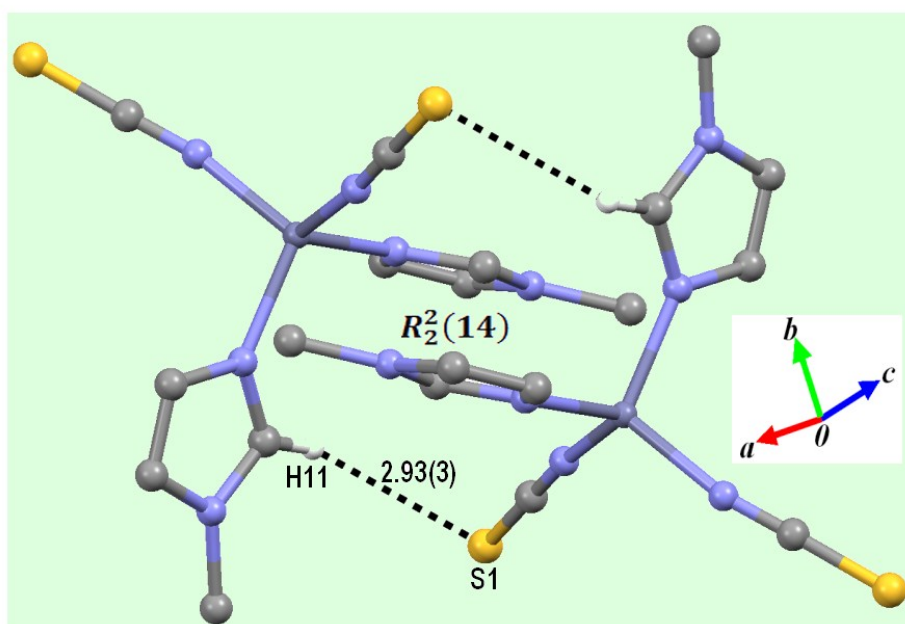


## Electronic Supplementary Information

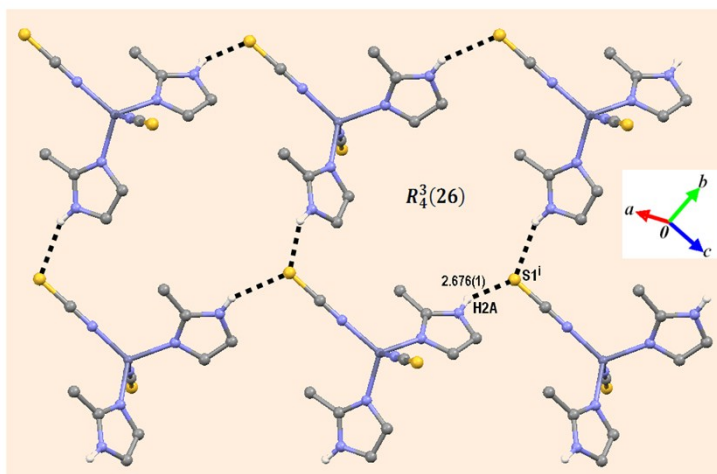
### “Exploring weak intermolecular interactions in thiocyanate-bonded Zn(II) and Cd(II) complexes with methylimidazole: Crystal structures, Hirshfeld surface analysis and luminescence properties”

Alejandro Di Santo<sup>1</sup>, Hiram Pérez<sup>2,\*</sup>, Gustavo A. Echeverría<sup>3,+</sup>, Oscar E. Piro<sup>3,+</sup>, Rodrigo A. Iglesias<sup>4,+</sup>, Raúl E. Carbonio<sup>4,+</sup>, Aida Ben Altabef<sup>1,+</sup>, Diego M. Gil<sup>1,+,\*</sup>

