ELECTRONIC SUPPLEMENTARY INFORMATION

Zinc(II)-methimazole complexes: synthesis and reactivity

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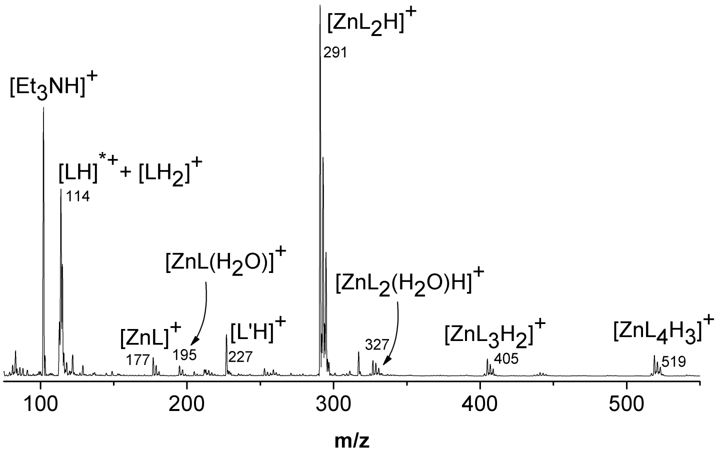


Fig. S1 Positive ion ESI-MS spectrum of [Zn(MeImS)$_2$], (3.45x10^{-5} M, CH$_3$CN); L = MeImS, L' = methimazole-disulfide ($C_8H_{10}N_4S_2$) (part of the released ligand from [ZnL$_2$H]$^+$, undergoes oxidation and formation of protonated methimazole-disulfide [($C_4H_5N_2S$)$_2$H]$^+$ (*m/z* 227). The signal at m/z 114 corresponds to a convoluted signals of the radical [MeImSH]$^{*+}$ (86%) and the [MeImHS+H$^+$]$^+$ (14%) species. In fact, the experimental pattern is due to a weighted combination of the isotopic pattern of the two molecules. The weights, namely the percentage in which each molecule is present, was obtained by multivariate regression analysis of the experimental data.

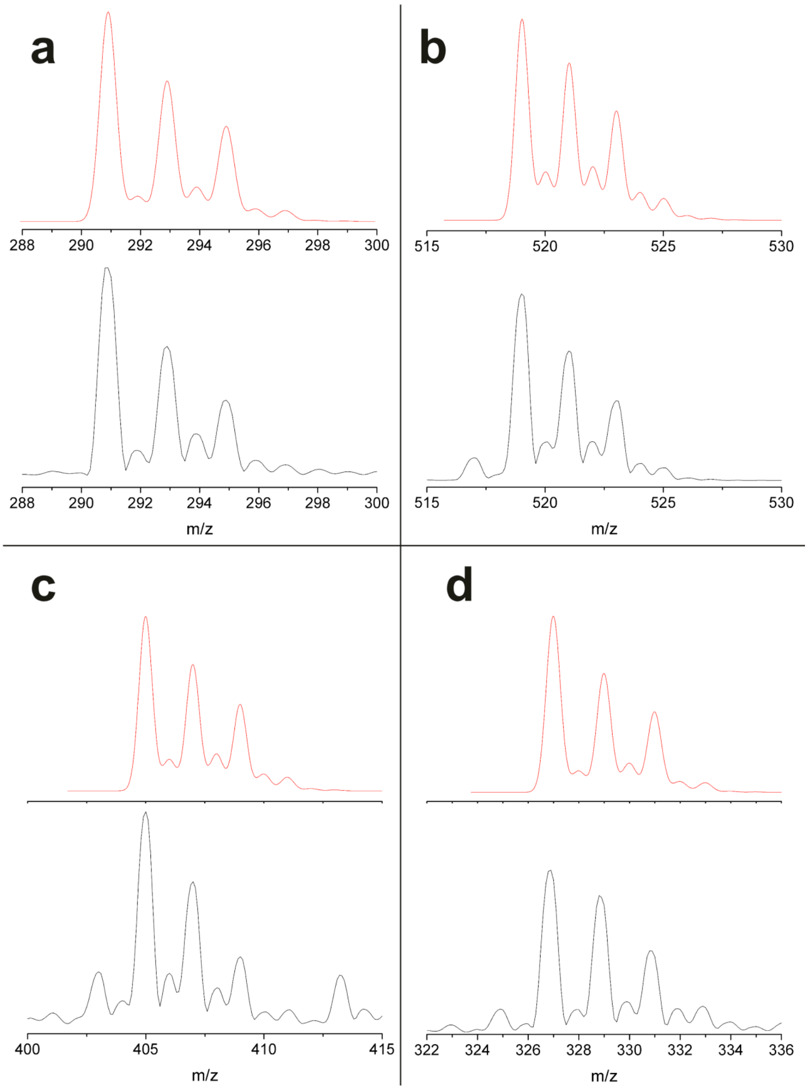


Fig. S2 Calculated (red) and experimental (black) isotopic patterns for $[ZnL_2H]^+$ (**a**), $[ZnL_4H_3]$ (**b**), $[ZnL_3H_2]^+$ (**c**), $[ZnL_2(H_2O)_2H_2]^+$ (**d**) ions, (L = MeImS).

