

Electronic Supplementary Information

Molecular evidence for sulfurization of molybdenum dithiocarbamates (MoDTC) by zinc dithiophosphates: a key process in their synergetic interactions and the enhanced preservation of MoDTC in formulated lubricants?

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Supplementary Material

Figure 1S: (a) Summed ion chromatogram m/z 725-732 obtained by HPLC-MS analysis of synthetic **2S-1d** (APPI, positive mode); (b) Mass spectrum of synthetic **2S-1d**

Figure 2S: (a) Summed ion chromatograms m/z 947-960; 1087-1101; 1227-1241 showing the distribution of synthetic mixture of MoDTC **2S-1a**; **2S-1b**; **2S-1c** obtained by HPLC-MS analysis (b) Summed mass spectra of the synthesized mixture of 2S-MoDTC **1a-1c** recorded between 7.1 and 9.1 min (HPLC-MS, APPI detection, positive mode).

Figure 3S: Oil samples collected over a period of 17-18 h during the oil ageing experiments involving 1 wt. % of 2S-MoDTC substrates **2S-1a-1c** in hydrocarbon base oils at 135 °C under (a) argon and (b) air bubbling.

Figure 4S: (a) Summed ion chromatograms m/z 931-944; 1071-1085; 1211-1225 showing the distribution of MoDTC **1S-1a**; **1S-1b**; **1S-1c** obtained by HPLC-MS analysis (b) Summed mass spectra of MoDTC complexes **1S-1a-1c** recorded between 7.1 and 9.1 min (HPLC-MS, APPI detection, positive mode) as oxidative degradation products of MoDTC complexes **2S-1a-1c** after 4 h under air condition at 135 °C.

Figure 5S: (a) Summed ion chromatograms (HPLC-MS, APPI, positive mode) m/z 896-916; 1036-1057; 1177-1198 showing the distribution of MoDTC **1O-1a**; **1O-1b**; **1O-1c** (b) Summed mass spectra between 7.5 and 12.5 min (HPLC-MS, APPI, positive mode) of MoDTC **1O-1a-1c** as oxidative degradation products of MoDTC **1a-1c** after 9 h under air bubbling at 135 °C.

Figure 6S: Evolution of the concentrations of MoDTC complexes **1O-1a-1c** as oxidative degradation products formed during the heating experiment involving 1 wt. % of MoDTC **1a-1c** under bubbling with (a) air and (b) NO₂ (2000 ppm) in air at 135 °C. IS: Internal standard. *Y-axis: arbitrary units. Error bars correspond to triplicate HPLC-MS analyses for each sample.

Figure 7S: Gas chromatogram (RIC; GC-MS, EI, 70 eV) of the ligands (analyzed as methylated derivatives) released after MeI treatment of di-isooctyl ZnDTP **2c**

Figure 1S: (a) Summed ion chromatogram m/z 725-732 obtained by HPLC-MS analysis of synthetic **2S-1d** (APPI, positive mode); (b) Mass spectrum of synthetic **2S-1d**