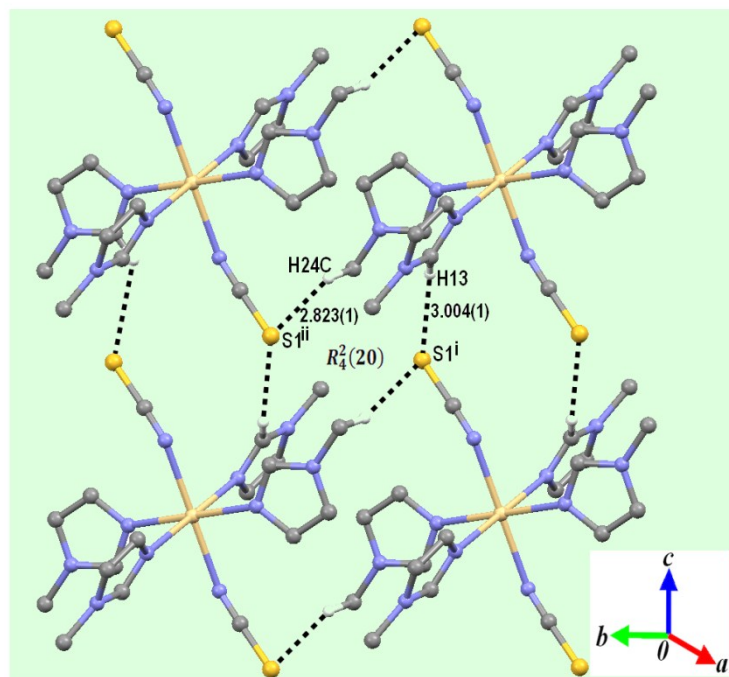
**Figure S1, ESI.** A view of intermolecular C-H...S hydrogen bonds (dashed lines) forming  $R_2^2(14)$  dimer sited at a crystallographic inversion centre of compound (**1**) solid. Hydrogen atoms not involved in the hydrogen bonding are omitted for the sake of clarity.



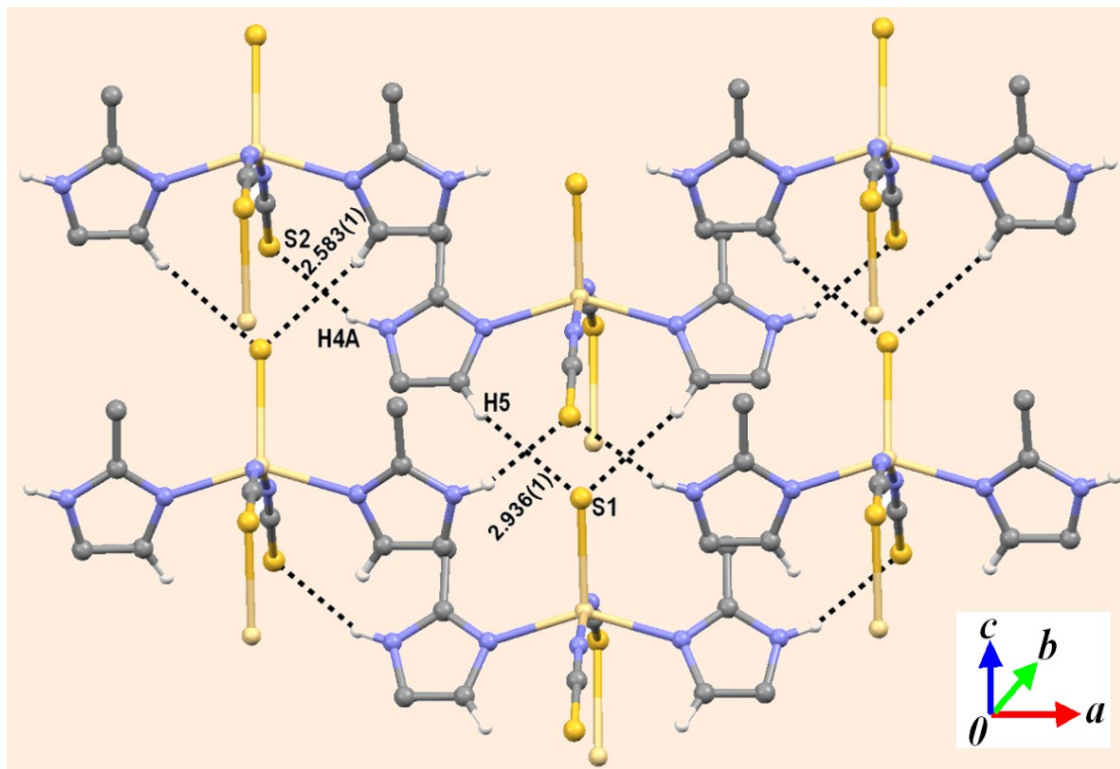
**Figure S2, ESI.** A view of intermolecular N-H...S hydrogen bonds (dashed lines) forming  $R_4^3(26)$  ring motifs for compound (**2**). Hydrogen atoms not involved in the hydrogen bonding are omitted for the sake of clarity.