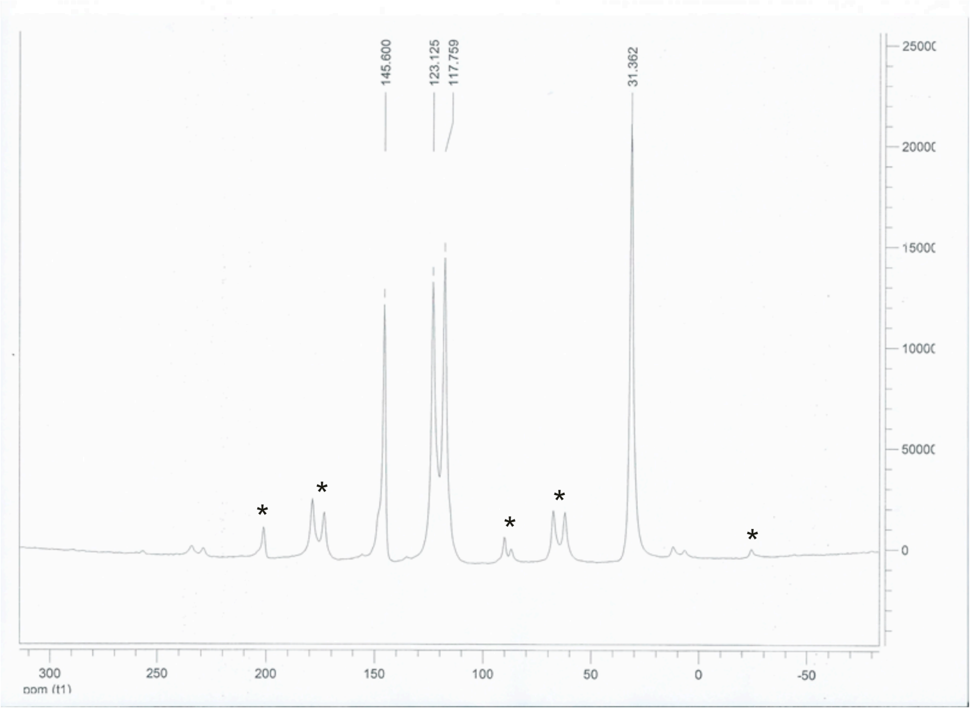


Fig. S3 MAS ^{13}C-NMR of complex [Zn(MeImS)$_2$].[1]

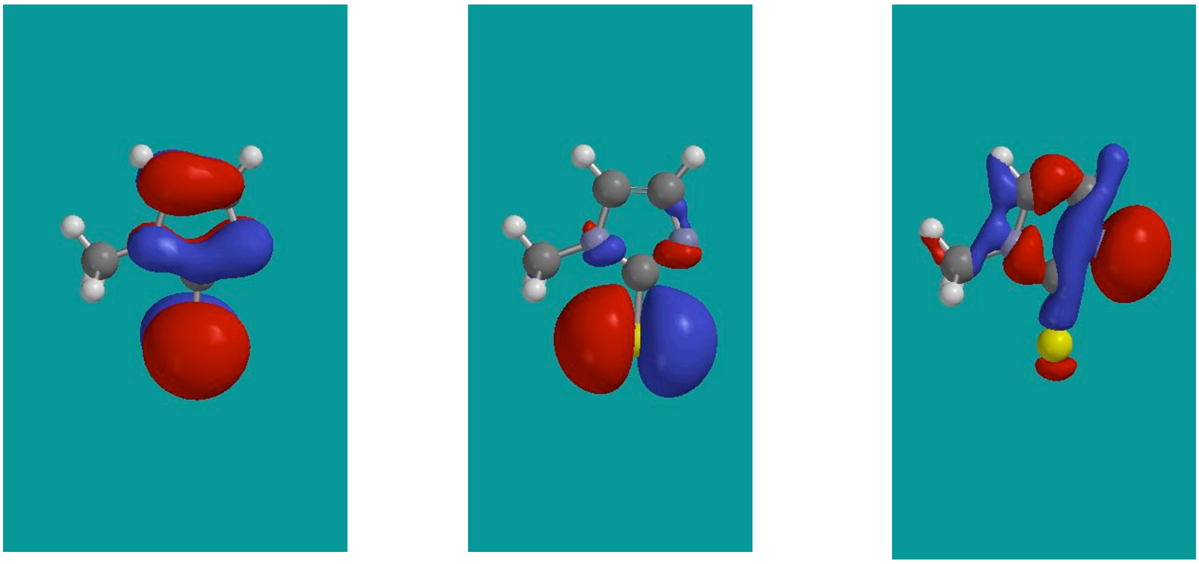


Fig. S4 Iso-surface drawings of Kohn–Sham HOMO (left), HOMO–1 (centre), and HOMO–3 (right) calculated for anion methimazole (MeImS).

