PERGAMON

Polyhedron 21 (2002) 1553–1559

POLYHEDRON

www.elsevier.com/locate/poly

Structural studies of pyrazineformamide N4-methylthiosemicarbazone and its zinc(II) and cadmium(II) complexes formed by electrochemical oxidation

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Received 15 November 2001; accepted 22 February 2002

Abstract

Reduction of cyanopyrazine by sodium in dry methanol in the presence of N(4)-methylthiosemicarbazide produces pyrazineformamide N(4)-methylthiosemicarbazone, HPzAm4M. Electrochemical synthesis in acetonitrile produced $[Zn(PzAm4M)_2]\cdot 2CH_3CN$ and $\cdot[Cd(PzAm4M)_2]\cdot 0.5CH_3CN$. The crystal structures of HPzAm4M and the two complexes have been obtained. Coordination of anionic PzAm4M in the two complexes is via the pyridyl nitrogen, imine nitrogen and thiolato sulfur and the ligands are in a meridional arrangement with the imine nitrogens trans. Hydrogen-bonding interactions are an important property of HPzAm4M and its complexes. Both pyrazine nitrogens are involved in hydrogen-bonding in HPzAm4M, and the non-coordinated pyrazine nitrogen is involved in both complexes. HPzAm4M and the coordinated PzAm4M ligands are quite planar.

Keywords: Pyrazineformamide; Thiosemicarbazone; Zinc; Cadmium; Crystal structures; Electrochemical synthesis

1. Introduction

Heterocyclic thiosemicarbazones and their metal complexes have been screened for antitumor activity [1] and studied to determine the range of stereochemistries and stoichiometries that their complexes can assume [2]. Although other heterocycles have received attention, the majority of such studies have dealt with pyridine derivatives, and most specifically, 2-acetylpyridine [3]. In addition, metal complexes prepared with 2-formylpyridine [4], 2-benzoylpyridine [5], di-2-pyridyl ketone [6] and recently, 2-pyridineformamide [7] N(4)-substituted thiosemicarbazones have also been isolated and characterized. In addition, complexes of formyl- [8] and acetylpyrazine [9] N(4)-substituted thiosemicarbazones have been studied. Here, we report the newly formed pyrazineformamide N4-methylthiosemicarbazone, HPzAm4M (Fig. 1) and its six-coordinate zinc(II) and cadmium(II) complexes, $[Zn(PzAm4M)_2]\cdot 2CH_3CN$ and $[Cd(PzAm4M)_2]\cdot 0.5CH_3CN$, which were prepared by electrochemical oxidation of the metals.

2. Experimental

2.1. Reagents, materials and syntheses

Cyanopyrazine and N(4)-methylthiosemicarbazide were both purchased from Aldrich and used as received. Following the literature procedure for the reduction of 2-cyanopyridine [10], sodium (0.092 g, 4.0 mmol) was added to 25 ml of MeOH, which had been dried over $CaSO_4$, and the solution stirred until complete dissolution occurred. Cyanopyrazine (2.615 g, 24.9 mmol) was added, and the mixture stirred for 1/2 h, and N(4)-methylthiosemicarbazide (2.60 g, 24.9 mmol) was then added in small portions over a period of 1/2 h. On

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0277-5387/02/$ - see front matter
PII: S0277-5387(02)01019-7

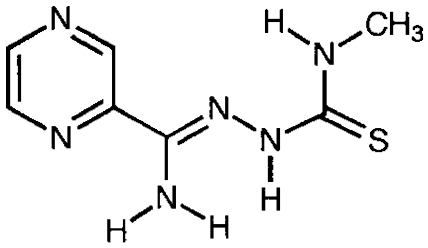

Fig. 1. Representation of pyrazineformamide N(4)-methylthiosemicarbazone, HPzAm4M.

addition of another 25 ml of MeOH, the mixture was refluxed for a minimum of 4 h. Slow evaporation of the MeOH produced the orange pyrazineformamide N4-methylthiosemicarbazone, HPzAm4M, NMR (DMSO-d_6): N(2)H at $\delta = 10.18$, N(4)H at $\delta = 9.72$, N–CH_3 at $\delta = 3.02$ (d), NH_2 at $\delta = 6.95$; m.p., 234–235 °C.