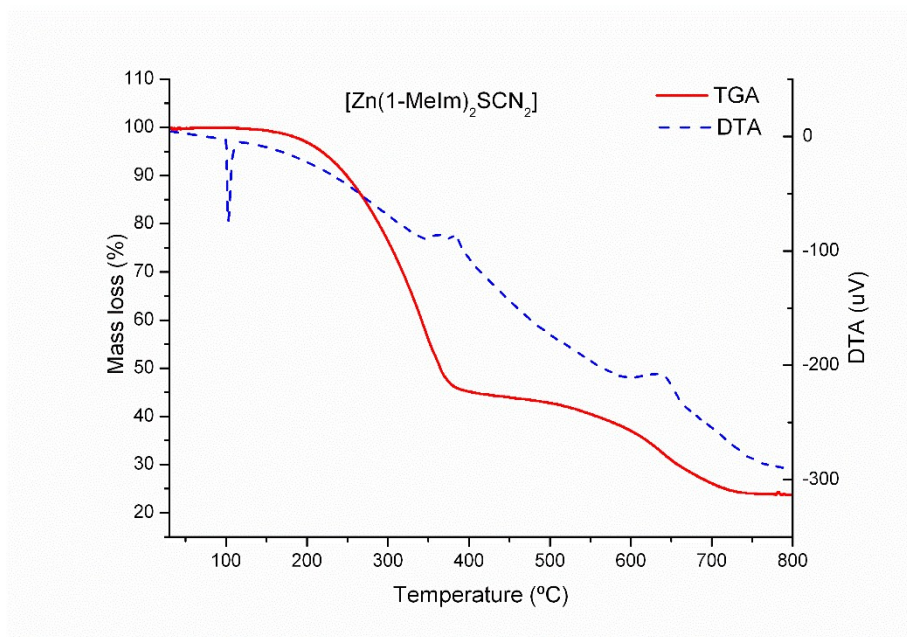
**Figure S3, ESI.** A view of intermolecular C-H...S hydrogen bonds (dashed lines) forming  $R_4^2(20)$  ring motifs for compound (**3**). Hydrogen atoms not involved in the hydrogen bonding are omitted for the sake of clarity.



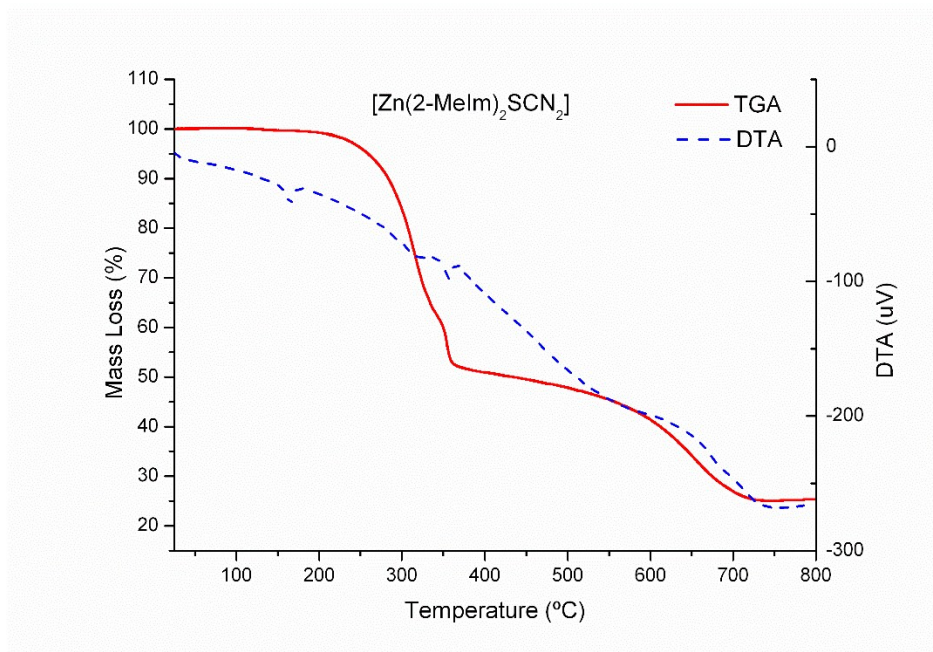
**Figure S4, ESI.** A view of 3D network showing intermolecular C-H...S hydrogen bonds (dashed lines) for polymeric (**4**). Hydrogen atoms not involved in the hydrogen bonding are omitted for the sake of clarity.



