metal-organic compounds

The effect of hydrogen-bonding anions on the structure of metal–sulfimide complexes

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Investigations into the effects of the choice of anion on the hydrogen-bonding interactions between anions and metal–sulfimide cationic complexes have led to the study of three novel compounds. Hexakis(S,S-diphenylsulfimide)cobalt(II) diiodide S,S-diphenylsulfimide acetonitrile disolvate, [Co-$(C_{12}H_{11}NS)_6]I_2 \cdot C_{12}H_{11}NS \cdot 2C_2H_3N$, crystallizes in the centrosymmetric space group $P\bar{1}$ with $Z = 2$. Six diphenylsulfimide ligands coordinate to the cobalt centre through their N atoms. Two iodide counter-ions hydrogen bond to the cation through N—H$\cdots$I interactions, with N$\cdots$I distances in the range 3.7302 (19)–3.8461 (19) Å. One extra molecule of sulfimide is included in the asymmetric unit, regardless of the metal–ligand ratio used in the synthesis, and this sulfimide molecule also hydrogen bonds to one of the iodide counter-ions through one N—H$\cdots$I hydrogen bond. The reaction of $FeCl_3 \cdot 6H_2O$ with S,S-diphenylsulfimide monohydrate yields hexakis(S,S-diphenylsulfimide)iron(III) trichloride, $[Fe(C_{12}H_{11}NS)_6]Cl_3$. The complex crystallizes in the centrosymmetric cubic space group $Pa\bar{3}$ and the asymmetric unit contains one-sixth of a formula unit. Two of the chloride anions each hydrogen bond to three sulfimide NH groups on opposite sides of the $[Fe(Ph_2SNH)_6]^{3+}$ cation. The third chloride anion does not take part in any strong hydrogen bonding; instead it is surrounded by aromatic groups and is involved in C—H$\cdots$Cl hydrogen bonds. The reaction of $[Pt(Ph_2SNH)_4]Cl_2$ with I_2 facilitates oxidation of the Pt^{II} metal centre to Pt^{IV}, producing tetrakis(S,S-diphenylsulfimide)diiodoplatinum(IV) dichloride dichloromethane disolvate, $[PtI_2(C_{12}H_{11}NS)_4]Cl_2 \cdot 2CH_2Cl_2$. The crystal structure is centrosymmetric, with the elongated octahedral cationic complex situated on an inversion centre. The chloride anions are hydrogen bonded to the cation through N—H$\cdots$Cl hydrogen bonds, with two *cis* NH groups hydrogen bonded to each anion. Strong hydrogen bonding within these three compounds is limited to N—H$\cdots$halide hydrogen bonds between the cation and two anions, with a three-up/three-down arrangement of the NH groups in the first two compounds. The anions also 'cap' the NH groups in

the third compound. In all three cases, the anions are also involved in weaker hydrogen bonds utilizing the plethora of relatively acidic aryl CH groups in the structures.

Comment

S,S-Diphenylsulfimide, Ph_2SNH, has proven to be an extremely useful ligand for later transition metal centres in so far as the complexes produced invariably exhibit strong hydrogen bonding between the sulfimide NH groups and the counterions. As a result, the complexes often show unusual structural properties; by way of example, the ostensibly simple reaction of the ligand with $Cu(BF_4)_2$ results in a multitude of products, including three polymorphs of $[Cu(Ph_2SNH)_4](BF_4)_2$, the inter-allogon $[Cu(Ph_2SNH)_4]_2(BF_4)_4$ and the mixed coordination system $[Cu(Ph_2SNH)_4][Cu(Ph_2SNH)_5](BF_4)_4$ (Holmes *et al.*, 2002).


(I)

(II)

