**Supplementary material**

**Cr(III) and Ni(II) complexes of isatin-hydrazone ligand: Preparation, characterization, DFT studies, biological activity, and ion-flotation separation of Ni(II)**

**Hany M. Youssef1,2\*, Yasir Kh. Abdulhamed2, T. A. Yousef 3,4, G. M. Abu El-Reash2**

1Department of Chemistry, College of Science and Humanities in Al-Kharj, Prince Sattam bin Abdulaziz University, Al-Kharj 11942, Saudi Arabia

2Department of Chemistry, Faculty of Science, Mansoura University, Mansoura 35516, Egypt

3Department of Chemistry, Science College, Imam Mohammad Ibn Saud Islamic University, (IMSIU), Riyadh, KSA, P.O. Box 90950, Riyadh 11623, Saudi Arabia

4Department of Toxic and Narcotic drug, Forensic Medicine, Mansoura Laboratory, Medicolegal organization, Ministry of Justice, Egypt

**Table 1S.** Selected bond lengths of H4MDI in using DFT-method from DMol3 calculations.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Bond** | **Length(Å)** | **Bond** | **Length(Å)** | **Bond** | **Length(Å)** |
| C(26)-C(27) | 1.417 | C(25)-C(26) | 1.422 | C(24)-C(25) | 1.422 |
| C(27)-C(23) | 1.423 | C(22)-C(24) | 1.411 | C(22)-C(23) | 1.443 |
| N(21)-C(22) | 1.392 | C(20)-O(28) | 1.264 | C(20)-N(21) | 1.417 |
| C(19)-C(23) | 1.452 | C(19)-C(20) | 1.47 | N(18)-C(19) | 1.353 |
| N(16)-N(18) | 1.374 | C(15)-O(17) | 1.263 | C(15)-N(16) | 1.41 |
| C(14)-C(15) | 1.522 | C(12)-C(14) | 1.51 | C(12)-O(13) | 1.28 |
| N(11)-C(12) | 1.396 | N(10)-N(11) | 1.358 | C(9)-N(10) | 1.357 |
| C(8)-O(29) | 1.353 | C(9)-C(8) | 1.449 | C(8)-N(7) | 1.354 |
| C(5)-C(9) | 1.46 | C(6)-C(5) | 1.422 | N(7)-C(4) | 1.382 |
| C(5)-C(4) | 1.461 | C(4)-C(3) | 1.417 | C(2)-C(3) | 1.415 |
| C(1)-C(6) | 1.425 | C(2)-C(1) | 1.425 |  |  |

**Table 2S.** Selected bond angles of H4MDI in using DFT-method from DMol3 calculations.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Angle** | **Degree (°)** | **Angle** | **Degree (°)** | **Angle** | **Degree (°)** |
| C(26)-C(25)-C(24) | 120.954 | C(26)-C(27)-C(23) | 118.468 | C(27)-C(26)-C(25) | 121.6 |
| C(27)-C(23)-C(19) | 133.619 | C(25)-C(24)-C(22) | 117.223 | C(27)-C(23)-C(22) | 119.094 |
| C(24)-C(22)-N(21) | 129.349 | C(22)-C(23)-C(19) | 107.222 | C(24)-C(22)-C(23) | 122.63 |
| O(28)-C(20)-N(21) | 122.69 | C(23)-C(22)-N(21) | 107.946 | C(22)-N(21)-C(20) | 111.484 |
| C(23)-C(19)-C(20) | 107.518 | O(28)-C(20)-C(19) | 131.426 | N(21)-C(20)-C(19) | 105.778 |
| C(19)-N(18)-N(16) | 117.396 | C(23)-C(19)-N(18) | 131.682 | C(20)-C(19)-N(18) | 120.497 |
| O(17)-C(15)-C(14) | 120.763 | N(18)-N(16)-C(15) | 123.496 | O(17)-C(15)-N(16) | 121.622 |
| C(14)-C(12)-O(13) | 125.537 | N(16)-C(15)-C(14) | 117.352 | C(15)-C(14)-C(12) | 119.108 |
| C(12)-N(11)-N(10) | 122.629 | C(14)-C(12)-N(11) | 118.568 | O(13)-C(12)-N(11) | 115.686 |
| N(10)-C(9)-C(5) | 135.286 | N(11)-N(10)-C(9) | 116.469 | N(10)-C(9)-C(8) | 120.693 |
| O(29)-C(8)-N(7) | 122.163 | C(8)-C(9)-C(5) | 104.002 | O(29)-C(8)-C(9) | 123.932 |
| C(5)-C(6)-C(1) | 119.131 | C(9)-C(8)-N(7) | 113.902 | C(8)-N(7)-C(4) | 105.468 |
| C(6)-C(5)-C(4) | 118.695 | C(9)-C(5)-C(6) | 136.809 | C(9)-C(5)-C(4) | 104.489 |
| C(5)-C(4)-C(3) | 121.46 | N(7)-C(4)-C(5) | 112.057 | N(7)-C(4)-C(3) | 126.481 |
| C(6)-C(1)-C(2) | 121.507 | C(4)-C(3)-C(2) | 118.814 | C(3)-C(2)-C(1) | 120.354 |

