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# Structures of 2-pyridineformamide thiosemicarbazone and its complexes with cadmium halides

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## Abstract

Reduction of 2-cyanopyridine by sodium in dry methanol in the presence of thiosemicarbazide produces 2-pyridineformamide thiosemicarbazone, HAM4DH. Complexes of HAM4DH with cadmium(II) chloride, bromide and iodide have been prepared and spectroscopically characterized, and crystal structures of [Cd(HAM4DH)Cl<sub>2</sub>].DMSO, [Cd(HAM4DH)Br<sub>2</sub>].H<sub>2</sub>O and [Cd(HAM4DH)I<sub>2</sub>] have been determined by X-ray diffractometry. In each of these complexes neutral HAM4DH coordinates via its pyridyl and imine nitrogens and sulfur, and the cadmium atom is pentacoordinated to the thiosemicarbazone and the two halo ligands. The coordination polyhedra of the three complexes are best described as square pyramidal, with [Cd(HAM4DH)Br<sub>2</sub>] having the greatest distortion toward a trigonal bipyramid. The hydrogens attached to nitrogens in coordinated HAM4DH form hydrogen bonds with oxygen atoms in solvent molecules and with halo ligands on adjacent molecules. © 2000 Elsevier Science Ltd. All rights reserved.

**Keywords:** 2-Pyridineformamide; Thiosemicarbazone; Crystal structures; Cadmium halides

## 1. Introduction

Although N(4)-substituted 2-formyl-, 2-acetyl- and 2-benzoylpyridine thiosemicarbazones [1–3] possess substantial in vitro activity against various human tumor lines [4], they are poorly soluble in water. Therefore, these thiosemicarbazones and their metal complexes are less promising when tested in vivo. In an attempt to enhance the water solubility of thiosemicarbazones and their complexes, a new series in which the thiosemicarbazone moiety is attached to an amide carbon rather than an aldehyde or ketone carbon has been

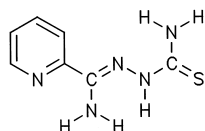


Fig. 1. 2-Pyridineformamide thiosemicarbazone, HAM4DH.

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prepared. Following our studies of complexes of 2-pyridineformamide N(4)-methylthiosemicarbazone, HAM4M [5,6], and of Group 12 metal complexes of various 2-acetylpyridine thiosemicarbazones [7–9], we recently communicated the structures of 2-pyridineformamide thiosemicarbazone (HAM4DH) (Fig. 1) and of its complexes with zinc chloride, bromide and iodide [10]. Here we present the structures of complexes of HAM4DH with cadmium chloride, bromide and iodide, and compare them to their zinc analogues and to previously studied cadmium complexes of heterocyclic thiosemicarbazones [11].

## 2. Experimental

Infrared spectra in KBr pellets (4000–400 cm<sup>-1</sup>) and Nujol mulls (500–100 cm<sup>-1</sup>) were recorded in a Bruker IFS 66V spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded in DMSO-*d*<sub>6</sub> solutions in a Bruker WM-300 spectrometer using TMS as internal reference. Elemental analysis was performed with a Carlo Erba 1108 elemental analyzer. The melting point was determined with a Büchi apparatus.

Table 1

Colors, melting points and partial elemental analyses of cadmium complexes of HAm4DH

Compound	Color	M.p. (°C)	%Found (Calc.)			
			C	H	N	S
[Cd(HAm4DH)Cl <sub>2</sub> ] $\cdot$ 0.25H <sub>2</sub> O	white	284	21.76 (21.95)	2.27 (2.50)	18.32 (18.28)	7.92 (8.37)
[Cd(HAm4DH)Br <sub>2</sub> ]	yellow	240	18.13 (17.99)	1.89 (1.94)	14.86 (14.98)	6.76 (6.86)
[Cd(HAm4DH)I <sub>2</sub> ]	yellow	210	15.12 (14.97)	1.57 (1.62)	12.47 (12.47)	5.48 (5.71)

The details of the preparation of HAm4DH were communicated in our earlier report on its zinc complexes [10]. The cadmium complexes were prepared as follows. A solution of CdCl<sub>2</sub>, CdBr<sub>2</sub> or CdI<sub>2</sub> (0.002 mol) in EtOH (30 mL) was mixed with a solution of HAm4DH (0.002 mol) in the same solvent (30 mL) and the mixture was stirred under reflux for 2 h. The resulting solids were filtered out, washed with anhydrous ether to apparent dryness, and placed on a warm plate at 35°C. Yields were 97.4, 94.3 and 83.5% for [Cd(HAm4DH)Cl<sub>2</sub>] $\cdot$ 0.25H<sub>2</sub>O, [Cd(HAm4DH)Br<sub>2</sub>] and [Cd(HAm4DH)I<sub>2</sub>], respectively. Their partial elemental analyses are listed in Table 1 with their melting points.