(III)
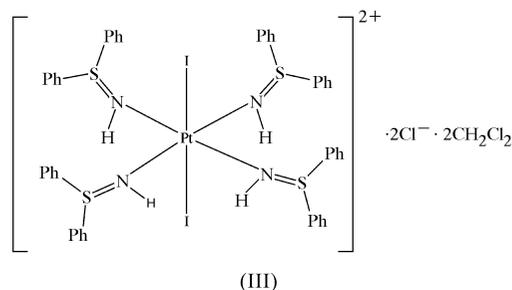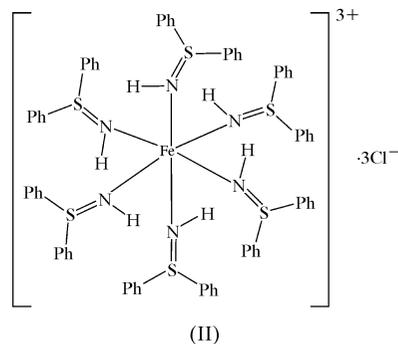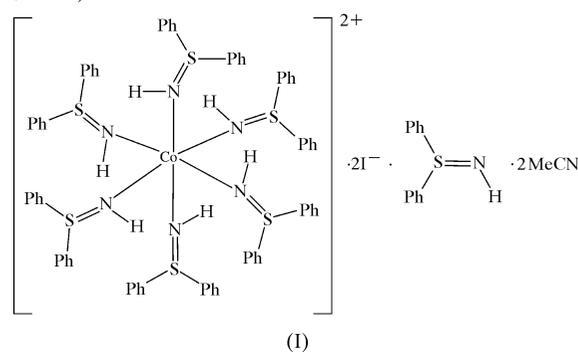
One of the first examples of a metal–sulfimide complex reported was $[Co(Ph_2SNH)_6]Cl_2$, in which the ligands are arranged around the metal centre in such a way as to maximize the hydrogen-bonding interactions between the sulfimide NH groups and the chloride counter-ions (Kelly *et al.*, 1998). Hence, each chloride ion acts as a trifurcated acceptor, with three NH bonds pointing upwards and three down. The isostructural nickel(II) complex has since been reported by Sellmann *et al.* (2001).

We describe here investigations into the effect of the modification of the anion on the hydrogen-bonding interactions between Co–, Fe– and Pt–sulfimide complexes and uncoordinated anions.

In the light of the successful study of $[Co(Ph_2SNH)_6]Cl_2$, the modification of the anion from the chloride to the larger, less electronegative, iodide was attempted. The reaction of Ph_2SNH with CoI_2 in acetonitrile results in pink crystals of $[Co(Ph_2SNH)_6]I_2 \cdot Ph_2SNH \cdot 2MeCN$, (I), which crystallizes in a triclinic space group, indicating that the crystallographically imposed symmetry of the chloride complex has been broken. The crystal structure of (I) is centrosymmetric and the asymmetric unit contains a complete formula unit. The Co^{II} centre is octahedrally coordinated by six sulfimide ligands, with *trans* angles lying between 178.44 (8) and 179.23 (8)° (Fig. 1 and Table 1). The ligands are arranged in the same way as in the chloride complex, with three sulfimide NH groups on either side of the metal. Each halide ion therefore acts as a trifurcated acceptor to the $[Co(Ph_2SNH)_6]^{2+}$ cation, with $N\cdots I$ distances in the range 3.7302 (19)–3.8461 (19) Å and $N-H\cdots I$ angles in the range 157 (2)–165 (2)° (Fig. 2 and Table 2). A mean distance of 3.66 (1) Å has been quoted for $N\cdots I$ contact distances for sp^2-hybridized NH groups (Desiraju & Steiner, 1999).

