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 Santo¹, Hiram Pérez²*, Gustavo A. Echeverría³+, Oscar E. Piro³+, Rodrigo A. Iglesias⁴+, Raúl E. Carbonio⁴+, Aida Ben Altabef⁴+, Diego M. Gil¹⁺,*

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 $R^3_4(26)$ 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 [Zn(1-Melm)$_2$(SCN)$_2$] (1) at 5 °C/min in air.

Figure S6, ESI. TG and DTA curves for the thermal decomposition of the complex [Zn(2-Melm)$_2$(SCN)$_2$] (2) at 5 °C/min in air.
**Figure S7, ESI.** TG and DTA curves for the thermal decomposition of the complex [Cd(1-MelIm)_4(SCN)_2] (3) at 5 °C/min in air.

![TG and DTA curves for the thermal decomposition of the complex [Cd(1-MelIm)_4(SCN)_2] (3) at 5 °C/min in air.](image1.png)

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

![TG and DTA curves for the thermal decomposition of the complex [Cd(2-MelIm)_2(SCN)_2]_n (4) at 5 °C/min in air.](image2.png)
**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-MeIm, 2-MeIm 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 $C_{XY}$ | 1   | 2   | 3   | 4   | 5   | 6   | 7   |
|------------------|-----|-----|-----|-----|-----|-----|-----|
| 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 cm\(^{-1}\)) for 2-methylimidazole and its Cd(II) and Zn(II) thiocyanate complexes together with their tentative assignment of modes.

|                  | 2-methylimidazole | [Cd(2-MeIm)\(_2\)(SCN)]\(_2\) | [Zn(2-MeIm)\(_2\)(SCN)]\(_2\) | Assignment                        |
|------------------|--------------------|-------------------------------|-------------------------------|-----------------------------------|
| **FT-IR**        | **Raman**          | **FT-IR**                     | **Raman**                     |                                   |
| 3182 (s)         | -                  | 3224 (m)                      | -                             | v NH                              |
| 3137 (s)         | 3134 (52)          | 3147 (s)                      | 3147(18)                      | v CH                              |
| 2961 (s)         | 2960 (23)          | 2954 (vvw)                    | -                             | v CH                              |
| 2926 (s)         | 2925 (53)          | 2933 (vvw)                    | 2934 (29)                     | v CH                              |
|                  | -                  | 2119 (vs)                     | 2118 (67)                     | v CN                              |
|                  | -                  | 2076 (vs)                     | 2077 (100)                    | v CN                              |
| 1597 (s)         | -                  | 1566 (s)                      | -                             | v C-C + v C-N                      |
| 1479 (vvw)       | 1479 (100)         | 1495 (vw)                     | 1497 (49)                     | v C-C + v CH\(_3\)                |
| 1447 (s)         | -                  | 1428 (w)                      | -                             | v CH\(_3\) + v CH\(_3\)          |
| 1371 (w)         | -                  | 1352 (w)                      | 1351 (16)                     | v CH\(_3\) + v CCH                |
| 1303 (m)         | 1303 (4)           | 1280 (s)                      | -                             | v ring                            |
| 1155 (m)         | -                  | 1159 (w)                      | 1157 (m)                      | v CCH                             |
| 1117 (s)         | 1113 (79)          | 1098 (w)                      | 1140 (s)                      | v CH\(_3\) + v C-N (ring)         |
| 1048             | -                  | 1038 (w)                      | 1046 (w)                      | v CH\(_3\) + v CH\(_3\) + v C-C  |
| 995              | 993 (15)           | 1012 (w)                      | 1023 (vvw)                    | v CH\(_3\) + v CH\(_3\) + v C-N  |
| 945 (s)          | 937 (9)            | 943 (vvw)                     | 930 (w)                       | v CH\(_3\) + v CH\(_3\) + v CCH  |
| 916 (s)          | 916 (10)           | 901 (vvw)                     | 929 (13)                      | v CH\(_3\) + v C-N (ring)         |
|                  | -                  | 970 (w)                       | 1023 (vvw)                    | v CH\(_3\) + v CH\(_3\) + v C-N  |
|                  | -                  | 765 (vvw)                     | 747 (w)                       | v CH\(_3\) + v CH\(_3\) + v C-N  |
| 683 (s)          | 682 (39)           | 672 (m)                       | 674 (12)                      | v CH\(_3\) + v CH\(_3\) + v C-N  |
| 629              | 629 (2)            | 624 (vvw)                     | 622 (ww)                      | v CH\(_3\) + v CH\(_3\) + v C-N  |
|                  | -                  | 469 (w)                       | 478 (s)                       | v CH\(_3\) + v CH\(_3\) + v C-N  |
|                  | -                  | 451 (vvw)                     | 470 (m)                       | v CH\(_3\) + v CH\(_3\) + v C-N  |
|                  | -                  | 269 (25)                      | 283 (13)                      | v CH\(_3\) + v CH\(_3\) + v C-N  |
|                  | -                  | 269 (25)                      | 283 (13)                      | v CH\(_3\) + v CH\(_3\) + v C-N  |
|                  | -                  | 254 (9)                       | 254 (9)                       | v CH\(_3\) + v CH\(_3\) + v C-N  |
|                  | -                  | 212 (17)                      | 212 (17)                      | v CH\(_3\) + v CH\(_3\) + v C-N  |
|                  | -                  | 208 (25)                      | 208 (25)                      | v CH\(_3\) + v CH\(_3\) + v C-N  |
|                  | -                  | 185 (12)                      | 185 (12)                      | v CH\(_3\) + v CH\(_3\) + v C-N  |
|                  | -                  | 174 (44)                      | 174 (44)                      | v CH\(_3\) + v CH\(_3\) + v C-N  |
|                  | -                  | 145 (49)                      | 145 (49)                      | v CH\(_3\) + v CH\(_3\) + v C-N  |
|                  | -                  | 112 (94)                      | 112 (94)                      | v CH\(_3\) + v CH\(_3\) + v C-N  |
|                  | -                  | 107 (96)                      | 107 (96)                      | v CH\(_3\) + v CH\(_3\) + v C-N  |
|                  | -                  | 82 (99)                       | 82 (99)                       | v CH\(_3\) + v CH\(_3\) + v C-N  |
|                  | 75 (99)            | 64 (99)                       | 75 (99)                       | v CH\(_3\) + v CH\(_3\) + v C-N  |
Table S3: IR and Raman bands (in cm\(^{-1}\)) for 1-methylimidazole Zn(II) and Cd(II) thiocyanate complex together with their tentative assignment of modes.