Crystals of [Cd(HAm4DH)Cl<sub>2</sub>] $\cdot$ DMSO were grown from a 1:1 v/v DMSO–EtOH mixture, and crystals of [Cd(HAm4DH)Br<sub>2</sub>] $\cdot$ H<sub>2</sub>O and [Cd(HAm4DH)I<sub>2</sub>] from 96% ethanol. The crystals were mounted on glass fibers and used for data collection in an automatic diffractometer (Enraf–Nonius MACH3 for [Cd(HAm4DH)Cl<sub>2</sub>] $\cdot$ DMSO and [Cd(HAm4DH)I<sub>2</sub>]; CAD4 for [Cd(HAm4DH)Br<sub>2</sub>] $\cdot$ H<sub>2</sub>O). Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of the diffraction data from 25 reflections in the ranges 9.422–20.833° for [Cd(HAm4DH)Cl<sub>2</sub>] $\cdot$ DMSO, 7.921–45.065° for [Cd(HAm4DH)Br<sub>2</sub>] $\cdot$ H<sub>2</sub>O and 9.327–21.137° for [Cd(HAm4DH)I<sub>2</sub>]. Data for [Cd(HAm4DH)Br<sub>2</sub>] $\cdot$ H<sub>2</sub>O were collected at 293(2) K using Cu K $\alpha$  radiation ( $\lambda$  = 1.54184 Å), and data for [Cd(HAm4DH)Cl<sub>2</sub>] $\cdot$ DMSO and [Cd(HAm4DH)I<sub>2</sub>] using Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å). The  $\omega$ -scan technique were employed for the three crystals and the data were corrected for Lorentz and polarization effects [12]. A semi-empirical absorption correction was made for the three crystals [13]. The structures were solved by direct methods [14], which showed the positions of all non-hydrogen atoms, and refined on  $F^2$  by a full-matrix least-squares procedure using anisotropic displacement parameters [15]. The positions of most hydrogens were calculated (C–H 0.93–0.97 Å) and refined using a riding model; the exceptions were the H<sub>2</sub>O hydrogens in the bromo complex, which were located from difference Fourier maps and refined isotropically. In [Cd(HAm4DH)Cl<sub>2</sub>] $\cdot$ DMSO a weak peak found near Cd(11) in the Fourier difference synthesis at 1.052 Å was included in the final

model as a Cd(12) atom; the occupancy factors refined to 0.93(1) for Cd(11) and 0.07(1) for Cd12. Atom scattering factors were taken from the International Tables for X-ray Crystallography [16]. Molecular graphics were generated with PLATON-98 [17] for [Cd(HAm4DH)Cl<sub>2</sub>] $\cdot$ DMSO and [Cd(HAm4DH)I<sub>2</sub>], and with ZORTEP [18] for [Cd(HAm4DH)Br<sub>2</sub>] $\cdot$ H<sub>2</sub>O.

### 3. Results and discussion

Crystal and structure refinement data for the three cadmium complexes are summarized in Table 2. Selected bond lengths and angles are listed in Tables 3 and 4. Perspective views of [Cd(HAm4DH)Cl<sub>2</sub>] $\cdot$ DMSO, [Cd(HAm4DH)Br<sub>2</sub>] $\cdot$ H<sub>2</sub>O and [Cd(HAm4DH)I<sub>2</sub>] are shown in Figs. 2–4, respectively. Hydrogen bonding parameters are compiled in Table 5, and the root-mean-square plane data in Table 6.

#### 3.1. Structures of the [Cd(HAm4DH)X<sub>2</sub>] complexes

In all three complexes HAm4DH coordinates via its pyridyl and imine nitrogens and its sulfur, and the two halo ligands bring the coordination number to five. As found previously with metal complexes of heterocyclic thiosemicarbazones [1–3], in [Cd(HAm4DH)Cl<sub>2</sub>] and [Cd(HAm4DH)Br<sub>2</sub>] the Cd–N(2) bond is shorter than the Cd–N(1) bond, by ca. 0.08 and 0.06 Å, respectively. The two Cd–X bond distances also differ, by ca. 0.06 Å in the chloro complexes and ca. 0.07 Å in the bromo compound. However, in [Cd(HAm4DH)I<sub>2</sub>] neither the two Cd–N bond lengths nor the two Cd–I distances differ significantly. Cd–N(1) is significantly shorter in the iodo complex than in the others (as also in the [Zn(HAm4DH)X<sub>2</sub>] series [10]), but the Cd–N(2) and Cd–S bond lengths are similar in all three. The average Cd–X distance increases in the expected order Cd–Cl < Cd–Br < Cd–I. Comparison of [Cd(HAm4DH)Cl<sub>2</sub>] with [Cd(HFo4DH)Cl<sub>2</sub>], where HFo4DH is 2-formylpyridine thiosemicarbazone, shows that Cd–N(2) is much shorter in the former, 2.307(6) compared to 2.350(3) Å [11], but the lengths of the other bonds are similar in the two compounds. The difference in Cd–N(2) is presumably due to the N(2) amino group of

Table 2  
Crystal and structure refinement data for [Cd(HAm4DH)Cl<sub>2</sub>]·(CH<sub>3</sub>)<sub>2</sub>SO, [Cd(HAm4DH)Br<sub>2</sub>]·H<sub>2</sub>O and [Cd(HAm4DH)I<sub>2</sub>] (HAm4DH = 2-pyridineformamide N(4)-thiosemicarbazone)

