibam*
a [Å]	7.0419(2)	15.911(3)	23.3377(11)	7.632(2)
b [Å]	10.3710(4)	17.930(4)	13.6311(7)	31.855(6)
c [Å]	11.3981(3)	9.098(2)	10.5163(5)	6.969(1)
a [°]	81.768(1)	90	90	90
β [°]	78.624(1)	90	108.391(1)	90
γ [°]	70.736(1)	90	90	90
Volume [Å^3]	767.63(4)	2595.5(9)	3174.6(3)	1684.3(6)
Z	2	4	8	4
D_c [Mg m^{-3}]	2.036	1.676	1.680	2.301
μ(Mo-K_α) [mm^{-1}]	1.758	1.069	0.891	9.395
F(000)	452	1296	1600	1096
Crystal size [mm]	0.25 × 0.05 × 0.05	0.42 × 0.26 × 0.06	0.35 × 0.20 × 0.10	0.80 × 0.25 × 0.05
T [K]	293	293	293	293
No. of reflections collected	5131	748	10 808	893
No. of indept. reflections	3674	432	3908	484
Goodness of fit on F^2	0.956	1.069	1.052	1.064
R[a]	0.0481	0.0836	0.0570	0.0212
$wR2$[b]	0.1092	0.1958	0.1476	0.0493

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [b] $wR2 = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2]/\Sigma(w|F_o^2|^2)\}^{1/2}$.

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