**Figure S5, ESI.** TG and DTA curves for the thermal decomposition of the complex  $[\text{Zn}(\text{1-MeIm})_2(\text{SCN})_2]$  (**1**) at 5 °C/min in air.

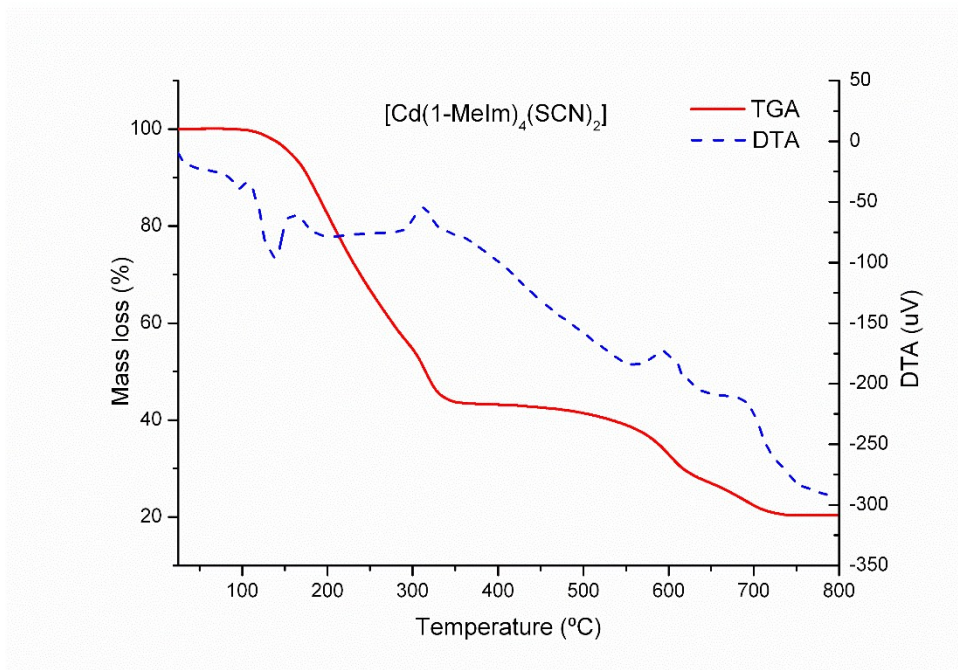


**Figure S6, ESI.** TG and DTA curves for the thermal decomposition of the complex  $[\text{Zn}(\text{2-MeIm})_2(\text{SCN})_2]$  (**2**) at 5 °C/min in air.