Empirical formula	C <sub>9</sub> H <sub>15</sub> CdCl <sub>2</sub> N <sub>5</sub> OS <sub>2</sub>	C <sub>7</sub> H <sub>11</sub> Br <sub>2</sub> CdN <sub>5</sub> OS	C <sub>7</sub> H <sub>9</sub> CdI <sub>2</sub> N <sub>5</sub> S
Color, habit	yellow, prism	yellow, prism	yellow, plate
Formula weight	456.68	485.49	561.45
Crystal size (mm)	0.25 × 0.20 × 0.15	0.35 × 0.25 × 0.15	0.30 × 0.30 × 0.10
Crystal system	monoclinic	triclinic	monoclinic
Space group	P2 <sub>1</sub> /c (no. 14)	P $\bar{1}$ (no. 2)	P2 <sub>1</sub> /c (no. 14)
Unit cell dimensions			
<i>a</i> (Å)	11.970(2)	7.525(2)	7.627(5)
<i>b</i> (Å)	10.737(2)	9.772(4)	14.980(4)
<i>c</i> (Å)	13.559(2)	10.398(4)	14.356(3)
$\alpha$ (°)	90.00(-)	80.856(17)	90.00(-)
$\beta$ (°)	108.19(1)	76.391(18)	121.978(1)
$\gamma$ (°)	90.00(-)	67.944(11)	90.00(-)
Volume (Å <sup>3</sup> )	1655.4(4)	686.6(4)	1391.3(10)
Z	4	2	4
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.832	2.348	2.680
Absorption coefficient (mm <sup>-1</sup> )	1.895	20.936	6.140
$\theta$ Range for data collection (°)	2.47–27.97	4.39–75.89	2.72–27.97
Index ranges (°)	–15 ≤ <i>h</i> ≤ 0, 0 ≤ <i>k</i> ≤ 14, –17 ≤ <i>l</i> ≤ 17	–9 ≤ <i>h</i> ≤ 6, –12 ≤ <i>k</i> ≤ 11, –13 ≤ <i>l</i> ≤ 6	0 ≤ <i>h</i> ≤ 10, 0 ≤ <i>k</i> ≤ 19, –10 ≤ <i>l</i> ≤ 16
Absorption correction	$\psi$ -scan	$\psi$ -scan	$\psi$ -scan
Reflections collected	4166	2986	1869
Independent reflections ( <i>R</i> <sub>int</sub> )	3984(5.67%)	2867(7.74%)	1869(0.00%)
Data/parameters	3984/193	2867/161	1869/145
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0518, <i>wR</i> <sub>2</sub> = 0.1252	<i>R</i> <sub>1</sub> = 0.0668, <i>wR</i> <sub>2</sub> = 0.1849	<i>R</i> <sub>1</sub> = 0.0372, <i>wR</i> <sub>2</sub> = 0.0692
<i>R</i> Indices (all data)	<i>R</i> <sub>1</sub> = 0.1824, <i>wR</i> <sub>2</sub> = 0.1580	<i>R</i> <sub>1</sub> = 0.0682, <i>wR</i> <sub>2</sub> = 0.1867	<i>R</i> <sub>1</sub> = 0.1275, <i>wR</i> <sub>2</sub> = 0.0861
Goodness-of-fit	0.977	1.086	0.970
Largest difference peak and hole (e Å <sup>-3</sup> )	0.891 and –0.791	2.338 and –2.193	0.689 and –0.537

HAm4DH having a larger inductive effect than the hydrogen in HFO4DH.

In the analogous series of zinc complexes only bond angles involving halogen atoms differed significantly [10]. The same is essentially true for the cadmium series, the greatest bond angle differences concerning X(1)–Cd–N(2) and X(2)–Cd–N(2), which respectively increase and decrease with increasing halogen size. The N(1)–Cd–S(1) angles, which reflect the two bite angles of the bichelate bonding system, average 142.6(3)°, as against 148.6(2)° for the analogous zinc complexes. These ligands may not be able to maintain N,N,S-coordination with larger metal ions: in [Hg(HAm4DH)<sub>2</sub>Br<sub>2</sub>] only the sulfurs are coordinated [19].

In all three complexes the thiosemicarbazone bond lengths (Table 3) differ slightly from their values in HAm4DH [10]. As in the zinc series [10], the S(1)–C(7) bonds shorten with increasing halogen size, and other bonds involving C(7) are consequently altered. By contrast, C(6)–N(2) is longest in [Cd(HAm4H)I<sub>2</sub>], which suggests that coordination via the thione sulfur is weakest, and bonding via the imine nitrogen strongest, in this sterically more crowded complex. Of the six known Group 12 metal complexes of HAm4DH, [Cd(HAm4DH)I<sub>2</sub>] differs most from HAm4DH in its thiosemicarbazone bond distances: for example, the

S(1)–C(7) distance is 1.671(15) Å in the complex and 1.698(2) Å in the ligand, and the C(6)–N(2) distance 1.322(16) Å in [Cd(HAm4DH)I<sub>2</sub>] and 1.293(2) Å in HAm4DH. The fact that the C–S bond is shorter in [Cd(HAm4DH)I<sub>2</sub>] than HAm4DH indicates the importance of intermolecular hydrogen bonding in the latter. Coordination also alters bond angles in the vicinity of the coordinating imine nitrogen, N(2), and the thione sulfur, S(1).