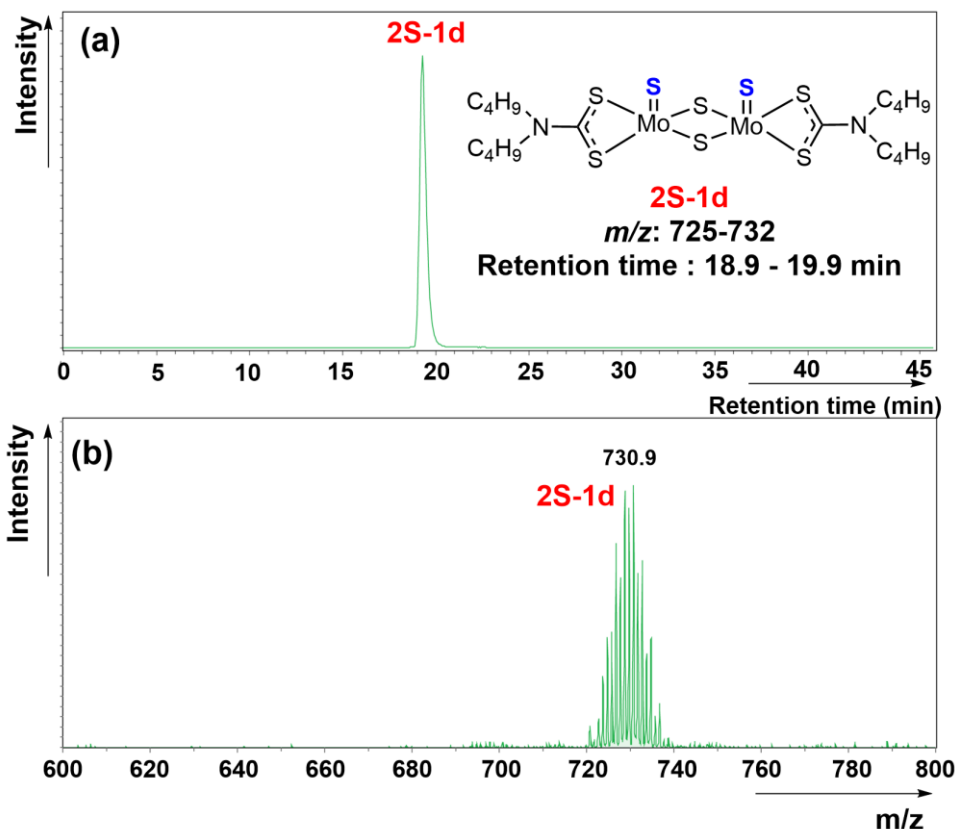


Figure 2S: (a) Summed ion chromatograms m/z 947-960; 1087-1101; 1227-1241 showing the distribution of synthetic mixture of MoDTC **2S-1a**; **2S-1b**; **2S-1c** obtained by HPLC-MS analysis (b) Summed mass spectra of the synthesized mixture of 2S-MoDTC **1a-1c** recorded between 7.1 and 9.1 min (HPLC-MS, APPI detection, positive mode).