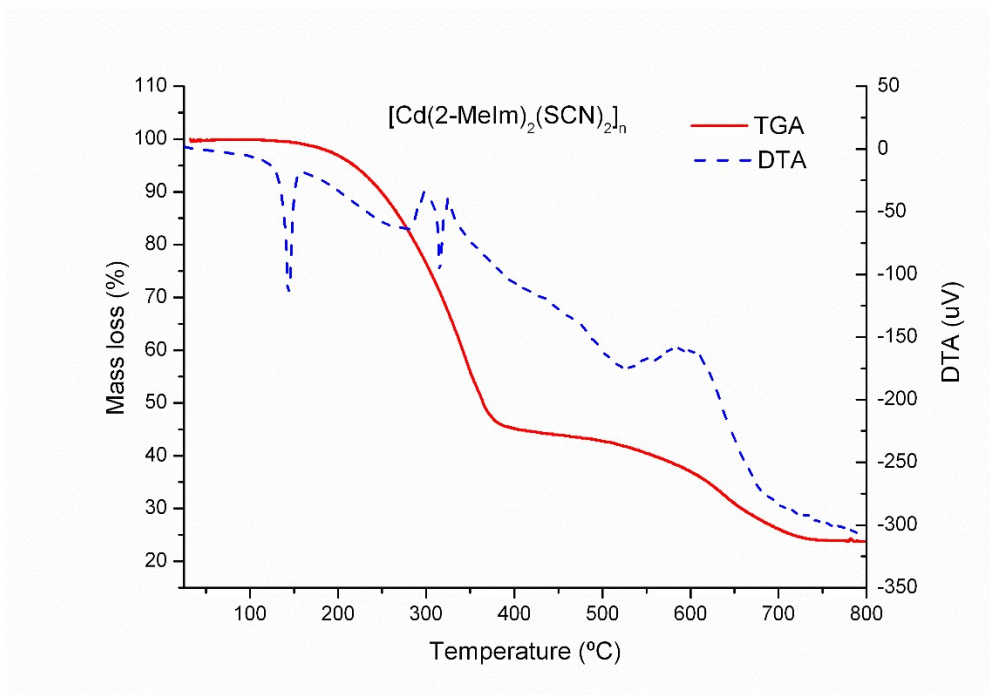




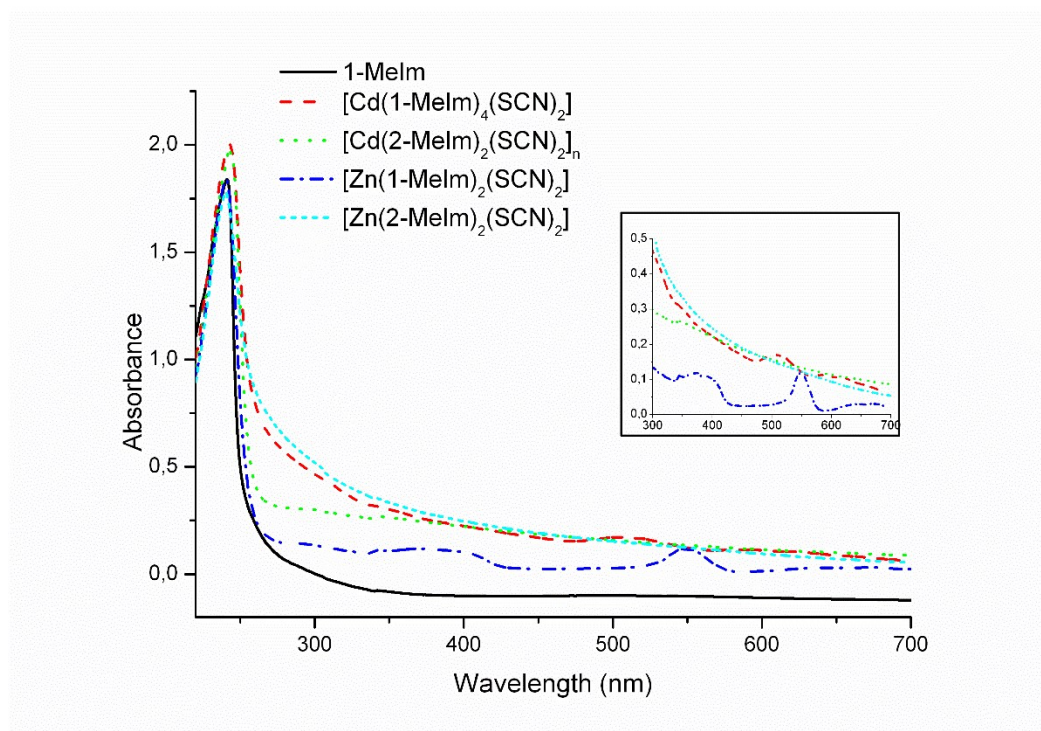
**Figure S7, ESI.** TG and DTA curves for the thermal decomposition of the complex  $[\text{Cd}(\text{1-MeIm})_4(\text{SCN})_2]$  (**3**) at 5 °C/min in air.