Table 3  
Selected bond lengths (Å) in [Cd(HAm4DH)Cl<sub>2</sub>]·(CH<sub>3</sub>)<sub>2</sub>SO, [Cd(HAm4DH)Br<sub>2</sub>]·H<sub>2</sub>O and [Cd(HAm4DH)I<sub>2</sub>]

Bond	[Cd(HAm4DH)- Cl <sub>2</sub> ]	[Cd(HAm4DH)- Br <sub>2</sub> ]	[Cd(HAm4DH)- I <sub>2</sub> ]
Cd(1)–N(1)	2.384(6)	2.385(7)	2.325(12)
Cd(1)–N(2)	2.307(6)	2.327(6)	2.313(12)
Cd(1)–S(1)	2.596(3)	2.579(2)	2.601(3)
Cd(1)–X(1)	2.455(2)	2.654(1)	2.7784(13)
Cd(1)–X(2)	2.515(2)	2.587(1)	2.780(2)
S(1)–C(7)	1.706(8)	1.693(7)	1.671(15)
C(6)–N(2)	1.281(9)	1.288(9)	1.322(16)
N(2)–N(3)	1.380(9)	1.375(8)	1.399(11)
N(3)–C(7)	1.332(9)	1.337(10)	1.340(15)
C(7)–N(4)	1.292(10)	1.333(9)	1.344(14)
C(6)–N(5)	1.367(9)	1.335(9)	1.342(18)

Table 4

Selected bond angles (°) in [Cd(HAm4DH)Cl<sub>2</sub>](CH<sub>3</sub>)<sub>2</sub>SO, [Cd(HAm4DH)Br<sub>2</sub>](H<sub>2</sub>O) and [Cd(HAm4DH)I<sub>2</sub>]

Bond	[Cd(HAm-4DH)Cl <sub>2</sub> ]	[Cd(HAm-4DH)Br <sub>2</sub> ]	[Cd(HAm-4DH)I <sub>2</sub> ]
S(1)–Cd(1)–N(11)	142.76(17)	143.60(16)	141.5(3)
S(1)–Cd(1)–N(2)	75.62(17)	75.97(15)	73.5(2)
S(1)–Cd(1)–X(1)	107.98(7)	101.38(5)	100.41(10) <sup>c</sup>
S(1)–Cd(1)–X(2)	106.30(8)	108.76(6)	108.06(8) <sup>c</sup>
X(1)–Cd(1)–N(1)	92.87(17)	91.97(16)	97.3(3)
X(1)–Cd(1)–N(2)	110.92(17)	115.45(15)	133.36(18)
X(1)–Cd(1)–X(2)	107.84(8)	120.87(4)	109.85(6)
N(1)–Cd(1)–N(2)	68.1(2)	67.7(2)	69.4(4)
X(2)–Cd(1)–N(1)	95.60(17)	92.32(16)	97.5(2)
X(2)–Cd(1)–N(2)	138.36(17)	120.54(15)	116.02(18)
Cd(1)–S(1)–C(7)	99.3(3)	99.2(2)	101.0(4)
Cd(1)–N(2)–C(6)	122.6(5)	122.6(5)	123.5(8)
Cd(1)–N(2)–N(3)	119.2(5)	118.5(4)	121.5(8)
N(5)–C(6)–N(2)	124.8(7)	126.6(7)	126.7(12)
C(5)–C(6)–N(2)	116.5(7)	115.8(6)	110.1(13)
C(6)–N(2)–N(3)	118.0(7)	118.9(6)	115.0(12)
N(2)–N(3)–C(7)	121.7(6)	121.3(6)	118.5(13)
N(3)–C(7)–N(4)	116.5(7)	115.3(7)	114.1(14)
N(3)–C(7)–S(1)	123.7(6)	124.8(5)	124.1(10)
N(4)–C(7)–S(1)	119.8(6)	119.9(6)	121.7(10)

In [Cd(HAm4DH)I<sub>2</sub>], which crystallized without an accompanying solvent molecule, N(3)–H(3), N(4)–H(4A) and N(5)–H(5B) all form hydrogen bonds with I(1) of one neighboring molecule while N(4)–H(4B) hydrogen bonds to I(2) of a second neighboring molecule (Table 5). In [Cd(HAm4DH)Cl<sub>2</sub>](DMSO), N(3)–H(3) and N(5)–H(5A) form hydrogen bonds with the oxygen of the DMSO molecule and N(4)–H(4A), N(4)–H(4B) and N(5)–H(5B) with Cl atoms on three different neighboring molecules. The hydrogen bonding in [Cd(HAm4DH)Br<sub>2</sub>](H<sub>2</sub>O) is similar to that of [Cd(HAm4DH)Cl<sub>2</sub>](DMSO), with the water molecule supplying the oxygen instead of DMSO; additionally, the hydrogens of the water molecule interact with the bromine ligands. The crystals of these cadmium complexes thus feature dense hydrogen bond networks, which contributes to their stability and helps to promote crystal growth.