**Table 3S.** Selected bond lengths of [Cr2(H2MDI)(H2O)2Cl4] in using DFT-method from DMol3 calculations.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Bond** | **Length(Å)** | **Bond** | **Length(Å)** | **Bond** | **Length(Å)** |
| C(4)-C(5) | 1.453 | Cr(31)-Cl(37) | 2.575 | Cr(31)-Cl(36) | 2.479 |
| O(33)-Cr(31) | 2.267 | Cr(30)-Cl(35) | 2.423 | Cr(30)-Cl(34) | 2.522 |
| O(32)-Cr(30) | 2.349 | O(29)-Cr(30) | 2.349 | O(28)-Cr(31) | 2.357 |
| C(26)-C(27) | 1.43 | C(25)-C(26) | 1.43 | C(24)-C(25) | 1.428 |
| C(27)-C(23) | 1.427 | C(22)-C(24) | 1.417 | C(22)-C(23) | 1.451 |
| N(21)-C(22) | 1.402 | C(20)-O(28) | 1.291 | C(20)-N(21) | 1.408 |
| C(23)-C(19) | 1.443 | C(19)-C(20) | 1.45 | N(18)-Cr(31) | 2.125 |
| N(18)-C(19) | 1.364 | O(17)-Cr(31) | 2.194 | N(16)-N(18) | 1.349 |
| C(15)-O(17) | 1.311 | C(15)-N(16) | 1.376 | C(14)-C(15) | 1.52 |
| O(13)-Cr(30) | 2.199 | C(12)-C(14) | 1.513 | C(12)-O(13) | 1.314 |
| N(11)-C(12) | 1.374 | N(10)-Cr(30) | 2.158 | N(10)-N(11) | 1.347 |
| C(9)-N(10) | 1.369 | C(8)-O(29) | 1.295 | C(8)-C(9) | 1.455 |
| C(8)-N(7) | 1.404 | C(9)-C(5) | 1.44 | C(5)-C(6) | 1.424 |
| C(4)-N(7) | 1.401 | C(3)-C(4) | 1.416 | C(2)-C(3) | 1.423 |
| C(6)-C(1) | 1.425 | C(1)-C(2) | 1.425 |  |  |