$[Zn(AmPz4M)]_2$ was prepared by electrochemical oxidation of zinc in a solution of HPzAm4M (0.186 mmol, 39.0 mg) in CH_3CN (40 ml) containing 10 mg of tetraethylammonium perchlorate for 1 h at 5 mA. A loss of 6.1 mg of the anode resulted. $[Cd(AmPz4M)]_2$ was prepared by electrochemical oxidation of cadmium in a solution of HAmPz4M (0.25 mmol, 52.5 mg) in CH_3CN (50 ml) containing 10 mg of tetraethylammonium perchlorate for 1 h at 5 mA. A loss of 13.4 mg of the anode resulted.

2.2. X-ray data collection and reduction

Orange crystals of HPzAm4M obtained by slow evaporation of ethanol, dark orange prismatic crystals of $[Zn(PzAm4M)_2]$ grown from MeCN and red prismatic hygroscopic crystals of $[Cd(PzAm4M)_2]$ obtained from MeCN were mounted on glass fibers and used for data collection. Data were collected on a Nonius MACH 3 diffractometer (HPzAm4M) or Bruker Smart CCD area-detector diffractometer at ambient conditions using Cu Kα radiation ($\lambda = 1.54184$ Å) for HPzAm4M and Mo Kα radiation ($\lambda = 0.71073$ Å) for $[Zn(PzAm4M)_2]$ and $[Cd(PzAm4M)_2]$. The structures were solved by direct methods [11] which revealed the position of all non-hydrogen atoms, and refined on F^2 by full-matrix least-square procedure using anisotropic displacement parameters [12]. The hydrogen atoms attached to carbons in the three compounds were located in their calculated positions and were refined using a riding model; the hydrogens attached to nitrogens were found and refined isotropically. Atomic scattering factors were taken from the International Table for X-ray Crystallography [13] and molecular graphics are from PLATON (HPzAm4M) [14] or ORTEP [15].

3. Results and discussion

The molecular structures of HPzAm4M, $[Zn(PzAm4M)_2]$ and $[Cd(PzAm4M)_2]$ are shown in Figs. 2–4, respectively. Table 1 has summaries of crystal data and intensity collection for the three compounds. A selection of bond distances and angles in the thiosemicarbazone fragment and coordination sphere of these complexes are listed in Tables 2 and 3. Hydrogen-bonding interactions for the three compounds are listed in Table 4 and their mean plane deviations, atoms showing the greatest deviation for each plane and the angles between planes are shown in Table 5.

3.1. Crystal structure of HPzAm4M

HPzAm4M crystallizes in the monoclinic space group $P2_1/c$ like 2-pyridineformamide N4-methylthiosemicarbazone, HAm4M [7], while 2-formylpyridine N4-methylthiosemicarbazone, HFo4M, crystallizes in the orthorhombic space group $P2_12_12_1$ with $Z = 4$ [16]. However, HAm4M [7] crystallizes with four unique molecules in the unit cell and $Z = 16$ compared with $Z = 4$ for HPzAm4M. HPzAmM, HAm4M and HFo4M are all E with respect to the imine C=N bond, the conformation that is most often found for heterocyclic N4-alkylthiosemicarbazones [16]. Like other heterocyclic N4-alkylthiosemicarbazones [7,16], the arrangement with respect to the N–C(S) bond, which has considerable double bond character, is also E. This allows for a weak interaction by N14H (Fig. 2) with the imine nitrogen, N12 and another weak interaction occurs between one of the N15 hydrogens and the pyrazine nitrogen, N11, that is unique to these recently studied heterocyclic amide thiosemicarbazones [7]. The bond distances for the thiosemicarbazone moiety of HPzAm4M, HAm4M [7] and HFo4M [16] are not very different except that the two amide thiosemicarbazones, HPzAm4M and HAm4M, have a C17–S1 bond that is approximately 0.05 Å longer and the C17–N13 and