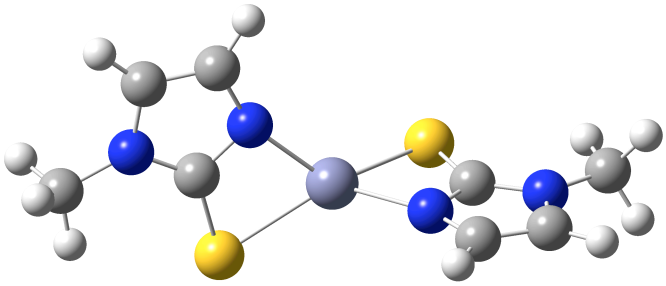
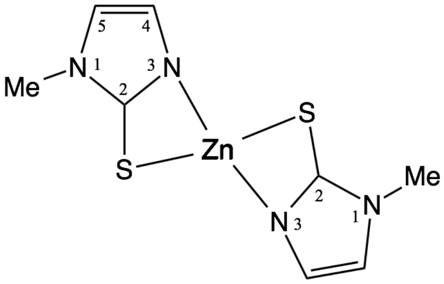


Fig. S5 Ball and stick representation of the structure of [Zn(MeImS)$_2$] optimised at DFT level.

Table S1 DFT calculated bond lengths (Å) and angles (°) for complex [Zn(MeImS)$_2$]; schematic structure and atom numbering of complex [Zn(MeImS)$_2$].

Bond		Angle	
N1-C2	1.358	N1-C2-S	130.98
N3-C2	1.345	N3-C2-S	119.34
N1-C5	1.390	N1-C2-N3	109.69
N2-C4	1.379	C5-N1-C2	107.58
C4-C5	1.364	C4-N3-C2	107.27
C2-S	1.746	N1-C5-C4	106.61
N1-C5	1.390	N3-C4-C5	108.90



Comments on the optimized structure of complex [Zn(MeImS)$_2$].

The zinc atom adopts a distorted tetrahedral geometry with both anions (*N,S*)-chelating. An examination of the metric parameters at the Zn centre provide evidence for a strain in the metallacycle formed under coordination [Zn-N(3)-C and N(3)-C-S = 94.68° and 119.34°, respectively; Zn-S-C = 72.69°]. Due to the S-C-N(3) narrow bite, the calculated S-Zn-N(3) angle

(73.24°) shows a great departure from ideal tetrahedral coordination geometry; however, a similar extent of distortion was also found in the (*N,S*)-chelating pyridine-2-thionate (py2S) complexes [MeHg(py2S)],[2a] [$Me_2Sn(py2S)_2$],[2b] and [$Me_2Tl(py2S)$],[2b] with thioamide angles of 58.5, 60.5, and 54.2°, respectively.

The calculated values of the bond lengths: *d*(Zn-N) 2.035 and *d*(Zn-S) 2.421 Å are consistent with those found in complex [$Zn_4O(MeImS)_6$],[3] which features MeImS acting as a (*N,S*)-bridging ligand that binds pairs of non-interacting zinc atoms [average *d*(Zn-N) 2.003(10), *d*(Zn-S) 2.337(3) Å]. Moreover, a comparison of the $Zn\text{-}N_{MeImS}$ bond distance with those reported for tetrahedral Zn-pyridine complexes[2c,d] (2.063-2.060 Å) shows that it is markedly shorter. Conversely, the calculated $Zn\text{-}S_{MeImS}$ bond distance is about 3% longer than the mean Zn-S bond distances reported for the neutral complexes listed in Table 1 [*d*($Zn\text{-}S_{thione}$) in the range 2.340–2.3581 Å], possibly due to the overestimation of the metal-sulphur bond lengths previously observed for the B3LYP functional.[4]

References and notes

1. MAS ^{13}C-NMR spectrum was recorded on a Varian 400 MHz spectrometer. The spectrum was calibrated such that the observed up field peak in the spectrum of adamantane is set to $\delta = 31.47$. The MAS rate was 5500 Hz. Acquisition was performed with standard MAS pulsing sequence using a 2.0 s delay between repetition, number of scans completed: 32000; $T = 23$ °C. Starred peaks are spinning side bands.
2. (*a*) H. Lynton, M. C. Sears, *Can. J. Chem.,* 1971, **49**, 3418–3424; (*b*) W. L. Steffen, G. J. Palenik, *Acta Crystallogr., Sect. B,* 1976, **32**, 298–300; (*c*) A. Castineiras, W. Hiller, J. Strahle, J. Bravo, J. Casa, M. Gayoso, J. Sordo, *J. Chem. Soc. Dalton Trans*., 1986, 1945–1948, (*d*) M. V. castano, A. Macias, A. Castineiras, A. S. Gonzales, E. G. Martinez, J. S. Casas, J. Sordo, W. Hiller, E. E. Castellano, *J. Chem. Soc. Dalton Trans*., 1990, 10011005.
3. R. Castro, J. A. Garcia-Vasquez, J. Romero, A. Sousa, Y. D. Chang, J. Zubieta, *Inorg. Chim. Acta*, 1995, **237**, 143–146.
4. M. Elstner, Q. Cui, P. Munih, E. Kaxiras, T. Frauenheim, M. Karplus, *J. Comp. Chem*., 2003, **24**, 565–581.