However, a seventh sulfimide ligand is included in the structure, this time acting as an outer- rather than an inner-sphere ligand. The ligand is not coordinated to the metal centre but interacts with the $[Co(Ph_2SNH)_6]I_2$ unit *via* an $N-H\cdots I$ hydrogen-bonding interaction, having an $N\cdots I$ distance of 3.987 (2) Å and a more linear $N-H\cdots I$ angle of 172 (2)°. Therefore, one of the iodide anions accepts four hydrogen bonds. Two acetonitrile molecules of crystallization are also included in the crystal structure.
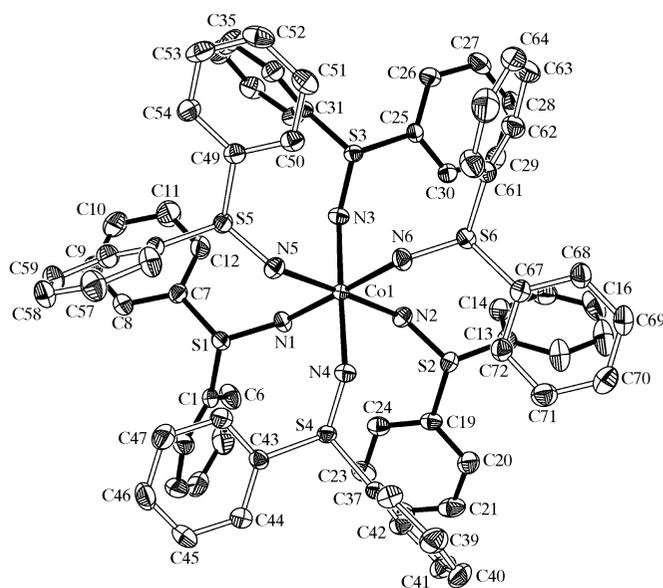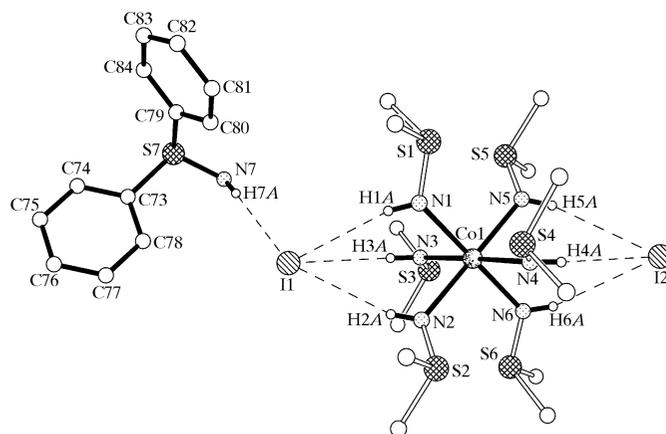
The structure appears rather asymmetric, with the second iodide anion only accepting three hydrogen bonds. It was expected that the system might, therefore, take up further units of Ph_2SNH. The addition of excess sulfimide, however, does not result in the incorporation of more of the free ligand. Compound (I) appears to be the only product, even in the presence of a large excess of sulfimide. The system also incorporates a number of weaker $C-H\cdots I$ hydrogen bonds using aromatic groups that surround the iodide anions. $C\cdots I$ contact distances lie in the range 4.072 (3)–4.423 (2) Å. A mean distance of 4.00 (2) Å has been quoted for the $C\cdots I$ contact distance for sp^2-hybridized CH groups (Desiraju & Steiner, 1999).

The 'capping' of the NH groups within the three-up/three-down arrangement through $N-H\cdots I$ hydrogen bonding in (I) clearly limits the extent of strong hydrogen bonding between complexes. $N-H\cdots I$ and $C-H\cdots I$ hydrogen bonds combine to create one-dimensional stacks of alternating cations and anions, propagating along the [223] direction. $C-H\cdots I$ interactions also link adjacent stacks together.

Interestingly, we have no evidence for the formation of simple $[Co(Ph_2SNH)_6]I_2$, even when exactly six molar equivalents (or slightly less) of sulfimide are used. It is not clear why the observed structure should be such a favourable arrangement, and this result serves to highlight the unpredictability and structural diversity of complexes of Ph_2SNH.

In the light of the fact that previous results indicate that the sulfimide ligands can readily adjust the relative orientations of the NH groups in order to facilitate the maximum degree of interaction with anions (*e.g.* multiple acceptors such as BF_4^-, *etc.*), the question of the effect of introducing a third halide into the basic $[ML_6]^{n+}$ unit becomes germane.

Attempts to prepare $[Co(Ph_2SNH)_6]Cl_3$ have proved unsuccessful; however, direct reaction of $FeCl_3$ with six equivalents of the ligand does provide a route to $[Fe(Ph_2SNH)_6]Cl_3$, (II), the first iron–sulfimide complex. Unlike $[Co(Ph_2SNH)_6]Cl_2$, which, though it has a low solubility in MeCN, may

Figure 1
A view of the cationic component of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity. Alternate Ph_2SNH ligands are shown using open bonds.