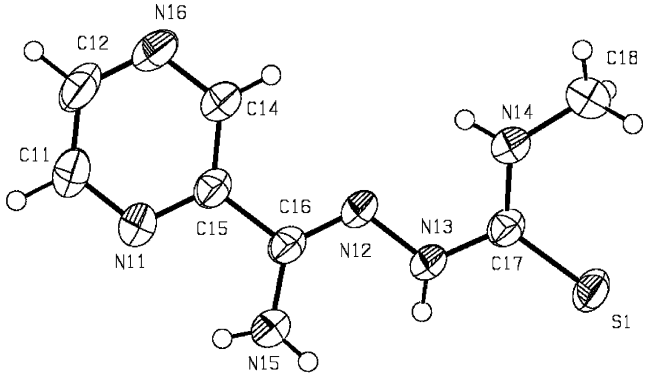

Fig. 2. ORTEP drawing of HPzAm4M with atom numbering scheme and displacement ellipsoids at 50% probability level.

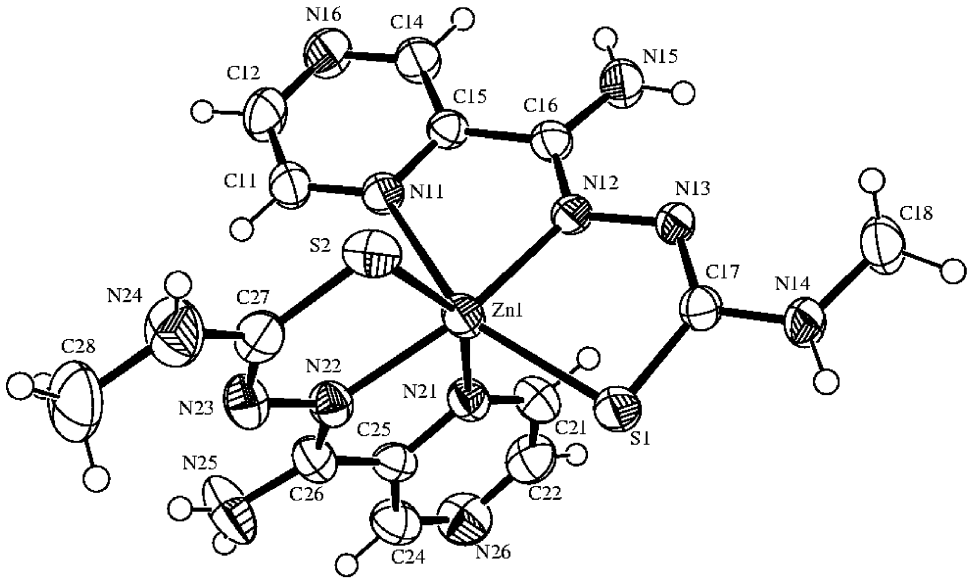

Fig. 3. ORTEP drawing of $[Zn(PzAm4M)_2]$ with atom numbering scheme and displacement ellipsoids at 50% probability level.

C17–N14 bonds are marginally shorter suggesting greater delocalization of electron density. While HPzAm4M and HAm4M have C15–C17–N12 bond angles of approximately 116°, this angle is more than 120° for HFo4M [16], which is consistent with a recent report comparing the structures of 4-formylpyridine and 4-acetylpyridine N(4)-methyl- and N(4)-ethylthiosemicarbazones [17]. The remainder of the thiosemicarbazone bond angles in HPzAm4M, HAm4M [7] and HFo4M [16] are more similar.