The planarity in HAm4DH of the pyridine ring and the thiosemicarbazone moiety is generally retained in the cadmium complexes; the greatest change in the thiosemicarbazone moiety occurs in [Cd(HAm4DH)I<sub>2</sub>] (Table 6). As in the zinc series [10], the angle between the best planes of the pyridine ring and the thiosemicarbazone moiety increases in the order [Cd(HAm4DH)Cl<sub>2</sub>] < [Cd(HAm4DH)Br<sub>2</sub>] < [Cd(HAm4DH)I<sub>2</sub>]. In the chloro and iodo complexes this angle is smaller for Cd than for Zn, while the reverse holds for the bromo complexes: [Cd(HAm4DH)Cl<sub>2</sub>], 2.04(24)°; [Zn(HAm4DH)Cl<sub>2</sub>], 5.46(11)°; [Zn(HAm4DH)Br<sub>2</sub>],

6.92(16)°; [Cd(HAm4DH)Br<sub>2</sub>], 8.22(36)°; [Cd(HAm4DH)I<sub>2</sub>], 9.25(61)° and [Zn(HAm4DH)I<sub>2</sub>], 11.44(58)°.

The values of the geometrical parameter  $\tau = (\beta - \alpha)/60$  [20], where  $\alpha = \text{Cl}(2)\text{--Cd--N}(2)$  and  $\beta = \text{N}(1)\text{--Cd--S}(1)$ , show that, like the Zn complexes, all three Cd complexes are closer to ideal square pyramid with X(1) apical than to a trigonal bipyramid (Table 7). However, [Cd(HAm4DH)Br<sub>2</sub>] ( $\tau = 0.39$ ) is closer to a trigonal bipyramid than any of the Group 12 complexes prepared with HAm4DH or any of the other Group 12 complexes listed in Table 7, which includes [Cd(HAc4DH)Cl<sub>2</sub>] [11] and six cadmium complexes of N(4)-substituted 2-acetylpyridine thiosemicarbazones [7–9].

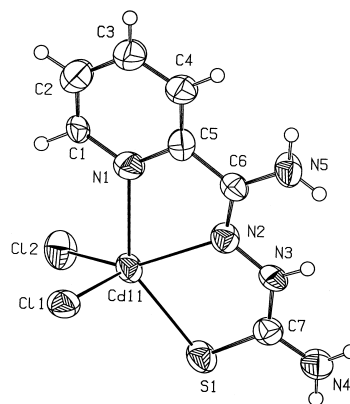


Fig. 2. Perspective view of dichloro(2-pyridineformamide thiosemicarbazone) cadmium(II), [Cd(HAm4DH)Cl<sub>2</sub>], showing 50% probability ellipsoids for the nonhydrogen atoms and the numbering scheme of the atoms in the molecule.

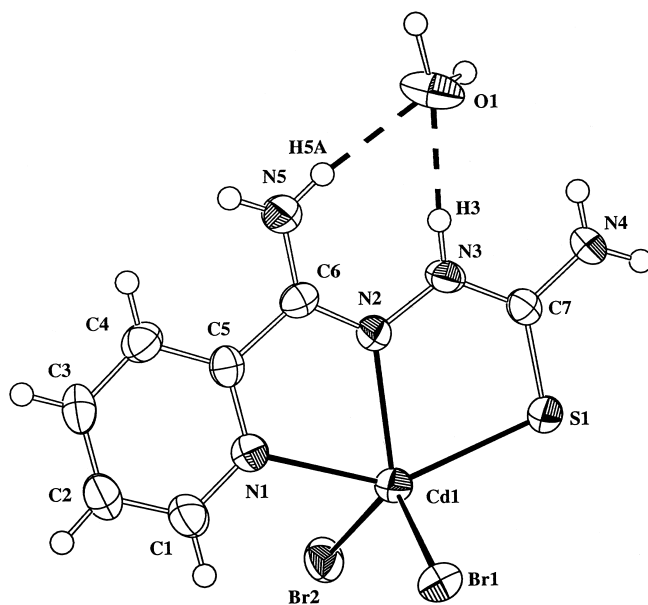


Fig. 3. Perspective view of dibromo(2-pyridineformamide thiosemicarbazone) cadmium(II) monohydrate, [Cd(HAm4DH)Br<sub>2</sub>](H<sub>2</sub>O), drawn with 50% probability ellipsoids. Some of the hydrogen bonds are shown by dashed lines.

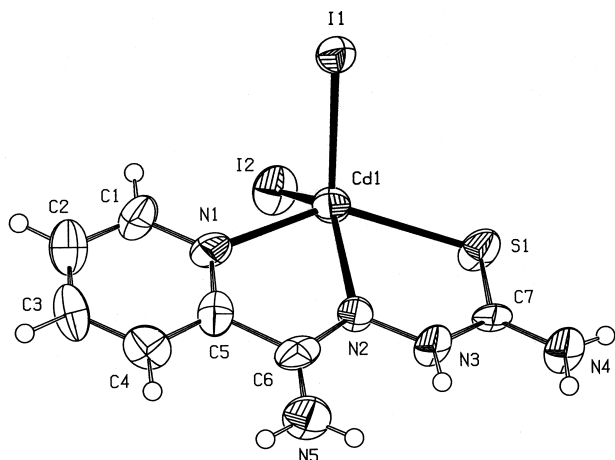


Fig. 4. Perspective view of diiodo(2-pyridineformamide thiosemicarbazone)cadmium(II),  $[\text{Cd}(\text{Am4DH})\text{I}_2]$  with thermal ellipsoids at 50% probability. The hydrogen atoms ( $\circ$ ) are drawn with an arbitrary radius of 0.1 Å.