Figure 2
A view of the hydrogen bonding present in (I). H atoms (except for those bound to N atoms), C atoms (apart from the Cα atoms of the phenyl rings) and two solvent molecules have been omitted for clarity. $N-S$ and $S-C$ bonds are shown as open bonds in the metal-coordinated ligands. Hydrogen bonding is indicated by dashed lines.

be recrystallized from the hot solvent, this product does not even show appreciable solubility upon heating. To circumvent this recrystallization problem, the reaction was performed without stirring after the initial mixing of reagents. This approach promoted the growth of small but usable crystals of (II). The product crystallizes in a cubic space group with one-sixth of an Fe^{III} centre on a site of $\bar{3}$ symmetry, one sulfimide ligand and a total of one-half of a chloride anion in the asymmetric unit (Fig. 3). Atom Cl1 lies on a site of threefold symmetry and has an occupancy of $\frac{1}{3}$, while atom Cl2 lies on a site of $\bar{3}$ symmetry and has an occupancy of $\frac{1}{6}$. The angle at the metal centre is distorted from 90 to 86.21 (9)° (Table 3). The complete structure contains three chloride anions, one of which is inequivalent to the other two. The arrangement of the sulfimide ligands is identical to that in the structure of $[Co(Ph_2SNH)_6]Cl_2$, with two Cl atoms, Cl1 and a symmetry-equivalent, placed above and below the metal centre, each accepting three hydrogen bonds (Fig. 4 and Table 4). The third Cl atom, Cl2, is isolated in the structure and is not involved in any strong hydrogen-bonding interactions. Atom Cl2 is instead surrounded by phenyl groups of the Ph_2SNH ligands and is involved in six symmetry-equivalent $C-H \cdots Cl$ hydrogen bonds, having a $C \cdots Cl$ distance of 3.607 (3) Å ($C-H = 0.95$ Å, $H \cdots Cl = 2.86$ Å and $C-H \cdots Cl = 136°$). In the light of the previously observed tendency of the sulfimide ligands to maximize the hydrogen bonding in the system, this is a surprising observation, especially as the chloride anion is a strong acceptor. This result clearly indicates that the hydrogen-bonding arrangement within the $[M(Ph_2SNH)_6]Cl_2$ unit is extremely stable.
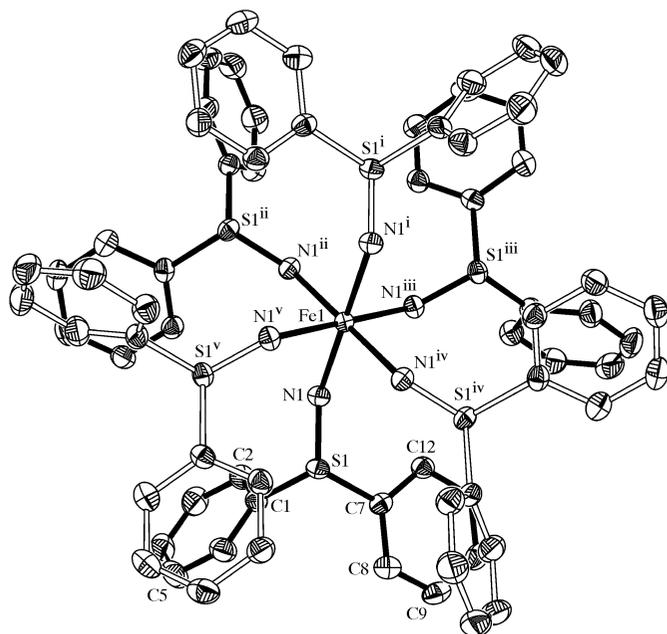
In the course of our investigations of metal–sulfimide complexes, we have observed two quite different types of reaction with platinum centres. When reacted with $(PPh_4)_2[PtCl_4]$ in CH_2Cl_2, a simple substitution to give $[Pt(Ph_2SNH)_4]Cl_2$ takes place (Kelly et al., 2000); in this product, the NH groups of the ligands are seen to orientate themselves in such a way as to maximize the hydrogen bonding to the anions. In reactions involving starting materials bearing nitrile ligands, the metal actually mediates addition reactions of the sulfimide to the nitriles; this phenomenon has been observed for Pt^{II} (Kelly & Slawin, 1999) and, most effectively, for Pt^{IV} starting materials (Makarycheva-Mikhailova et al., 2003).