As indicated previously, two weak intramolecular hydrogen bonds, N14–H14···N12 and N15–H15B···N11, are present in HPzAm4M. Although the arrangement of HFo4M [16] is the same, the N14–H14···N12 interaction was not found because of the inductive effect of a the aldehyde hydrogen compared with the electron donating amino function. In the four unique molecules of HAm4M, the N14–H14···N12 interaction has an average non-bonding distance of 2.575(5) Å and average angle of 113(4)° which are similar to the values for HPzAm4M (Table 4). The distances and angles for the N15H15B···N11 interaction are essentially the same for HPzAm4M and HAm4M. Unique to HPzAm4M is that H14 is also involved in an interaction with the second nitrogen of the pyrazine ring, N16, which is weaker, based on the H14···N distances, than its intramolecular interaction with N12. The second N15 hydrogen, H15A, interacts weakly with the thione sulfur of a second neighboring molecule.

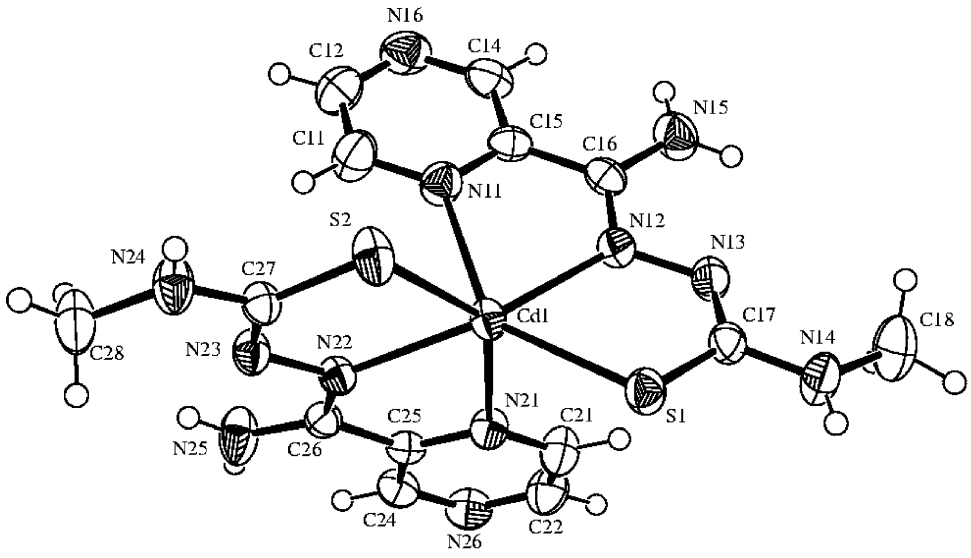

Fig. 4. ORTEP drawing of $[Cd(PzAm4M)_2]$ with atom numbering scheme and displacement ellipsoids at 50% probability level.

Table 1
Crystal data and structure refinement for HPzAm4M, $[Zn(PzAm4M)_2]\cdot 2CH_3CN$, and $[Cd(PzAm4M)_2]\cdot 0.5CH_3CN$