### 3.2. Infrared spectra

The IR bands that are most useful for determining the coordination mode of the thiosemicarbazone are given in Table 8. As many as four bands can be assigned to  $\nu(\text{NH})$ . The highest energy band in the spectrum of HAm4DH at  $3421\text{ cm}^{-1}$ , is attributable to  $\nu_a(\text{N14H}_2)$  on the basis of previous studies of thiosemicarbazones [11]. In the complexes there are substantial shifts to lower energy of the other three bands, which in view of

the distances listed in Table 5 is probably due to the stronger hydrogen bonding interactions of coordinated HAm4DH. The fact that the  $\nu(\text{C}=\text{N})$  band at  $1590\text{ cm}^{-1}$  in the spectrum of HAm4DH shifts to smaller wavenumbers in the spectra of the cadmium complexes indicates coordination of the imine nitrogen, as does the band in the  $344\text{--}400\text{ cm}^{-1}$  range assigned to  $\nu(\text{CdN}(2))$  [21]. This range for  $\nu(\text{CdN}(2))$  is lower than is found for cobalt(II), nickel(II) and copper(II) complexes of related thiosemicarbazones [5,6], which is consistent with the larger size and longer bonds of cadmium. Coordination of the sulfur is indicated by a similar decrease in energy of the thioamide IV band, which derives considerable intensity from  $\nu(\text{CS})$ , and by the appearance of a band in the  $247\text{--}316\text{ cm}^{-1}$  range assignable to  $\nu(\text{CdS})$  [22,23]. Coordination of the pyridyl nitrogen shifts the out-of-plane ring deformation  $\rho(\text{py})$  some  $18\text{--}21\text{ cm}^{-1}$  to higher frequencies. In the  $100\text{--}500\text{ cm}^{-1}$  region, assignment to  $\nu(\text{Cd-X})$  of two strong bands with energies increasing in the order  $[\text{Cd}(\text{HAm4DH})\text{I}_2] < [\text{Cd}(\text{HAm4DH})\text{Br}_2] < [\text{Cd}(\text{HAm4DH})\text{Cl}_2]$  affords  $\nu(\text{Cd-Br})/\nu(\text{Cd-Cl})$  and  $\nu(\text{Cd-I})/\nu(\text{Cd-Cl})$  ratios of ca. 0.63 and 0.60, respectively (Table 8).

### 3.3. NMR spectra

Also included in Table 8 are  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{113}\text{Cd}$  NMR spectral assignments for HAm4DH and its cadmium complexes. As in other studies of heterocyclic thiosemicarbazones [1–3],  $\text{N}(13)\text{H}$  interacts with the solvent

Table 5  
Hydrogen bond parameters (Å, °) in  $[\text{Cd}(\text{HAm4DH})\text{Cl}_2]\cdot(\text{CH}_3)_2\text{SO}$ ,  $[\text{Cd}(\text{HAm4DH})\text{Br}_2]\cdot\text{H}_2\text{O}$  and  $[\text{Cd}(\text{HAm4DH})\text{I}_2]$

Compound	D–H⋯A	$d(\text{D–H})$	$d(\text{H⋯A})$	$d(\text{D⋯A})$	$\angle(\text{DHA})$
$[\text{Cd}(\text{HAm4DH})\text{Cl}_2]^a$	$\text{N}(3)\text{--H}(3)\text{--O}(1) \# 1$	0.86	1.96	2.779(9)	158.3
	$\text{N}(4)\text{--H}(4\text{A})\text{--Cl}(2) \# 2$	0.86	2.90	3.531(7)	132.0
	$\text{N}(4)\text{--H}(4\text{B})\text{--Cl}(1) \# 3$	0.86	2.49	3.300(7)	156.5
	$\text{N}(5)\text{--H}(5\text{A})\text{--O}(1) \# 1$	0.86	2.05	2.862(9)	157.9
	$\text{N}(5)\text{--H}(5\text{B})\text{--Cl}(1) \# 4$	0.86	2.48	3.224(6)	145.6
$[\text{Cd}(\text{HAm4DH})\text{Br}_2]^b$	$\text{N}(3)\text{--H}(3)\text{--O}(1)$	0.86	1.96	2.818(9)	176.7
	$\text{N}(4)\text{--H}(4\text{A})\text{--Br}(2) \# 1$	0.86	3.02	3.722(7)	139.9
	$\text{N}(4)\text{--H}(4\text{B})\text{--Br}(1) \# 2$	0.86	2.82	3.588(7)	149.1
	$\text{N}(5)\text{--H}(5\text{A})\text{--O}(1)$	0.86	2.07	2.921(11)	172.3
	$\text{N}(5)\text{--H}(5\text{B})\text{--Br}(1) \# 3$	0.86	2.76	3.526(7)	148.6
	$\text{O}(1)\text{--H}(1\text{A})\text{--Br}(2) \# 4$	1.06(1)	2.70(1)	3.507(8)	132(9)
	$\text{O}(1)\text{--H}(1\text{A})\text{--Br}(2) \# 1$	1.06(1)	2.71(1)	3.524(8)	133(9)
	$\text{O}(1)\text{--H}(1\text{B})\text{--Br}(1) \# 4$	0.69(5)	2.64(2)	3.329(7)	177(16)
$[\text{Cd}(\text{HAm4DH})\text{I}_2]^c$	$\text{N}(3)\text{--H}(3)\text{--I}(1) \# 1$	0.86	2.82	3.623(12)	156.7
	$\text{N}(4)\text{--H}(4\text{A})\text{--I}(1) \# 1$	0.86	3.10	3.859(13)	148.8
	$\text{N}(4)\text{--H}(4\text{B})\text{--I}(2) \# 2$	0.86	2.92	3.711(11)	169.0
	$\text{N}(5)\text{--H}(5\text{A})\text{--I}(1) \# 1$	0.86	3.06	3.849(12)	153.7