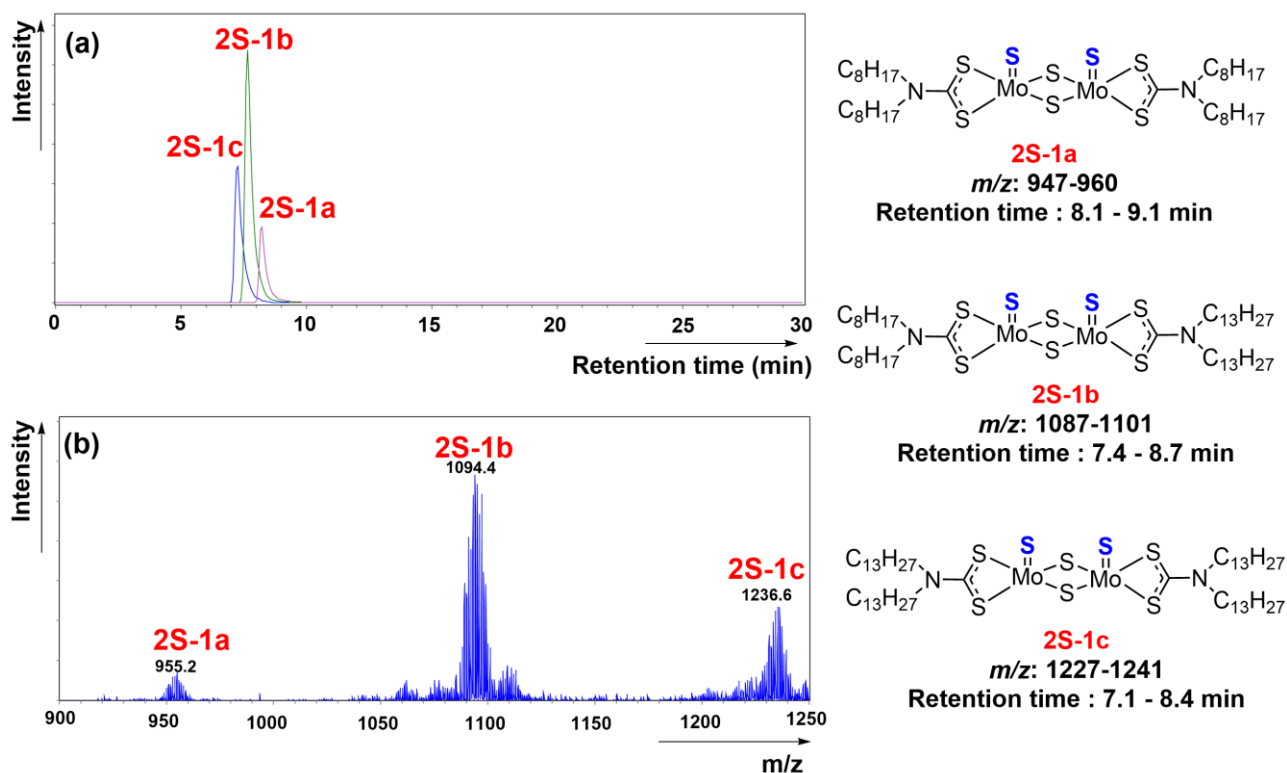


Figure 3S: Oil samples collected over a period of 17-18 h during the oil ageing experiments involving 1 wt. % of 2S-MoDTC substrates **2S-1a-1c** in hydrocarbon base oils at 135 °C under **(a)** argon and **(b)** air bubbling.

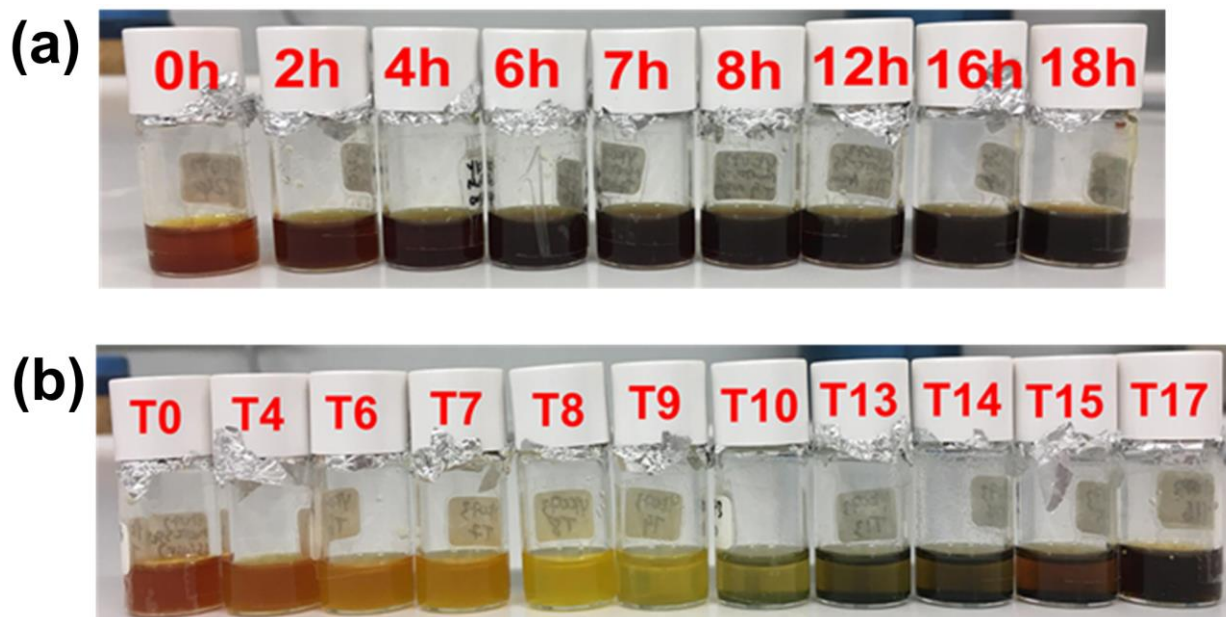


Figure 4S: **(a)** Summed ion chromatograms m/z 931-944; 1071-1085; 1211-1225 showing the distribution of MoDTC **1S-1a**; **1S-1b**; **1S-1c** obtained by HPLC-MS analysis **(b)** Summed mass spectra of MoDTC complexes **1S-1a-1c** recorded between 7.1 and 9.1 min (HPLC-MS, APPI detection, positive mode) as oxidative degradation products of MoDTC complexes **2S-1a-1c** after 4 h under air condition at 135 °C.

