The 18th International Electronic Conference on Synthetic Organic Chemistry
November 2014

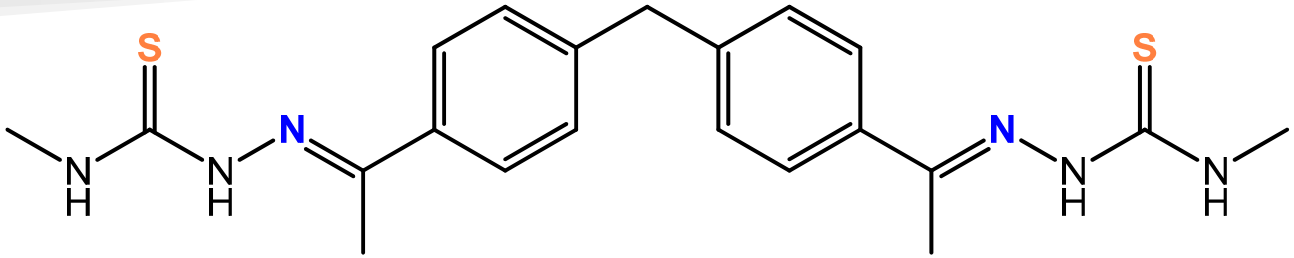
Synthesis and X-ray crystal structure of the thiosemicarbazone ligand *bis*(4-*N*-methyl-thiosemicarbazone)-4,4'-diacetylphenylmethane

Rocío Carballido, Rosa Pedrido, Ana M. González-Noya, Manuel R. Bermejo, Esther Gómez-Fórneas, Marcelino Maneiro

Department of Inorganic Chemistry
University of Santiago de Compostela
Spain

The interest of this ligand molecule…

Thiosemicarbazones represent one class of versatile multidonor ligands, which have been demonstrated to possess a wide biological activity



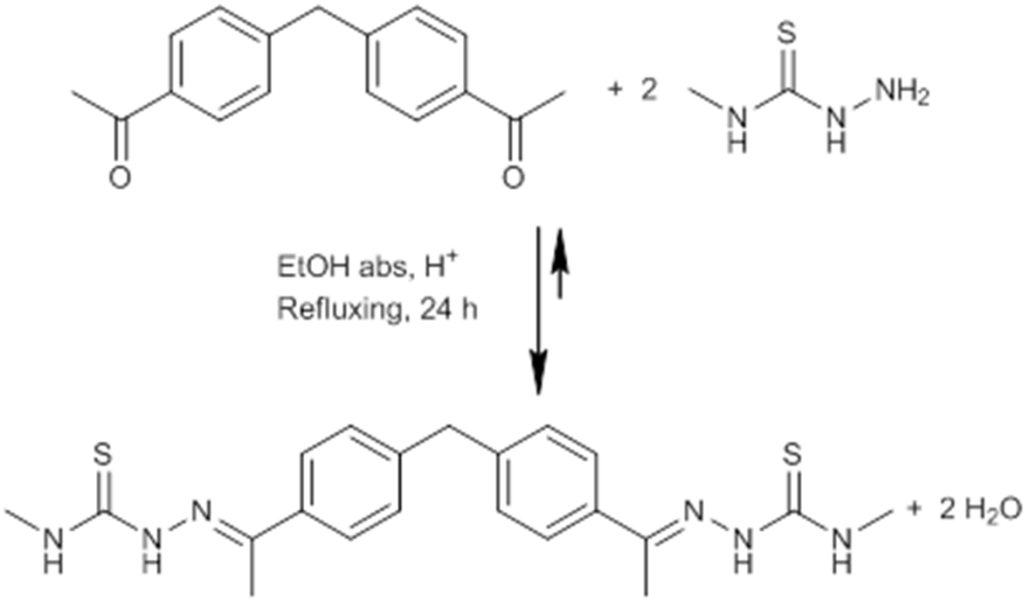
Thiosemicarbazone ligand **1**

Our aim…

Taking into account the versatility of tetradentate tiosemicarbazones and the supramolecular structures derived from ligands containing the spacer *bis*phenylmethane, in this work we try to combine both structural factors in order to obtain the ligand 1, potentially precursor of helical metal complexes