<sup>a</sup> Symmetry transformations used to generate equivalent atoms:  $\# 1: x-1, -y+1/2, z-1/2$ ;  $\# 2: -x, -y+1, -z$ ;  $\# 3: -x, y+1/2, -z+1/2$ ;  $\# 4: -x, y-1/2, -z+1/2$ .

<sup>b</sup> Symmetry transformations used to generate equivalent atoms:  $\# 1: -x+1, -y+1, -z+1$ ;  $\# 2: -x, -y+1, -z+1$ ;  $\# 3: -x+1, -y+1, -z$ ;  $\# 4: x, y+1, z$ .

<sup>c</sup> Symmetry transformations used to generate equivalent atoms:  $\# 1: x, -y+1/2, z-1/2$ ;  $\# 2: -x+1, y-1/2, -z+3/2$ .

Table 6

Root-mean square planes in [Cd(HAm4DH)Cl<sub>2</sub>·(CH<sub>3</sub>)<sub>2</sub>SO, [Cd(HAm4DH)Br<sub>2</sub>]·H<sub>2</sub>O and [Cd(HAm4DH)I<sub>2</sub>]

Compound	Plane	Root-mean square deviation	Largest deviation	Angle with previous plane
[Cd(HAm4DH)Cl <sub>2</sub> ]	C(6)/N(2)/N(3)/C(7)/N(4)/S(1)	0.0176	N(3), 0.035(6)	
	N(1)/C(1)/C(2)/C(3)/C(4)/C(5)	0.0105	C(2), 0.017(7)	2.0(2)
[Cd(HAm4DH)Br <sub>2</sub> ]	C(6)/N(2)/N(3)/C(7)/N(4)/S(1)	0.0118	N(3), 0.022(6)	
	N(1)/C(1)/C(2)/C(3)/C(4)/C(5)	0.0023	C(5), 0.004(5)	8.2(4)
[Cd(HAm4DH)I <sub>2</sub> ]	C(6)/N(2)/N(3)/C(7)/N(4)/S(1)	0.0578	N(2), 0.097(6)	
	N(1)/C(1)/C(2)/C(3)/C(4)/C(5)	0.0050	C(4), 0.007(7)	9.3(6)

Table 7

Deviation from tetragonal-pyramidal coordination in Group 12 metal thiosemicarbazone complexes [M(NNS)X<sub>2</sub>] {M = Zn(II), Cd(II), Hg(II); X = Cl, Br, I}

Compound	$\beta$ (N–M–X)	$\alpha$ (S–M–N)	$\beta - \alpha$	$\tau = (\beta - \alpha)/60$	Ref.
[Cd(HAm4DH)Cl <sub>2</sub> ]	142.8	138.4	4.4	0.07	this work
[Cd(HAm4DH)Br <sub>2</sub> ]	143.6	120.5	23.1	0.39	this work
[Cd(HAm4DH)I <sub>2</sub> ]	141.5	133.4	8.1	0.14	this work
[Cd(HAc4DH)Cl <sub>2</sub> ]	141.5	137.7	3.8	0.06	[11]
[Cd(HAc4M)Cl <sub>2</sub> ]	139.8	136.7	3.1	0.05	[7]
[Cd(HAc4M)Br <sub>2</sub> ]	139.9	135.3	4.6	0.08	[7]
[Cd(HAc4M)I <sub>2</sub> ]	140.1	135.2	4.9	0.08	[7]
[Cd(HAc4DM)Cl <sub>2</sub> ]	145.2	135.5	9.7	0.16	[9]
[Cd(HAc4DM)I <sub>2</sub> ]	145.4	131.6	13.8	0.23	[9]
[Cd(HAc4Ph)Br <sub>2</sub> ]	136.1	139.5	3.4	0.06	[8]
[Zn(HAm4DH)Cl <sub>2</sub> ]	149.7	141.8	7.9	0.13	[10]
[Zn(HAm4DH)Br <sub>2</sub> ]	146.0	148.4	2.4	0.04	[10]
[Zn(HAm4DH)I <sub>2</sub> ]	150.1	136.3	13.8	0.23	[10]
[Hg(HAc4M)Cl <sub>2</sub> ]	138.7	132.4	6.3	0.11	[7]