Empirical formula	$C_7H_{10}N_6S$	$C_{18}H_{24}N_{14}S_2Zn$	$C_{15}H_{19.5}CdN_{12.5}S_2$
Color; Habit	orange, prism	dark orange, prism	red, prism
Formula weight	210.27	566.0	551.45
Temperature (K)	293(2)	293(2)	293(2)
Crystal size (mm)	$0.32 \times 0.24 \times 0.12$	$0.20 \times 0.20 \times 0.12$	$0.26 \times 0.17 \times 0.12$
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_1/c$ (#14)	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)
Unit cell dimensions			
a (Å)	11.1334(8)	7.9278(12)	9.6613(16)
b (Å)	5.0612(3)	11.036(1)	11.1091(18)
c (Å)	17.9215(11)	16.000(2)	11.831(2)
α (°)	90(0)	78.117(16)	89.329(5)
β (°)	99.569(5)	88.668(14)	73.568(5)
γ (°)	90(0)	68.428(14)	64.279(4)
Volume (Å^3)	995.80(11)	1271.8(4)	1088.1(3)
Z	4	2	2
Density (Mg m^{-3})	1.403	1.478	1.683
Absorption coefficient (mm^{-1})	2.669	1.167	1.227
θ Range for data collect. (°)	4.03–74.92	2.61–30.43	1.81–30.58
Index ranges	$-13 \le h \le 13$, $0 \le k \le 6$, $0 \le l \le 22$	$-11 \le h \le 11$, $-15 \le k \le 15$, $-22 \le l \le 0$	$-12 \le h \le 13$, $-15 \le k \le 15$, $-16 \le l \le 16$
Absorption correction	ψ-scan	ψ-scan	SADABS
Reflections collected	2103	7944	19424
Independent reflections (R_{int})	2031 (0.0406)	7688 (0.0861)	6577 (0.0434)
Max., min. transmissions	0.967, 0.916	0.8727, 0.8001	0.8668, 0.7410
Data/restraints/parameters	2031/0/167	7688/0/326	6576/0/289
Final R Indices [$I > 2\sigma(I)$]	$R_1 = 0.0360$, $wR_2 = 0.0999$	$R_1 = 0.0466$, $wR_2 = 0.0795$	$R_1 = 0.0321$, $wR_2 = 0.0604$
R Indices (all data)	$R_1 = 0.0484$, $wR_2 = 0.1061$	$R_1 = 0.2042$, $wR_2 = 0.1063$	$R_1 = 0.0584$, $wR_2 = 0.0666$
Goodness-of-fit	1.060	0.959	0.925
Largest difference peak/hole (e Å^{-3})	0.189/−0.215	0.463/−0.724	0.706/−0.451

The thiosemicarbazone moiety of HPzAm4M, C16–N12–N13–C17–S1–N14, has a larger mean plane deviation (Table 5) than HAm4M, 0.0339 Å. The mean plane of the pyridine ring forms an angle of 9.912(12)° with the thiosemicarbazone moiety mean plane, which is smaller than found for HAm4M, 14.1(4)°.

Table 2
Selected bond distances (Å) for HPzAm4M (**1**); $[Zn(PzAm4M)_2]\cdot 2CH_3CN$ (**2**); and $[Cd(PzAm4M)_2]\cdot 0.5CH_3CN$ (**3**)

Bond	**1**	Bond	**2**	Bond	**3**
S1–C17	1.6939(15)	S1–C17	1.743(3)	S1–C17	1.756(3)
C16–N12	1.290(2)	C16–N12	1.298(3)	C16–N12	1.295(3)
N12–N13	1.3879(18)	N12–N13	1.389(3)	N12–N13	1.389(3)
N13–C17	1.351(2)	N13–C17	1.316(3)	N13–C17	1.307(3)
C17–N14	1.324(2)	C17–N14	1.346(4)	C17–N14	1.349(3)
C16–N15	1.350(2)	C16–N15	1.349(4)	C16–N15	1.361(3)
		S2–C27	1.750(3)	S2–C27	1.744(2)
		C26–N22	1.298(4)	C26–N22	1.292(3)
		N22–N23	1.401(3)	N22–N23	1.391(2)
		N23–C27	1.297(4)	N23–C27	1.317(3)
		C27–N24	1.366(4)	C27–N24	1.343(3)
		C26–N25	1.347(4)	C26–N25	1.348(3)
		Zn–S1	2.4056(10)	Cd–S1	2.5805(7)
		Zn–S2	2.4405(10)	Cd–S2	2.5693(8)
		Zn–N12	2.072(2)	Cd–N12	2.327(2)
		Zn–N22	2.071(2)	Cd–N22	2.2987(19)
		Zn–N11	2.415(2)	Cd–N11	2.481(2)
		Zn–N21	2.333(2)	Cd–N21	2.5260(19)

Table 3
Selected bond angles (°) for HPzAm4M (**1**); $[Zn(PzAm4M)_2]\cdot 2CH_3CN$ (**2**); and $[Cd(PzAm4M)_2]\cdot 0.5CH_3CN$ (**3**)