**Table 4S.** Selected bond angles of [Cr2(H2MDI)(H2O)2Cl4] in using DFT-method from DMol3 calculations.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Angle** | **Degree (°)** | **Angle** | **Degree (°)** | **Angle** | **Degree (°)** |
| Cl(37)-Cr(31)-Cl(36) | 163.633 | Cl(37)-Cr(31)-O(33) | 80.414 | Cl(37)-Cr(31)-O(28) | 87.542 |
| Cl(37)-Cr(31)-N(18) | 99.586 | Cl(37)-Cr(31)-O(17) | 93.183 | Cl(36)-Cr(31)-O(33) | 83.38 |
| Cl(36)-Cr(31)-O(28) | 95.074 | Cl(36)-Cr(31)-N(18) | 96.737 | Cl(36)-Cr(31)-O(17) | 92.717 |
| O(33)-Cr(31)-O(28) | 107.104 | O(33)-Cr(31)-N(18) | 176.198 | O(33)-Cr(31)-O(17) | 103.172 |
| O(28)-Cr(31)-N(18) | 76.682 | O(28)-Cr(31)-O(17) | 149.393 | N(18)-Cr(31)-O(17) | 73.026 |
| Cl(35)-Cr(30)-Cl(34) | 88.083 | Cl(35)-Cr(30)-O(32) | 89.292 | Cl(35)-Cr(30)-O(29) | 105.971 |
| Cl(35)-Cr(30)-O(13) | 105.071 | Cl(35)-Cr(30)-N(10) | 176.693 | Cl(34)-Cr(30)-O(32) | 173.184 |
| Cl(34)-Cr(30)-O(29) | 93.978 | Cl(34)-Cr(30)-O(13) | 97.988 | Cl(34)-Cr(30)-N(10) | 91.698 |
| O(32)-Cr(30)-O(29) | 80.702 | O(32)-Cr(30)-O(13) | 88.768 | O(32)-Cr(30)-N(10) | 91.283 |
| O(29)-Cr(30)-O(13) | 146.996 | O(29)-Cr(30)-N(10) | 77.335 | O(13)-Cr(30)-N(10) | 71.69 |
| Cr(30)-O(29)-C(8) | 105.446 | Cr(31)-O(28)-C(20) | 105.864 | C(26)-C(27)-C(23) | 118.249 |
| C(27)-C(26)-C(25) | 121.099 | C(26)-C(25)-C(24) | 121.366 | C(25)-C(24)-C(22) | 117.414 |
| C(27)-C(23)-C(22) | 119.773 | C(27)-C(23)-C(19) | 134.08 | C(22)-C(23)-C(19) | 106.122 |
| C(24)-C(22)-C(23) | 122.045 | C(24)-C(22)-N(21) | 129.399 | C(23)-C(22)-N(21) | 108.522 |
| C(22)-N(21)-C(20) | 110.017 | O(28)-C(20)-N(21) | 127.024 | O(28)-C(20)-C(19) | 125.886 |
| N(21)-C(20)-C(19) | 106.97 | C(23)-C(19)-C(20) | 108.353 | C(23)-C(19)-N(18) | 136.495 |
| C(20)-C(19)-N(18) | 114.82 | Cr(31)-N(18)-C(19) | 116.553 | Cr(31)-N(18)-N(16) | 119.735 |
| C(19)-N(18)-N(16) | 122.355 | Cr(31)-O(17)-C(15) | 113.202 | N(18)-N(16)-C(15) | 111.598 |
| O(17)-C(15)-N(16) | 121.975 | O(17)-C(15)-C(14) | 120.596 | N(16)-C(15)-C(14) | 117.069 |
| C(15)-C(14)-C(12) | 111.08 | Cr(30)-O(13)-C(12) | 115.209 | C(14)-C(12)-O(13) | 121.759 |
| C(14)-C(12)-N(11) | 116.732 | O(13)-C(12)-N(11) | 121.058 | C(12)-N(11)-N(10) | 111.607 |
| Cr(30)-N(10)-N(11) | 120.428 | Cr(30)-N(10)-C(9) | 115.095 | N(11)-N(10)-C(9) | 122.575 |
| N(10)-C(9)-C(8) | 114.957 | N(10)-C(9)-C(5) | 136.789 | C(8)-C(9)-C(5) | 108.088 |
| O(29)-C(8)-C(9) | 127.029 | O(29)-C(8)-N(7) | 125.625 | C(9)-C(8)-N(7) | 107.013 |
| C(8)-N(7)-C(4) | 110.285 | C(5)-C(6)-C(1) | 118.749 | C(9)-C(5)-C(6) | 135.064 |
| C(9)-C(5)-C(4) | 106.387 | C(6)-C(5)-C(4) | 118.547 | N(7)-C(4)-C(5) | 108.22 |
| N(7)-C(4)-C(3) | 129.101 | C(5)-C(4)-C(3) | 122.679 | C(4)-C(3)-C(2) | 117.679 |
| C(3)-C(2)-C(1) | 120.524 | C(6)-C(1)-C(2) | 121.814 |  |  |