and is assigned to the signal furthest downfield, and the N(14)H<sub>2</sub> protons are assigned to the two resonances in the region around 7.85 ppm, which disappear on addition of D<sub>2</sub>O to the sample. The N(15)H<sub>2</sub> protons are assigned to the resonance at 6.91 ppm, which is similar to the chemical shift found for HAm4M, 6.86 ppm [6]. None of these signals shifts significantly upon coordination to cadmium. Of the <sup>13</sup>C NMR signals of the free ligand, the signal for the thione carbon, C(7), does not shift significantly on complexation, but the signal of the imine carbon, C(6), shifts from 142.0 to 144.6–144.8 ppm in the complexes, as has also been observed for other thiosemicarbazone complexes with Group 12 dihalides [7–9].

The <sup>113</sup>Cd NMR spectra show a single signal between 387 ppm, for [Cd(HAm4DH)Cl<sub>2</sub>], and 291 ppm, for [Cd(HAm4DH)I<sub>2</sub>]. The metal atom is in each case less deshielded than in the corresponding dihalide (CdX<sub>2</sub>) in DMSO [24]. These findings are consistent with those obtained for other complexes of cadmium(II) halides with thiosemicarbazones [6–9] and are compatible with pentacoordination of the metal [25].

#### 4. Conclusion

These three cadmium complexes are similar in their structural and spectral properties. The results presented here form a basis for future comparison with complexes of the same ligand with other metals, and with cadmium complexes of N(4)-substituted 2-pyridineformamide thiosemicarbazones. The strong intermolecular hydrogen bonds of HAm4DH become even stronger in the cadmium complexes, particularly when a solvate molecule is present in the crystal.

#### 5. Supplementary material

Crystallographic data for C<sub>10</sub>H<sub>15</sub>CdCl<sub>2</sub>N<sub>5</sub>OS<sub>2</sub> {[Cd(HAm4DH)Cl<sub>2</sub>]·DMSO, CCDC-139834}, C<sub>7</sub>H<sub>11</sub>Br<sub>2</sub>CdN<sub>5</sub>OS {[Cd(HAm4DH)Br<sub>2</sub>]·H<sub>2</sub>O, CCDC-139835} and C<sub>7</sub>H<sub>9</sub>CdI<sub>2</sub>N<sub>5</sub>SCd {[Cd(HAm4DH)I<sub>2</sub>], CCDC-139836} have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-1003/m. Copies of available material can be

Table 8

IR and  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{113}\text{Cd}$  NMR data ( $[\text{d}_2]$ -DMSO) for HAm4DH and its cadmium complexes <sup>a</sup>

Assignment	HAm4DH	$[\text{Cd}(\text{HAm4DH})\text{Cl}_2]$ <sup>b</sup>	$[\text{Cd}(\text{HAm4DH})\text{Br}_2]$	$[\text{Cd}(\text{HAm4DH})\text{I}_2]$
<i>IR</i>				
$\nu(\text{NH})$	3421s 3360s 3283s 3234s 3208m 3184m	3370s 3288s 3191s	3422m 3385m 3315s 3235s	3461w 3389s 3281s 3173m
$\nu(\text{NH})$	1663m	1704s	1697s 1674m	1664s
$\nu(\text{CN}) + \nu(\text{CC})$	1612m 1590s 1568m 1524s	1635sh 1623s 1583s	1610s 1587s 1569m	1598s 1542s
$\nu(\text{CS})$	854m	857m	845m	831w
$\rho(\text{py})$	618m	636m	636w	639w
$\nu(\text{CdN})$		400m	368m	344m
$\nu(\text{CdS})$		316s	261m	247s
$\nu_{\text{a}}(\text{CdX})$		256s	160s	154m
$\nu_{\text{s}}(\text{CdX})$		225s	148s	147s
<i>NMR</i>				
$\text{N13H}$	10.05	10.05	10.05	10.05
$\text{N14H}_2$	7.93 7.78 <sup>c</sup>	7.95 7.81 <sup>c</sup>	7.94 7.81 <sup>c</sup>	7.94 7.81 <sup>c</sup>
$\text{N15H}_2$	6.91	6.92	6.92	6.92
$\text{C}(7)_{(\text{thioamide})}$	176.7	176.7	177.1	177.1
$\text{C}(6)_{(\text{imine})}$	142.0	144.6	144.8	144.6
$^{113}\text{Cd}$		387.27	361.06	291.39

<sup>a</sup> Recorded as ground crystals.<sup>b</sup>  $\nu(\text{SO})$  at  $997\text{ cm}^{-1}$ ,  $\nu(\text{CS})$  at  $829\text{ cm}^{-1}$  for DMSO.<sup>c</sup> Overlapping.

obtained, free of charge, on application to: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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