Angle	**1**	Angle	**2**	Angle	**3**
N15–C16–N12	127.74(15)	N15–C16–N12	123.1(3)	N15–C16–N12	124.1(2)
C15–C16–N12	115.97(14)	C15–C16–N12	116.5(3)	C15–C16–N12	116.8(2)
C16–N12–N13	115.87(14)	C16–N12–N13	113.3(2)	C16–N12–N13	114.09(19)
N12–N13–C17	118.27(14)	N12–N13–C17	113.6(2)	N12–N13–C17	114.57(19)
N13–C17–N14	116.99(14)	N13–C17–N14	115.6(3)	N13–C17–N14	116.2(2)
N13–C17–S1	119.40(12)	N13–C17–S1	127.8(2)	N13–C17–S1	128.70(18)
N14–C17–S1	123.59(13)	N14–C17–S1	116.6(2)	N14–C17–S1	115.1(2)
		N25–C26–N22	123.7(3)	N25–C26–N22	123.6(2)
		C25–C26–N22	116.1(3)	C25–C26–N22	117.1(2)
		C26–N22–N23	113.6(2)	C26–N22–N23	113.38(19)
		N22–N23–C27	113.5(3)	N22–N23–C27	115.00(19)
		N23–C27–N24	116.0(3)	N23–C27–N24	115.2(2)
		N23–C27–S2	128.3(2)	N23–C27–S2	128.93(17)
		N24–C27–S2	115.7(3)	N24–C27–S2	115.91(18)
		S1–Zn1–N22	115.08(7)	S1–Cd1–N22	136.06(5)
		S1–Zn1–N12	81.81(7)	S1–Cd1–N12	74.74(5)
		S1–Zn1–N11	151.79(6)	S1–Cd1–N11	139.83(5)
		S1–Zn1–N21	90.54(7)	S1–Cd1–N21	96.93(5)
		S1–Zn1–S2	105.31(4)	S1–Cd1–S2	104.41(2)
		S2–Zn1–N22	80.97(7)	S2–Cd1–N22	75.99(5)
		S2–Zn1–N12	112.29(7)	S2–Cd1–N12	130.97(5)
		S2–Zn1–N11	93.33(6)	S2–Cd1–N11	91.39(5)
		S2–Zn1–N21	153.25(6)	S2–Cd1–N21	142.08(5)
		N11–Zn1–N22	88.28(9)	N11–Cd1–N22	83.26(7)
		N11–Zn1–N12	71.47(8)	N11–Cd1–N12	67.231(7)
		N11–Zn1–N21	81.21(8)	N11–Cd1–N21	92.06(7)
		N21–Zn1–N22	72.75(9)	N21–Cd1–N22	66.97(6)
		N21–Zn1–N12	90.90(9)	N21–Cd1–N12	84.59(7)
		N12–Zn1–N22	155.91(9)	N12–Cd1–N22	138.23(7)
		Zn1–S1–C17	94.06(10)	Cd1–S1–C17	97.06(8)
		Zn1–N12–C16	124.7(2)	Cd1–N12–C16	123.04(16)
		Zn1–N12–N13	122.01(17)	Cd1–N12–N13	122.85(14)
		Zn1–S2–C27	94.02(11)	Cd1–S2–C27	97.05(8)
		Zn1–N22–C26	123.0(2)	Cd1–N22–C26	123.58(15)
		Zn1–N22–N23	123.18(19)	Cd1–N22–N23	122.58(13)

Table 4
Hydrogen-bonding interactions for HPzAm4M (**1**); $[Zn(PzAm4M)_2]\cdot 2CH_3CN$ (**2**); and $[Cd(PzAm4M)_2]\cdot 0.5CH_3CN$ (**3**)