We present here the results of an investigation into the reaction of $[Pt(Ph_2SNH)_4]Cl_2$ with iodine. This reaction was undertaken for two reasons: firstly, it would ascertain whether or not a stable Pt^{IV}–sulfimide complex (as opposed to a sulfimide/nitrile hybrid) could be isolated. Note that some previous examples of iodo–Pt^{IV} species containing S,N-donor ligands have proven to be unstable; for example, the Pt^{II} species $Pt(S_2N_2H)I(PMe_2Ph)$ is the only isolable product from the reaction of $Pt(S_2N_2H)(PMe_2Ph)_2$ with iodine (Jones et al., 1988). In addition, the aim was to observe the effect that introduction of the iodo ligands would have on the hydrogen-bonding arrangements of the sulfimide ligands.

Reaction of $[Pt(Ph_2SNH)_4]Cl_2$ with iodine in CH_2Cl_2 takes place rapidly, and the product $[Pt(Ph_2SNH)_4I_2]Cl_2$, (III), appears stable both in solution and in the solid state. A structure determination confirms that oxidation to Pt^{IV} has taken place, giving an elongated octahedral coordination with the Pt^{IV} ion situated on an inversion centre (Fig. 5 and Table 5); the asymmetric unit contains one-half of a formula unit and the two I atoms adopt mutually trans positions. It is likely that
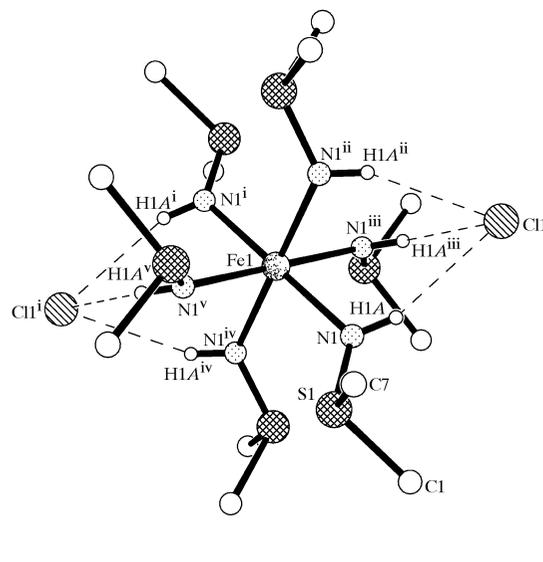

Figure 3
A view of the cationic component of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity. Alternate Ph_2SNH ligands are shown using open bonds. [Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $z-\frac{1}{2}, \frac{1}{2}-x, 1-y$; (iii) $\frac{1}{2}-y, 1-z, \frac{1}{2}+x$; (iv) $\frac{1}{2}-z, \frac{1}{2}+x, y$; (v) $y-\frac{1}{2}, z, \frac{1}{2}-x$.]

Figure 4
A view of the hydrogen bonding present in (II). H atoms (except for those bound to N atoms) and C atoms (apart from the Cα atoms of the phenyl rings) have been omitted for clarity. N—S and S—C bonds are shown as open bonds. Hydrogen bonding is indicated by dashed lines. [Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $z-\frac{1}{2}, \frac{1}{2}-x, 1-y$; (iii) $\frac{1}{2}-y, 1-z, \frac{1}{2}+x$; (iv) $\frac{1}{2}-z, \frac{1}{2}+x, y$; (v) $y-\frac{1}{2}, z, \frac{1}{2}-x$.]

this conformation is favoured because it allows the NH units of the sulfimide to become involved in significant hydrogen-bonding interactions with the chloride counter-ions (Table 6). As in the Pt^{II} analogue (and indeed other homoleptic complexes of Ph$_2$SNH), the ligands arrange themselves in such a way that the two pairs of *cis* S atoms extend from opposite sides of the MN$_4$ plane; as a result, each pair of NH groups can co-operate in hydrogen bonding to a different chloride ion. The average H···Cl distance is thus 2.46 Å (somewhat longer than in the Pt^{II} analogue, where the H···Cl distance is 2.25 Å; Kelly *et al.*, 2000), with average N—H···Cl angles of 166°. Although strong hydrogen bonds are limited to within the [Pt(Ph$_2$SNH)$_4$I$_2$]Cl$_2$ unit, weaker C—H···Cl hydrogen bonds (Table 6) are apparent between aryl CH groups and atom Cl3.

The structure of (III) contains two molecules of dichloromethane solvent per cationic complex; thus, the asymmetric unit contains one molecule of dichloromethane, which was found to be disordered. The solvent molecule was modelled over two sets of positions with a refined major occupancy of 80.6 (11)%. The metal-bound iodide has a close contact with one of the Cl atoms of the solvent molecule [I1···Cl2(x, y + 1, z) = 3.815 (4) Å].