Synthesis of 1

Ligand **1** has been prepared by treatment of 4,4'-diacetylphenylmethane (1.00 g, 3.96 mmol) with 4-*N*-methyl-3-thiosemicarbazide (0.83 g, 7.92 mmol) in a 1:2 molar ratio, under standard reflux conditions during 24 hours in absolute ethanol, in presence of a catalytic quantity of p-toluenesulfonic acid (Scheme 1).

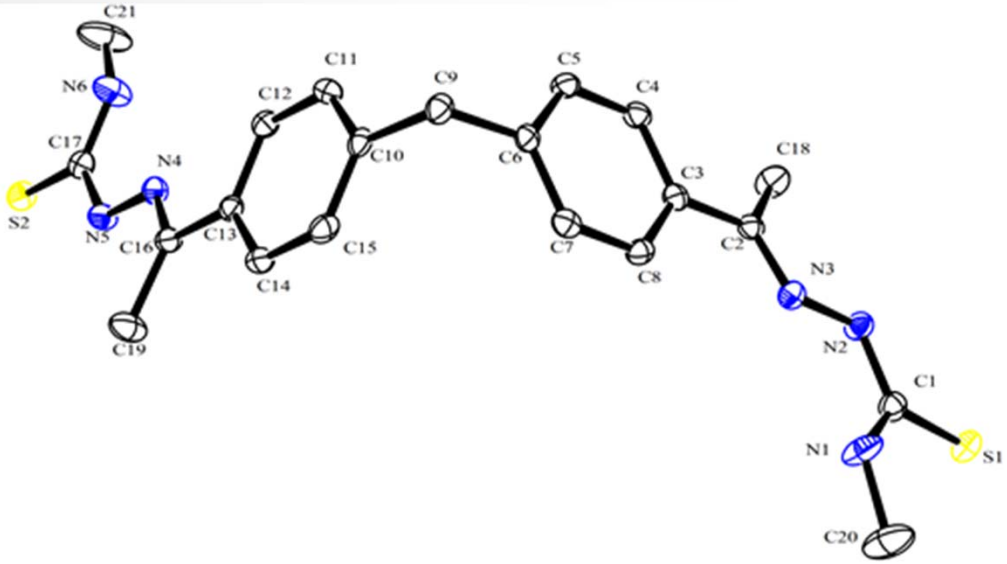


Scheme 1

Ligand **1**: M.p. 205 ºC. Yield 1.57 g (93%) Elemental analysis, Calc. for $C_{21}H_{26}N_6S_2$: C, 59.13; H, 19.70; N, 6.14; S, 15.03. Found: C, 59.11; H, 19.25; N, 5.80; S, 14.70 %. MS ESI$^-$ (m/z): 426.59 ([1]$^+$); IR (KBr, cm^{-1}): ν(N-H) 3365, 3284, 3225, ν(C=N + C-N) 1545, 1493, ν(C=S) 1105, 818. ^{1}H NMR (DMSO-d_6, ppm), δ (m, nH): 10.17 (s, 2H), 8.41 (s, 2H), 7.83 (d, 4H), 7.25 (d, 4H), 3.99 (s, 2H), 3.02 (d, 6H), 2.24 (s, 6H).

Our results...

X-ray diffraction studies



-the two thiosemicarbazone arms adopt an *E* conformation in relation to the two imine bonds

-this *E* conformation is mainly determined by the existence of both intra- and intermolecular hydrogen bonds

-considering the presence of a large and semi-flexible spacer and the optimal conformation taken by the free ligand, helical supramolecular metal assemblies are expected