Compound	D–H···A	d(D–H)	d(H···A)	d(D···A)	∠ (DHA)
1[a]	N14–H14···N12	0.84(2)	2.20(2	2.614(2)	110.3(17)
	N14–H14···N16#1	0.84(2)	2.45(2)	3.124(2)	138.0(18)
	N15–H15A···S1#2	0.84(3)	2.84(3)	3.2886(18)	116(2)
	N15–H15B···N11	0.80(3)	2.26(3)	2.681(2)	113(2)
2[b]	N14–H14···N16#1	0.77(3)	2.29(3)	3.027(4)	163(3)
	N15–H15A···N13	0.80(3)	2.25(3)	2.588(4)	106(2)
	N15–H15B···S2#2	0.92(4)	2.53(4)	3.445(3)	172(3)
	N25–N25B···N23	0.83(4)	2.21(4)	2.612(5)	109(3)
	N25–H25B···N1(MeCN)#3	0.87(4)	2.26(4)	3.117(5)	166(3)
3[c]	N14–H14···N26#1	0.79(3)	2.65(3)	3.358(3)	150(3)
	N24–H24···N26#2	0.79(3)	2.36(3)	3.112(3)	161(3)
	N15–H15A···S2#3	0.93(3)	3.00(3)	3.518(3)	116.5(19)
	N15–H15A···N13	0.93(2)	2.25(3)	2.626(4)	103(2)
	N25–H25A···S1#4	0.81(3)	2.76(3)	3.526(3)	159(3)
	N25–H25BN23	0.81(3)	2.19(3)	2.596(3)	111(2)

Symmetry transformations used to generate equivalent atoms: [a]#1: $-x+3$, $y+1/2$, $-z+3/2$; #2: $-x+2$, $-y$, $-z+1$.[b]#1: $x+1$, $y-1$, z; #2: $-x+1$, $-y+2$, $-z+1$; #3: x, y, $z+1$. [c]#1: $x+1$, y, z; #2: x, $y+1$, z; #3: $-x+2$, $-y+1$, $-z$; #4: $-x+1$, $-y+1$, $-z+1$.

Table 5
Rms planes for HPzAm4M (**1**); $[Zn(PzAm4M)_2]\cdot 2CH_3CN$ (**2**); and $[Cd(PzAm4M)_2]\cdot 0.5CH_3CN$ (**3**)

Compound	Plane	rms dev.	Largest dev.	∠ with previous plane
1	N11–C11–C12–N16–C14–C15	0.0083	C15, 0.0116(0.0014)	
	C16–N12–N13–C17–S1–N14	0.0449	N12, 0.0906(0.0013)	9.912(0.12)
2	N11–C11–C12–N16–C14–C15	0.0012	C12, 0.0017(0.0024)	
	C16–N12–N13–C17–S1–N14	0.0451	C16, 0.0683(0.0016)	7.05(0.14)
	C26–N22–N23–C27–S2–N24	0.0195	N22, 0.0375(0.0021)	89.86(0.06)
	N21–C21–C22–N26–C24–C25	0.0083	C25, 0.0117(0.0021)	5.62(0.19)
3	N11–C11–C12–N16–C14–C15	0.0024	N11, 0.0040(0.0018)	
	C16–N12–N13–C17–S1–N14	0.0637	N12, 0.1112(0.0017)	8.88(0.13)
	C26–N22–N23–C27–S2–N24	0.0248	N23, 0.0445(0.0018)	75.83(0.04)
	N21–C21–C22–N26–C24–C25	0.0013	C24, 0.0019(0.0017)	6.50(0.07)

3.2. Crystal structure of [Zn(PzAm4M)$_2$] and of [Cd(PzAm4M)$_2$]

In both complexes, the metal center has a coordination number of six binding the imine and the pyridine nitrogen atoms, as well as the thiolato sulfur, of two anionic tridentate thiosemicarbazone ligands. The coordinated polyhedron about the metal in both complexes is distorted octahedral with the two ligands in a meridional arrangement. This distortion from octahedral symmetry is illustrated by the three angles defined by pairs of *trans* donor atoms and the metal atom, in the range of 151.77(6)°–155.91(9)° for $[Zn(PzAm4M)_2]$ and 138.23(7)°–142.10(5)° for $[Cd(PzAm4M)_2]$, significantly different from 180°. The small bite angle of chelate rings is the main source of distortion as found previously with Group 12 metal complexes, as well as iron(III), cobalt(III) and nickel(II) complexes with bis(heterocylic thiosemicarbazone) metal centers [7a]. The bond angles (Table 3) of the two ligands, which involve the metal ions, are similar in the two complexes, and, in particular, those angles involving donor atoms within the same ligand. The greatest difference occurs in comparing analogous angles between the two ligands; for example, S1–Zn1–N22 is 115.08(7)°, but S2–Zn1–N12 is 112.29(7)°. The difference is even larger in $[Cd(PzAm4M)_2]$, S1–Cd1-N22 is 136.07(5)° and S2–Cd1–N12 is 130.97(5)°. As would be expected due to the larger size of cadmium(II) compared with zinc(II), the bond angles involving the metals ions in the two complexes are significantly different.