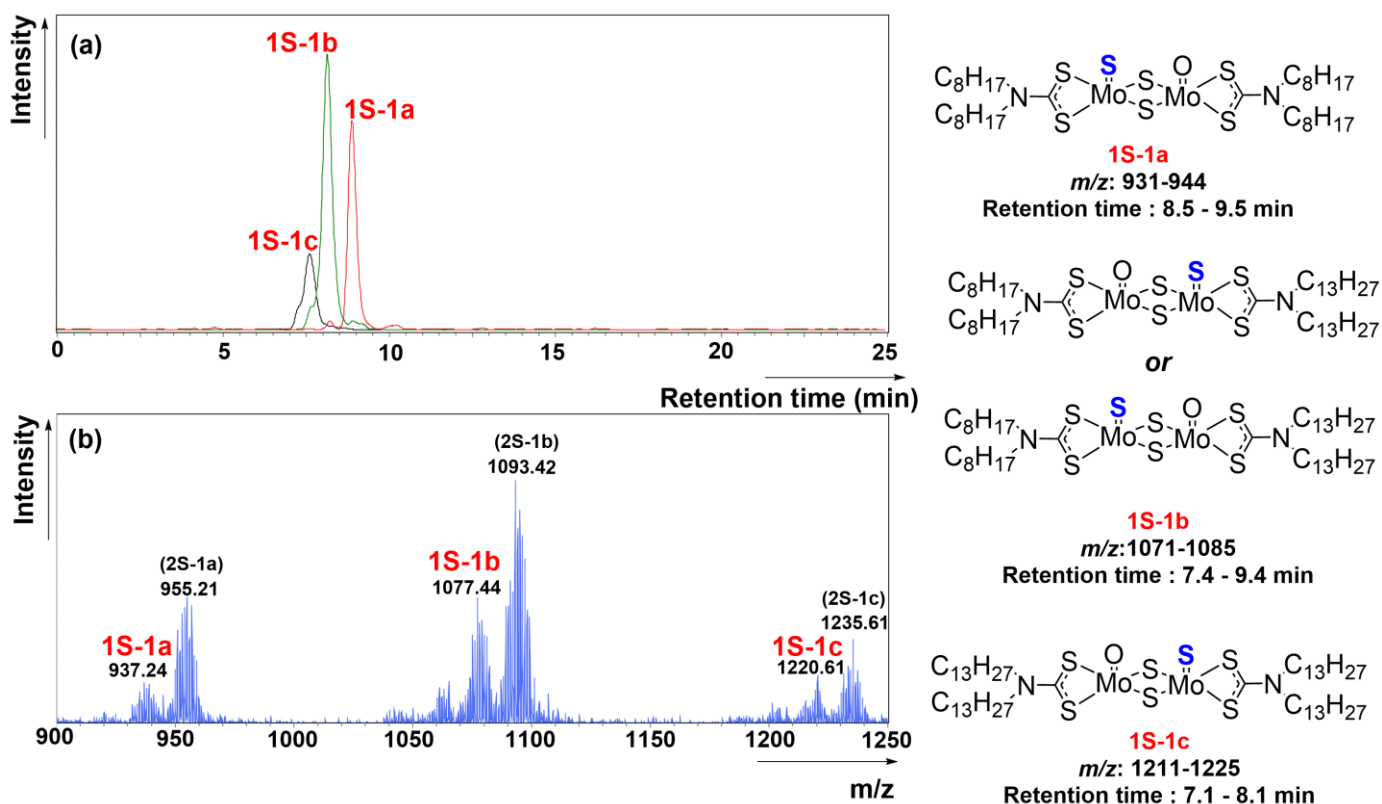


Figure 5S: (a) Summed ion chromatograms (HPLC-MS, APPI, positive mode) m/z 896-916; 1036-1057; 1177-1198 showing the distribution of MoDTC **10-1a**; **10-1b**; **10-1c** (b) Summed mass spectra between 7.5 and 12.5 min (HPLC-MS, APPI, positive mode) of MoDTC **10-1a-1c** as oxidative degradation products of MoDTC **1a-1c** after 9 h under air bubbling at 135 °C.