| 1-Methylimidazole | \([\text{Cd(1-MeIm)}_4(\text{SCN})_2]\) | \([\text{Zn(1-MeIm)}_2(\text{SCN})_2]\) | Assignment |
|-------------------|--------------------------------|--------------------------------|------------|
| FT-IR             | Raman                        | FT-IR                          | Raman      | Assignment |
| -                 | 3134 (39)                     | 3145 (vw)                      | 3146 (17)  | \(\nu\) CH |
| 3127 (vw)         | -                             | 3125 (w)                       | 3127 (13)  | \(\nu\) CH |
| 3111 (vs)         | 3109 (35)                     | 3111 (m)                       | 3117 (8)   | \(\nu\) CH |
| 2983              | -                             | 2984 (vw)                      | -          | \(\nu\) CH₃ |
| 2952 (m)          | 2955 (36)                     | 2958 (s)                       | 2959 (10)  | \(\nu\) CH₃ |
| 2812 (w)          | 2816 (11)                     | -                              | 2815 (2)   | \(\nu\) CH₃ |
| -                 | -                             | 2083 (vs)                      | -          | \(\nu\) C·N |
| -                 | -                             | 2066 (s)                       | 2074 (100) | \(\nu\) C·N |
| 1669              | 1671 (vw)                     | -                              | -          | \(\nu\) C·N \(\delta\) CH₃ |
| 1619              | -                             | 1621 (vw)                      | -          | \(\nu\) C·C \(\delta\) CH₃ |
| 1522 (vs)         | 1519 (15)                     | 1534 (m)                       | 1533 (3)   | \(\delta\) CH₃ |
| -                 | -                             | 1516 (m)                       | 1518 (3)   | \(\delta\) CH₃ |
| 1422              | 1422 (9)                      | 1421 (vw)                      | 1419 (4)   | \(\nu\) C·N \(\delta\) CH₃ |
| -                 | -                             | 1413 (vw)                      | -          | \(\nu\) C·N \(\delta\) CH₃ |
| 1363 (m)          | -                             | 1369 (vs)                      | 1369 (9)   | \(\nu\) ring \(\delta\) CH₃ |
| 1329              | 1328 (20)                     | 1339 (vwv)                     | 1335 (18)  | \(\nu\) ring \(\delta\) CH₃ |
| 1288              | 1288 (21)                     | 1282 (m)                       | 1283 (5)   | \(\nu\) ring |
| 1237              | 1238 (9)                      | 1237 (s)                       | 1239 (2)   | \(\nu\) C·N \(\delta\) HCN |
| 1026 (m)          | 1032 (33)                     | 1027 (vw)                      | 1030 (2)   | \(\rho\) CH₃ |
| -                 | -                             | 1023 (vw)                      | -          | \(\rho\) CH₃ |
| 925 (vs)          | -                             | 937 (s)                        | 937 (4)    | \(\nu\) C·N \(\delta\) CNC |
| 836 (vs)          | -                             | 838 (s)                        | 833 (2)    | \(\gamma\) C·H |
| -                 | -                             | 769 (m)                        | -          | \(\nu\) C·S |
| -                 | -                             | 764 (m)                        | 768        | \(\nu\) C·S |
| 661               | -                             | 670 (w)                        | 669 (12)   | \(\gamma\) C·H |
| 620 (vs)          | 619 (3)                       | 619 (s)                        | 622 (2)    | \(\gamma\) C·H |
| -                 | -                             | 473 (w)                        | 471 (1)    | \(\delta\) SCN |
| -                 | -                             | 464 (w)                        | 473 sh     | \(\delta\) SCN |
| -                 | 355 (7)                       | -                              | 368 (3)    | \(\delta\) N·CH₃ |
| -                 | -                             | -                              | -          | \(\nu\) Zn-N (ring) |
| -                 | -                             | 202 (19)                       | -          | \(\nu\) Zn-N (SCN) |
| -                 | -                             | 142 (40)                       | -          | \(\nu\) Cd-N (SCN) |
| -                 | -                             | 87 (56)                        | -          | \(\rho\) SCN |
| -                 | -                             | 65 (33)                        | -          | \(\tau\) CH₃ |
Table S4: Steps for the thermal decomposition of complexes 1-4 and % of mass loss.

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