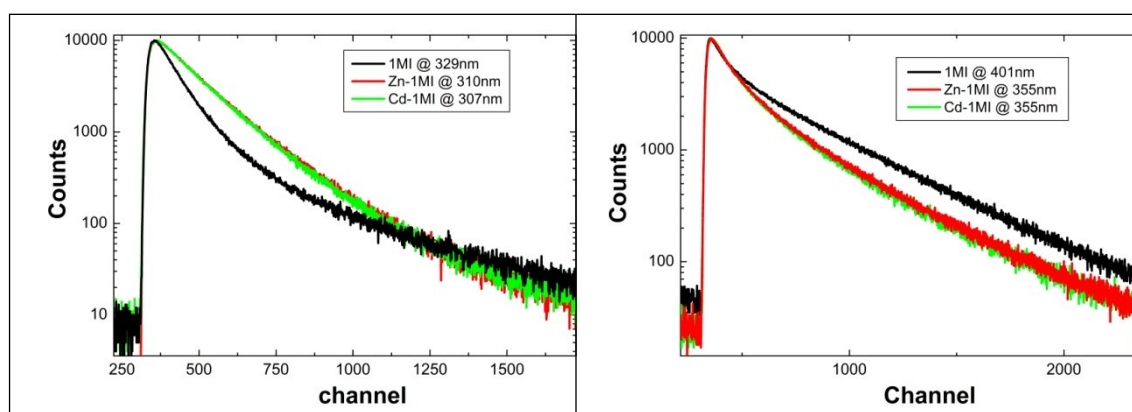
**Figure S8, ESI.** TG and DTA curves for the thermal decomposition of the complex  $[\text{Cd}(\text{2-MeIm})_2(\text{SCN})_2]_n$  (**4**) at 5 °C/min in air.



**Figure S9, ESI.** Electronic spectra of the ligands and complexes 1-4 in acetonitrile solutions ( $10^{-3}$  M).



**Figure S10, ESI.** Decay of the photoluminescence intensity integrated over the whole spectral range of 1-Melm, 2-Melm and complexes 1-4.



**Table S1, ESI†.** Hirshfeld contact surfaces  $C_{XY}$  (%)\*, proportion of chemical type on the molecular surface  $S_x$  (%) and random contacts  $R_{XY}$  (%) of the main intermolecular interactions for compounds **1-7**.

Contact $C_{XY}$	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>	<b>7</b>
H··H	23.3	24.5	41.9	21.4	41.2	37.4	43.5
C··H	20.7	22.2	22.8	21.2	11.0	10.9	9.7
N··H	13.9	12.4	11.1	16.6	7.3	9.7	8.0
S··H	33.7	30.1	21.6	31.2	-	-	-
O··H	-	-	-	-	-	4.6	-
Cl··H	-	-	-	-	33.9	-	-
Br··H	-	-	-	-	-	32.3	26.0
C··C	-	0.5	1.0	0.0	1.3	1.6	2.0
C··S	-	3.9	-	4.3	-	-	-
N··S	-	3.3	-	-	-	-	-
Cl··C	-	-	-	-	1.6	-	-
N··C	-	-	-	-	-	-	1.6
Surface $S_x$							
H	57.6	56.9	69.7	55.9	67.9	66.3	65.4
C	14.4	14.0	12.7	13.4	8.2	7.9	7.6
N	9.0	9.8	6.3	10.2	5.0	6.5	5.5
S	19.0	19.0	11.3	19.3	-	-	-
O	-	-	-	-	-	2.4	-
Cl	-	-	-	-	18.3	-	-
Br	-	-	-	-	-	16.7	17.7
Random contacts $R_{XY}$							
H··H	33.2	32.4	48.5	31.3	46.0	44.0	42.8
C··H	16.5	16.0	17.7	15.0	11.0	10.5	9.9
N··H	10.4	11.2	8.7	11.4	7.0	8.6	7.2
S··H	21.9	21.6	15.7	21.5	-	-	-
O··H	-	-	-	-	-	3.2	-
Cl··H	-	-	-	-	24.8	-	-
Br··H	-	-	-	-	-	22.1	23.2
C··C	2.1	2.0	1.6	1.8	0.7	0.6	0.6
C··S	5.5	5.3	-	5.2	-	-	-
N··S	-	3.7	-	-	-	-	-
Cl··C	-	-	-	-	3.0	-	-
N··C	2.6	-	-	-	-	-	0.8

\*Data obtained from CrystalExplorer3.0, including reciprocal contacts.



**Table S2:** IR and Raman bands (in  $\text{cm}^{-1}$ ) for 2-methylimidazole and its Cd(II) and Zn(II) thiocyanate complexes together with their tentative assignment of modes.