**Table 5S.** Selected bond lengths of [Ni2(MDI)(H2O)6].4H2O in using DFT-method from DMol3 calculations.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Bond** | **Length(Å)** | **Bond** | **Length(Å)** | **Bond** | **Length(Å)** |
| C(4)-C(5) | 1.464 | C(26)-C(27) | 1.424 | C(25)-C(26) | 1.429 |
| C(24)-C(25) | 1.426 | C(27)-C(23) | 1.427 | C(22)-C(24) | 1.422 |
| C(22)-C(23) | 1.466 | N(21)-C(22) | 1.384 | C(20)-O(28) | 1.299 |
| C(20)-N(21) | 1.388 | C(23)-C(19) | 1.44 | C(19)-C(20) | 1.47 |
| N(18)-C(19) | 1.385 | N(16)-N(18) | 1.384 | C(15)-O(17) | 1.315 |
| C(15)-N(16) | 1.37 | C(14)-C(15) | 1.524 | C(12)-C(14) | 1.518 |
| C(12)-O(13) | 1.305 | N(11)-C(12) | 1.375 | N(10)-N(11) | 1.346 |
| C(9)-N(10) | 1.359 | C(8)-O(29) | 1.301 | C(8)-C(9) | 1.466 |
| C(8)-N(7) | 1.382 | C(9)-C(5) | 1.436 | C(5)-C(6) | 1.423 |
| C(4)-N(7) | 1.386 | C(3)-C(4) | 1.422 | C(2)-C(3) | 1.426 |
| C(6)-C(1) | 1.427 | C(1)-C(2) | 1.433 | O(35)-Ni(31) | 2.275 |
| O(34)-Ni(31) | 2.387 | O(33)-Ni(31) | 2.416 | O(37)-Ni(30) | 2.476 |
| O(36)-Ni(30) | 2.435 | O(32)-Ni(30) | 2.224 | O(29)-Ni(30) | 2.358 |
| O(28)-Ni(31) | 2.39 | N(18)-Ni(31) | 2.107 | O(17)-Ni(31) | 2.238 |
| O(13)-Ni(30) | 2.264 | N(10)-Ni(30) | 2.057 |  |  |