Comparison of the metal–nitrogen bond lengths in the three title complexes (Tables 1, 3 and 5) shows that the Co—N bond lengths [mean 2.143 (6) Å] are significantly longer than the Pt—N [2.042 (3) Å] and Fe—N [2.078 (2) Å] bond lengths.

From the investigations presented here, it is clear that the three-up/three-down conformation of the $[M(\text{Ph}_2\text{SNH})_6]^{n+}$ ion is extremely stable. Attempts to alter this conformation through the introduction of less electronegative anions, or even extra anions, still leads to the same conformation being observed in (I) and (II), while the introduction of iodide

ligands to give an elongated octahedron in (III) still allows two sulfimide NH groups on each side of the complex to hydrogen bond to the chloride anions. In all three compounds, there are weaker hydrogen-bonding interactions between relatively acidic CH groups and the halide anions, resulting from the halide anions being positioned in the gaps between close-packed Ph$_2$SNH ligands.

Experimental

For the preparation of compound (I), CoI$_2$ (51 mg, 0.16 mmol) was dissolved in MeCN (5 ml), and a solution of Ph$_2$SNH·H$_2$O (250 mg, 1.14 mmol) in MeCN (5 ml) was added with stirring to give an intense blue-coloured solution containing a pink precipitate. This solid was redissolved by heating to give a clear solution from which pink crystals of (I) were grown by slow cooling. For the preparation of compound (II), FeCl$_3$·6H$_2$O (44 mg, 0.16 mmol) was dissolved in MeCN (10 ml) and a solution of Ph$_2$SNH·H$_2$O (250 mg, 1.14 mmol) in MeCN (10 ml) was added. The solution was stirred only to mix the two solutions and was then left to stand. The product has very limited solubility in MeCN, and precipitation of an orange solid was observed, but, on standing, small yellow crystals of (II) formed overnight. For the preparation of compound (III), [PtI$_2$-(Ph$_2$SNH)$_4$]Cl$_2$ was first prepared by the equimolar reaction of [Pt(Ph$_2$SNH)$_4$]Cl$_2$ with iodine in CH$_2$Cl$_2$, followed by removal of the solvent *in vacuo*. Crystals of (III) were grown by slow diffusion of ether into a solution of the product in CH$_2$Cl$_2$.

Compound (I)

Crystal data

[Co(C$_{12}$H$_{11}$NS)$_6$]I$_2$·C$_{12}$H$_{11}$NS·2C$_2$H$_3$N	$Z = 2$
$M_r = 1803.86$	$D_x = 1.429$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 13.0776$ (6) Å	Cell parameters from 49 288
$b = 15.1667$ (7) Å	reflections
$c = 22.4675$ (11) Å	$\theta = 2.3–28.5°$
$\alpha = 73.557$ (2)°	$\mu = 1.17$ mm^{-1}
$\beta = 87.490$ (2)°	$T = 150$ (2) K
$\gamma = 78.807$ (2)°	Block, pink
$V = 4192.5$ (3) Å^3	0.18 × 0.11 × 0.06 mm

Data collection

Bruker SMART 1000 CCD diffractometer	19 601 independent reflections
ω scans	12 795 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)	$R_{int} = 0.027$
$T_{min} = 0.818$, $T_{max} = 0.933$	$\theta_{max} = 29.0°$
49 288 measured reflections	$h = -17 \rightarrow 17$
	$k = -20 \rightarrow 19$
	$l = -30 \rightarrow 30$

Figure 5
A view of (III), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level, H atoms are represented by circles of arbitrary radii and hydrogen bonding is indicated by dashed lines. Solvent molecules and H atoms, except for those bound to N atoms, have been omitted for clarity. [Symmetry code: (i) $-x$, $1 - y$, $-z$.]

Table 1
Selected geometric parameters (Å, °) for (I).