<i>2-methylimidazole</i>		<i>[Cd(2-MeIm)<sub>2</sub>(SCN)<sub>2</sub>]<sub>n</sub></i>		<i>[Zn(2-MeIm)<sub>2</sub>(SCN)<sub>2</sub>]</i>		Assignment
FT-IR	Raman	FT-IR	Raman	FT-IR	Raman	
3182 (s)	-	3224 (m)	-	3319 (vs)	-	$\nu$ NH
3137 (s)	3134 (52)	3147 (s)	3147(18)	3160 (w)	3160 (26)	$\nu$ CH
2961 (s)	2960 (23)	2954 (vvw)	-	2967 (vvw)	-	$\nu_a$ CH <sub>3</sub>
2926 (s)	2925 (53)	2933 (vvw)	2934 (29)	2934 (vw)	2934 (36)	$\nu_s$ CH <sub>3</sub>
-	-	2119 (vs)	2118 (67)	2100 (vs)	2102 (100)	$\nu$ CN
-	-	2076 (vs)	2077 (100)	2077 (vs)	2077 (51)	$\nu$ CN
1597 (s)	-	1566 (s)	-	1565 (vs)	-	$\nu$ C-C + $\nu$ C-N
1479 (vvw)	1479 (100)	1495 (vw)	1497 (49)	1500 (m)	1502 (100)	$\nu$ C-C + $\delta_a$ CH <sub>3</sub>
1447 (s)	-	1428 (w)	-	1430 (m)	-	$\delta_a$ CH <sub>3</sub>
1371 (w)	-	1352 (w)	-	1351 (m)	1353 (16)	$\delta_s$ CH <sub>3</sub>
1303 (m)	1303 (4)	1280 (s)	-	1279 (w)	1279 (17)	
1155 (m)	-	1159 (w)	-	1157 (m)		$\nu$ ring
1117 (s)	1113 (79)	1098 (w)	-	1140 (s)	1140 (55)	$\delta$ CCH
1048	-	1038 (w)	-	1046 (w)	-	$\rho$ CH <sub>3</sub>
995	993 (15)	1012 (w)	-	1023 (vw)	-	$\rho$ CH <sub>3</sub> + $\nu$ C-N (ring)
945 (s)	937 (9)	943 (vw)	-	930 (w)	929 (13)	$\rho$ CH <sub>3</sub> + $\delta$ CCH
916 (s)	916 (10)	901 (vvw)	-	-	-	$\delta$ ring
-	-	770 (w)	857 (25)	757 (w)	-	$\nu$ CS
-	-	765 (vvw)	-	747 (w)	-	$\nu$ CS
683 (s)	682 (39)	672 (m)	674 (12)	666(vw)	684 (9)	$\gamma$ CH
629	629 (2)	624 (vvw)	-	622 (vw)	620 (6)	$\gamma$ NH
-	-	469 (w)	-	478 (s)	481 (5)	$\delta$ SCN
-	-	451 (vw)	-	470 (m)	-	$\delta$ SCN
-	269 (25)	-	283 (13)	-	284 (15)	G CNCN
-	-	-	-	-	254 (9)	$\nu$ Zn-N(ring)
-	-	-	-	-	212 (17)	$\nu$ Zn-N (SCN)
-	-	-	208 (25)	-	-	$\nu$ Cd-N (2Au)
-	-	-	185 (12)	-	-	$\nu$ Cd-N (NCS)
-	-	-	174 (44)	-	-	$\nu$ Cd-N (ring)
-	-	-	145 (49)	-	-	$\nu$ Cd-S (B1g)
-	-	-	112 (94)	-	-	$\nu$ Cd-N(ring)
-	-	-	107 (96)	-	-	$\nu$ Cd-N(SCN)
-	-	-	-	-	82 (99)	$\rho$ SCN
-	-	-	75 (99)	-	64 (99)	$\tau$ CH <sub>3</sub>

**Table S3:** IR and Raman bands (in  $\text{cm}^{-1}$ ) for 1-methylimidazole Zn(II) and Cd(II) thiocyanate complex together with their tentative assignment of modes.