In both complexes the M–N(imine) bonds (i.e. M–N12, M–N22) are the shortest metal–ligand distances and in $[Cd(PzAm4M)_2]$ the Cd–S distances are longer than the Cd–N(pyridine) distances. However, in $[Zn(PzAm4M)_2]$ the Zn–S and Zn–N(pyridine) bond distances are similar. $[Fe(Am4M)_2]ClO_4$ and $[Co(Am4M)_2]ClO_4$ have the same order of ligand bond distances [7a] as $[Cd(PzAm4M)_2]$. To date the only zinc and cadmium complexes of HAm4M for which we have obtained crystals are four-coordinate, $[Zn(Am4M)OAc]_2$ and five-coordinate $[Cd(HAm4M)Cl_2]\cdot DMSO$ [18]. Compared with the bond distances of the thiosemicarbazone moiety of HPzAm4M, the following bond distances have been altered in $[Zn(PzAm4M)_2]$ and $[Cd(PzAm4M)_2]$: C17–S1 (and C27–S2) is longer consistent with it formally changing from a double bond to a single bond, N13–C17 (and N23–C27) is shorter consistent with it formally changing from a single bond to a double bond and C17–N14 (and C27–N24) is marginally longer. The remaining bond distances of the thiosemicarbazone moiety, as well as C16–N15 (and C26–N25) are unchanged in the two complexes from their distances in HPzAm4M. The bond angles of the thiosemicarbazone moieties (Table 3) also are different in the two complexes than in HPzAm4M; N13–C17–S1 (and N23–C27–S2) and N14–C17–S1 (and N24–C27–S2) show the largest differences.

These complexes of 2-pyridineformamide thiosemicarbazones feature hydrogen-bonding involving the amide hydrogens, $N15H_2$ [7,18]. One of the hydrogens from both ligands in $[Zn(PzAm4M)_2]\cdot 2CH_3CN$ is involved in hydrogen-bonding, one to sulfur of the other ligand in a neighboring molecule, and the other to the nitrogen of an acetonitrile solvent molecule. In $[Cd(PzAm4M)_2]\cdot 0.5CH_3CN$ only N25–H25...S1 is present, and it is substantially weaker than the analogous interaction in $[Zn(PzAm4M)_2]\cdot 2MeCN$. Unique to these pyrazine thiosemicarbazones is hydrogen-bonding to the second ring nitrogen, N16. Both complexes, as well as HPzAm4M, involve the atom in an intermolecular interaction and it is either of comparable strength or a stronger interaction in the complexes.

Formation of the anion on coordination retains the planarity of the thiosemicarbazone moiety in the two complexes. The average of the mean planes of the two ligands in $[Zn(PzAm4M)_2]$ is less than that of HPzAm4M, but the mean plane average of the two ligands in $[Cd(PzAm4M)_2]$ is comparable to HPzAm4M. Both ligands in each complex have angles between the mean planes of the pyrazine ring and the thiosemicarbazone moiety that are marginally less than

found for HPzAm4M. This is expected because of the greater conjugation present in the anionic ligand compared with the neutral molecule.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-172573 for HPzAm4M, and, CCDC-172574 for $[Zn(PzAm4M)_2]\cdot 2CH_3CN$, and CCDC-172575 for $[Cd(PzAm4M)_2]\cdot 0.5CH_3CN$. Copies of available material can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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