Co1—N1	2.1486 (19)	Co1—N4	2.1400 (19)
Co1—N2	2.1679 (19)	Co1—N5	2.1454 (19)
Co1—N3	2.1187 (19)	Co1—N6	2.1367 (19)
N1—Co1—N2	84.82 (7)	N2—Co1—N6	95.46 (7)
N1—Co1—N3	85.63 (7)	N3—Co1—N4	178.54 (8)
N1—Co1—N4	95.19 (7)	N3—Co1—N5	96.10 (7)
N1—Co1—N5	94.28 (7)	N3—Co1—N6	93.68 (7)
N1—Co1—N6	179.23 (8)	N4—Co1—N5	85.06 (7)
N2—Co1—N3	85.11 (7)	N4—Co1—N6	85.50 (7)
N2—Co1—N4	93.75 (7)	N5—Co1—N6	85.45 (7)
N2—Co1—N5	178.44 (8)		

Table 2
Hydrogen-bonding geometry (Å, °) for (I).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1$A\cdots$I1	0.80 (2)	3.07 (2)	3.8337 (19)	159 (2)
N2—H2$A\cdots$I1	0.78 (2)	3.09 (2)	3.8207 (19)	157 (2)
N3—H3$A\cdots$I1	0.81 (2)	2.95 (2)	3.7302 (19)	163 (2)
N4—H4$A\cdots$I2	0.80 (2)	2.97 (2)	3.7413 (19)	165 (2)
N5—H5$A\cdots$I2	0.81 (2)	3.09 (2)	3.8461 (19)	156 (2)
N6—H6$A\cdots$I2	0.79 (2)	3.09 (2)	3.831 (2)	157 (2)
N7—H7$A\cdots$I1	0.84 (2)	3.16 (2)	3.987 (2)	172 (2)

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.064$
$S = 0.89$
19 601 reflections
987 parameters

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0244P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.64$ e Å^{-3}
$\Delta\rho_{min} = -0.34$ e Å^{-3}

Compound (II)

Crystal data

$[Fe(C_{12}H_{11}NS)_6]Cl_3$
$M_r = 1369.93$
Cubic, $Pa\bar{3}$
$a = 18.8566 (4)$ Å
$V = 6704.9 (2)$ Å^3
$Z = 4$
$D_x = 1.357$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 28 769 reflections
$\theta = 2.9-27.5°$
$\mu = 0.58$ mm^{-1}
$T = 120 (2)$ K
Block, yellow
$0.10 \times 0.08 \times 0.05$ mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{min} = 0.942$, $T_{max} = 0.970$
64 482 measured reflections

2572 independent reflections
1840 reflections with $I > 2\sigma(I)$
$R_{int} = 0.133$
$\theta_{max} = 27.5°$
$h = -24 \rightarrow 24$
$k = -24 \rightarrow 21$
$l = -24 \rightarrow 23$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.113$
$S = 1.04$
2572 reflections
138 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.052P)^2 + 4.568P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.66$ e Å^{-3}
$\Delta\rho_{min} = -0.89$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0011 (2)

Table 3
Selected geometric parameters (Å, °) for (II).

Fe1—N1	2.078 (2)	N1—Fe1—N1^{ii}	86.21 (9)

Symmetry code: (ii) $z - \frac{1}{2}, \frac{1}{2} - x, 1 - y$.

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1$A\cdots$Cl1	0.82 (3)	2.50 (3)	3.272 (2)	157 (3)

Compound (III)

Crystal data

$[PtI_2(C_{12}H_{11}NS)_4]Cl_2\cdot2CH_2Cl_2$
$M_r = 1494.75$
Monoclinic, $P2_1/n$
$a = 13.7287 (5)$ Å
$b = 10.8620 (4)$ Å
$c = 18.3936 (6)$ Å
$\beta = 93.864 (2)°$
$V = 2736.64 (17)$ Å^3
$Z = 2$
$D_x = 1.814$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 15 561 reflections
$\theta = 2.2-28.8°$
$\mu = 4.18$ mm^{-1}
$T = 150 (2)$ K
Block, red
$0.28 \times 0.17 \times 0.16$ mm

Data collection

Bruker SMART 1000 CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min} = 0.357$, $T_{max} = 0.511$
23 077 measured reflections
6442 independent reflections

5859 reflections with $I > 2\sigma(I)$
$R_{int} = 0.016$
$\theta_{max} = 28.8°$
$h = -18 \rightarrow 18$
$k = -13 \rightarrow 14$
$l = -24 \rightarrow 24$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.143$
$S = 1.07$
6442 reflections
338 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.078P)^2 + 27.27P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 3.60$ e Å^{-3}
$\Delta\rho_{min} = -3.70$ e Å^{-3}

Table 5
Selected geometric parameters (Å, °) for (III).