<i>1-Methylimidazole</i>		<i>[Cd(1-MeIm)<sub>4</sub>(SCN)<sub>2</sub>]</i>		<i>[Zn(1-MeIm)<sub>2</sub>(SCN)<sub>2</sub>]</i>		Assignment
FT-IR	Raman	FT-IR	Raman	FT-IR	Raman	
-	3134 (39)	3145 (vw)	3146 (17)	3142	3143 (4)	$\nu$ CH
3127 (vvw)	-	3125(w)	3127 (13)	3120	3124 (3)	$\nu$ CH
3111(vs)	3109 (35)	3111 (m)	3117 (8)	-	-	$\nu$ CH
2983	-	2984 (vw)	-	-	-	$\nu$ a CH <sub>3</sub>
2952 (m)	2955 (36)	2958 (s)	2959 (10)	2967	2959 (8)	$\nu$ a CH <sub>3</sub>
2812 (w)	2816 (11)	-	2815 (2)	-	-	$\nu$ s CH <sub>3</sub>
-	-	2083 (vs)	-	2098	2086 (100)	$\nu$ C-N
-	-	2066 (s)	2074 (100)	2083	2070 (93)	$\nu$ C-N
1669	-	1671 (vw)	-	-	-	$\nu$ C-N + $\delta$ a CH <sub>3</sub>
1619	-	1621 (vw)	-	-	-	$\nu$ C-C + $\delta$ a CH <sub>3</sub>
1522 (vs)	1519 (15)	1534 (m)	1533 (3)	1545	1541 (21)	$\delta$ a CH <sub>3</sub>
-	-	1516 (m)	1518 (3)	1525	1522 (30)	$\delta$ a CH <sub>3</sub>
1422	1422 (9)	1421 (vw)	1419 (4)	1421	1414 (20)	$\nu$ C-N + $\delta$ a CH <sub>3</sub>
-	-	1413 (vw)	-	-	-	$\nu$ C-N + $\delta$ a CH <sub>3</sub>
1363(m)	-	1369 (vs)	1369 (9)	1372	1370 (50)	$\nu$ ring + $\delta$ a CH <sub>3</sub>
1329	1328 (20)	1339 (vvw)	1335 (18)	1338	1336 (66)	$\nu$ ring + $\delta$ a CH <sub>3</sub>
1288	1288 (21)	1282 (m)	1283 (5)	1286	1284 (5)	$\nu$ ring
1237	1238 (9)	1237 (s)	1239 (2)	1240	1242 (10)	$\nu$ C-N + $\delta$ HCN
1026 (m)	1032 (33)	1027 (vw)	1030 (2)	1047	1041 (3)	$\rho$ CH <sub>3</sub>
-	-	1023 (vw)	-	1025	1024 (66)	$\rho$ CH <sub>3</sub>
925 (vs)	-	937 (s)	937 (4)	956	954 (33)	$\nu$ C-N + $\delta$ CNC
836 (vs)	-	838 (s)	833 (2)	828	837 (77)	$\gamma$ C-H
-	-	769 (m)	-	768	760 (7)	$\nu$ C-S
		764 (m)	-	753	-	$\nu$ C-S
661	-	670 (w)	669 (12)	673	670 (65)	$\gamma$ C-H
620 (vs)	619 (3)	619 (s)	622 (2)	619	618 (16)	$\gamma$ C-H
		473 (w)	471 (1)	478	477 (6)	$\delta$ SCN
-	-	464 (w)	-	473 sh	-	$\delta$ SCN
-	355 (7)	-	368 (3)	-	366 (21)	$\delta$ N-CH <sub>3</sub>
-	-	-	-	-	246 (32)	$\nu$ Zn-N(ring)
			-	-	214 (31)	$\nu$ Zn-N (SCN)
-	-	-	202 (19)	-	-	$\nu$ Cd-N (SCN)
-	-	-	142 (40)	-	-	$\nu$ Cd-N (ring)
-	-	-	87 (56)	-	82 (58)	$\rho$ SCN
-	-	-	65 (33)	-	-	$\tau$ CH <sub>3</sub>

**Table S4:** Steps for the thermal decomposition of complexes **1-4** and % of mass loss.

<b>Complex</b>	<b>Steps</b>	<b>Temperature range (°C)</b>	<b>Theoretical mass loss (%)</b>	<b>Observed mass loss (%)</b>
<b>1</b>	1	200-390	47.5	47.0
	2	500-750	28.9	29.0
	Total	-	76.4	76.0
<b>2</b>	1	250-375	47.5	48.0
	2	500-700	28.9	28.0
	Total	-	76.4	76.0
<b>3</b>	1	150-350	58.0	56.4
	2	500-750	19.0	23.6
	Total	-	77.0	80.0
<b>4</b>	1	200-390	42.0	43.0
	2	500-750	25.0	22.0
	Total	-	67.0	65.0