**Table 6S.** Selected bond angles of [Ni2(MDI)(H2O)6].4H2O in using DFT-method from DMol3 calculations.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Angle** | **Degree (°)** | **Angle** | **Degree (°)** | **Angle** | **Degree (°)** |
| C(26)-C(27)-C(23) | 118.24 | C(27)-C(26)-C(25) | 121.523 | C(26)-C(25)-C(24) | 121.087 |
| C(25)-C(24)-C(22) | 118.261 | C(27)-C(23)-C(22) | 120.139 | C(27)-C(23)-C(19) | 135.594 |
| C(22)-C(23)-C(19) | 104.254 | C(24)-C(22)-C(23) | 120.749 | C(24)-C(22)-N(21) | 127.065 |
| C(23)-C(22)-N(21) | 112.173 | C(22)-N(21)-C(20) | 106.593 | O(28)-C(20)-N(21) | 126.705 |
| O(28)-C(20)-C(19) | 122.673 | N(21)-C(20)-C(19) | 110.35 | C(23)-C(19)-C(20) | 106.619 |
| C(23)-C(19)-N(18) | 134.078 | C(20)-C(19)-N(18) | 119.066 | C(19)-N(18)-N(16) | 116.8 |
| N(18)-N(16)-C(15) | 112.796 | O(17)-C(15)-N(16) | 123.276 | O(17)-C(15)-C(14) | 119.825 |
| N(16)-C(15)-C(14) | 116.547 | C(15)-C(14)-C(12) | 110.396 | C(14)-C(12)-O(13) | 119.091 |
| C(14)-C(12)-N(11) | 117.887 | O(13)-C(12)-N(11) | 122.956 | C(12)-N(11)-N(10) | 112.432 |
| N(11)-N(10)-C(9) | 120.983 | N(10)-C(9)-C(8) | 117.174 | N(10)-C(9)-C(5) | 136.627 |
| C(8)-C(9)-C(5) | 106.198 | O(29)-C(8)-C(9) | 121.917 | O(29)-C(8)-N(7) | 126.844 |
| C(9)-C(8)-N(7) | 111.192 | C(8)-N(7)-C(4) | 105.832 | C(5)-C(6)-C(1) | 117.876 |
| C(9)-C(5)-C(6) | 134.355 | C(9)-C(5)-C(4) | 104.306 | C(6)-C(5)-C(4) | 121.302 |
| N(7)-C(4)-C(5) | 112.434 | N(7)-C(4)-C(3) | 127.676 | C(5)-C(4)-C(3) | 119.872 |
| C(4)-C(3)-C(2) | 118.36 | C(3)-C(2)-C(1) | 121.543 | C(6)-C(1)-C(2) | 120.929 |
| O(35)-Ni(31)-O(34) | 97.739 | O(35)-Ni(31)-O(33) | 96.808 | O(35)-Ni(31)-O(28) | 88.636 |
| O(35)-Ni(31)-N(18) | 157.753 | O(35)-Ni(31)-O(17) | 92.649 | O(34)-Ni(31)-O(33) | 89.622 |
| O(34)-Ni(31)-O(28) | 77.995 | O(34)-Ni(31)-N(18) | 96.991 | O(34)-Ni(31)-O(17) | 168.506 |
| O(33)-Ni(31)-O(28) | 167.068 | O(33)-Ni(31)-N(18) | 99.872 | O(33)-Ni(31)-O(17) | 84.253 |
| O(28)-Ni(31)-N(18) | 78.237 | O(28)-Ni(31)-O(17) | 107.283 | N(18)-Ni(31)-O(17) | 74.592 |
| O(37)-Ni(30)-O(36) | 172.36 | O(37)-Ni(30)-O(32) | 88.903 | O(37)-Ni(30)-O(29) | 90.373 |
| O(37)-Ni(30)-O(13) | 85.808 | O(37)-Ni(30)-N(10) | 91.09 | O(36)-Ni(30)-O(32) | 83.458 |
| O(36)-Ni(30)-O(29) | 91.501 | O(36)-Ni(30)-O(13) | 96.047 | O(36)-Ni(30)-N(10) | 96.546 |
| O(32)-Ni(30)-O(29) | 103.214 | O(32)-Ni(30)-O(13) | 105.233 | O(32)-Ni(30)-N(10) | 179.136 |
| O(29)-Ni(30)-O(13) | 151.204 | O(29)-Ni(30)-N(10) | 77.65 | O(13)-Ni(30)-N(10) | 73.906 |
| Ni(30)-O(29)-C(8) | 106.377 | Ni(31)-O(28)-C(20) | 104.776 | Ni(31)-N(18)-C(19) | 112.479 |
| Ni(31)-N(18)-N(16) | 116.916 | Ni(31)-O(17)-C(15) | 110.036 | Ni(30)-O(13)-C(12) | 109.557 |
| Ni(30)-N(10)-N(11) | 120.834 | Ni(30)-N(10)-C(9) | 116.241 |  |  |



**Figure 1S.** Infrared spectra of H4MDI and its metal complexes.



**Figure 2S.** Electronic spectra of H4MDI and its metal complexes.



**Figure 3S.** TGA curves of (a) [Cr2(H2MDI)(H2O)2Cl4] and (b) [Ni2(MDI)(H2O)6].4H2O.