Pt1—N1	2.046 (5)	Pt1—I1	2.6470 (5)
Pt1—N2	2.038 (5)		
N1—Pt1—N2	87.8 (2)	N2—Pt1—I1	87.89 (16)
N1—Pt1—I1	87.39 (15)		

Table 6
Hydrogen-bonding geometry (Å, °) for (III).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1$A\cdots$Cl3	0.77 (3)	2.46 (4)	3.210 (5)	165 (8)
N2—H2$A\cdots$Cl3	0.78 (3)	2.47 (7)	3.242 (5)	168 (8)
C3—H3$\cdots$Cl3^{ii}	0.95	2.93	3.567 (7)	126
C4—H4$\cdots$Cl3^{ii}	0.95	2.99	3.601 (9)	123
C10—H10$\cdots$Cl3^{iii}	0.95	2.76	3.626 (9)	153
C14—H14$\cdots$Cl3	0.95	2.84	3.716 (8)	154
C21—H21$\cdots$Cl3^{iv}	0.95	2.82	3.546 (7)	134

Symmetry codes: (ii) $-\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iii) $-\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (iv) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$.

In all three structures, C-bound H atoms were placed geometrically [C—H = 0.95 (aromatic), 0.99 (CH$_2$) and 0.98 Å (methyl)] and refined using a riding model. H atoms of NH groups were located in a difference Fourier map and their coordinates were refined freely in (I) and (II), and using restraints on the N—H bond length [target value 0.80 (3) Å in (III)]. $U_{iso}(H)$ values were set at $1.2U_{eq}(C)$ for aryl H atoms, $1.2U_{eq}(C)$ for CH$_2$ H atoms, and $1.5U_{eq}(N,C)$ for NH and methyl H atoms. The CH$_2$Cl$_2$ molecule of crystallization in (III) was

found to be disordered and was modelled over two sets of positions using restraints on the anisotropic displacement parameters of the C and Cl atoms. The major and minor disorder components had refined occupancies of 80.6 (11) and 19.4 (11)%, respectively.

For compounds (I) and (III), data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*. For compound (II), data collection: *COLLECT* (Hooft, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*. For all three compounds, program(s) used to solve structure: *SHELXTL* (Sheldrick, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1594). Services for accessing these data are described at the back of the journal.

References

Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.

Bruker (2001). *SMART* (Version 5.611) and *SAINT* (Version 6.02a). Bruker AXS Inc., Madison, Wisconsin, USA.

Desiraju, G. R. & Steiner, T. (1999). *The Weak Hydrogen Bond in Structural Chemistry and Biology*, pp. 246–253. New York: Oxford University Press.

Holmes, K. E., Kelly, P. F. & Elsegood, M. R. J. (2002). *CrystEngComm*, **4**, 545–547.

Hooft, R. (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.

Jones, R., Kelly, P. F., Williams, D. J. & Woollins, J. D. (1988). *J. Chem. Soc. Dalton Trans.* pp. 1569–1576.

Kelly, P. F., Macklin, A. C., Slawin, A. M. Z. & Waring, K. W. (2000). *Polyhedron*, **19**, 2077–2081.

Kelly, P. F. & Slawin, A. M. Z. (1999). *Chem. Commun.* pp. 1081–1082.

Kelly, P. F., Slawin, A. M. Z. & Waring, K. W. (1998). *Inorg. Chem. Commun.* **1**, 249–250.

Makarycheva-Mikhailova, A. V., Bokach, N. A., Kukushkin, V. Yu., Kelly, P. F., Gilby, L. M., Kuznetsov, M. L., Holmes, K. E., Haukka, M., Parr, J., Stonehouse, J. M., Elsegood, M. R. J. & Pombeiro, A. J. L. (2003). *Inorg. Chem.* **42**, 301–311.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.

Sellmann, D., Geipel, F. & Heinemann, F. W. (2001). *Z. Anorg. Allg. Chem.* **627**, 1034–1038.

Sheldrick, G. M. (2000). *SHELXTL*. Version 6.10. Bruker AXS Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (2003). *SADABS*. Version 2.10. University of Göttingen, Germany.