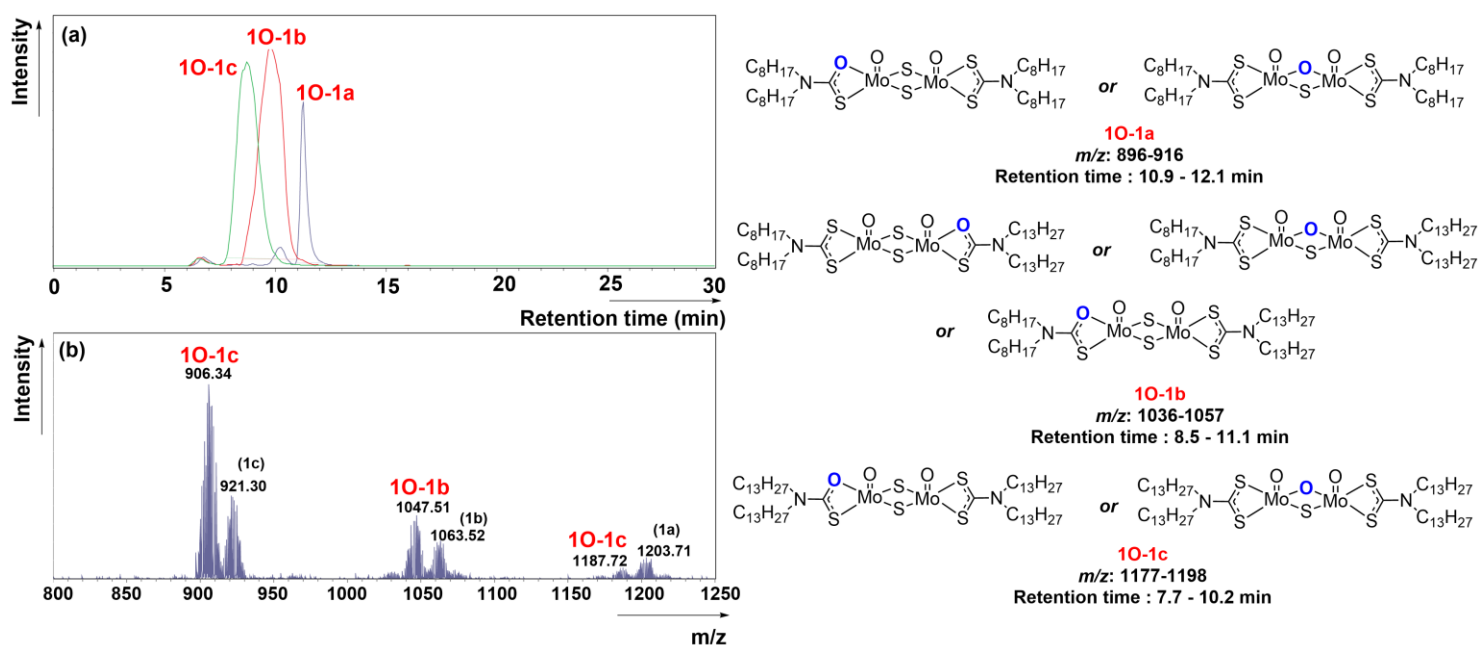


Figure 6S: Evolution of the concentrations of MoDTC complexes **10-1a-1c** as oxidative degradation products formed during the heating experiment involving 1 wt. % of MoDTC **1a-1c** under bubbling with (a) air and (b) NO₂ (2000 ppm) in air at 135 °C. IS: Internal standard. *Y-axis: arbitrary units. Error bars correspond to triplicate HPLC-MS analyses for each sample.

