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Graphical abstract

Nabil S. Youssef, Ahmed M.A. El-Seidy, Marco Schiavoni, Brunilde Castano, Fabio Ragaini, Emma Gallo, Alessandro Caselli

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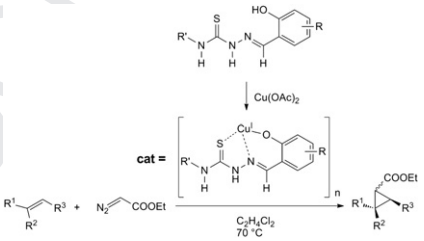
Thiosemicarbazone copper complexes as competent catalysts for olefin cyclopropanations

New copper complexes of several thiosemicarbazones have been prepared and characterized. Cyclopropanation reactions of several olefins by ethyldiazoacetate (EDA) in the presence of catalytic amounts of the complexes were examined. Cyclopropanes were obtained in high yields (up to 97%, TON up to 18,400) with moderate to excellent diastereoselectivities (up to >99%).



Highlights

► Neutral copper (I) complexes of thiosemicarbazones have been obtained in high yields. ► All complexes have been isolated and characterized. ► Copper complexes show outstanding catalytic activity in cyclopropanation reactions. ► TON up to 18,400 have been obtained. ► Diastereoselectivities up to 99% have been observed.

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Thiosemicarbazone copper complexes as competent catalysts for olefin cyclopropanations

Q4 Nabil S. Youssef [a], Ahmed M.A. El-Seidy [a], Marco Schiavoni [b], Brunilde Castano [b], Fabio Ragaini [b], Emma Gallo [b], Alessandro Caselli [b,*]

[a] Inorganic Chemistry Department, National Research Centre, P.O. 12622, Dokki, Giza, Egypt

Q1 [b] Dipartimento di Chimica Inorganica, Metallorganica e Analitica "Lamberto Malatesta", Università degli Studi di Milano and ISTM-CNR, Via Venezian 21, 20133 Milano, Italy

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ABSTRACT

New copper complexes of several thiosemicarbazones have been prepared and characterized. All complexes have been prepared by employing Cu (II) acetate hydrate, but analytical and spectroscopical data for the isolated complexes revealed that in most cases a reduction to copper (I) occurred. Cyclopropanation reactions of several olefins by ethyldiazoacetate (EDA) in the presence of catalytic amounts of the complexes were examined. The reported results showed that all complexes are competent catalysts for the cyclopropanation reaction of unactivated olefins. Cyclopropanes were obtained in high yields (up to 97%, TON up to 18,400) with moderate to excellent diastereoselectivities (up to >99%).

1. Introduction

Cyclopropane derivatives are an important family of chemical compounds that plays a prominent role in organic chemistry [1]. Naturally occurring and synthetic cyclopropanes are endowed with a rich spectrum of biological properties [2] and a large number of compounds carrying a cyclopropane ring have been synthesized and described in the literature. As a result, great efforts have been made to develop efficient stereoselective methods for the synthesis of cyclopropanes [3]. A particularly versatile method is the metal-catalysed cyclopropanation of olefins with diazo compounds, for which several efficient homogeneous catalysts have been developed [4]. Nevertheless, the synthesis of these compounds remains a considerable challenge, especially due to their interesting biological properties as well as their use as starting materials and intermediates in organic synthesis. Among transition metal catalysts for this reaction, copper complexes have attracted increasing interest in the last years [5–15], especially due to their high efficiency and to their lower cost when compared to other metal derivatives, such as catalysts based on rhodium [16–18] or ruthenium [19–21]. A variety of copper (II) and copper (I) sources are known to catalyse the cyclopropanation reaction although copper (I) rather than copper (II) was established as the active catalyst, where diazo compounds were found to reduce Cu (II) salts to Cu (I) [22]. Nevertheless Cu (I) complexes are challenging to synthesize and isolate due to the intrinsic instability of cuprous compounds [11]: under many conditions disproportionation of Cu (I) to Cu (0) and Cu (II) is thermodynamically favoured. We have recently reported that Schiff bases derived from the condensation of hydrazinecarbothioamide or phenyl thiosemicarbazone with 3-acetyl-2*H*-chromen-2-one are suitable ligands for the synthesis of copper (II) complexes very active as cyclopropanation catalysts [23,24]. The structure of the thiosemicarbazide moiety confers a good chelating capacity and the latter can be increased by employing a suitable aldehyde or ketone for the formation of the Schiff base possessing a further donor atom to render the ligand tridentate [25].

We report here that Schiff bases derived from the condensation reaction of hydrazinecarbothioamide with substituted salicylaldehydes are suitable ligands for copper and that the derived complexes are competent catalysts for the cyclopropanation of olefins with ethyldiazoacetate (EDA). Rarely metal complexes can give high selectivities in cyclopropanation reactions together with high turnover number (TON) [26]. In this work, different ligands have been synthesized and characterized, by changing the steric and electronic properties of the starting aldehyde employed in the condensation reaction.

Q2 * Corresponding author. Tel.: +39 02 50314372; fax: +39 02 50314405.
E-mail address: alessandro.caselli@unimi.it (A. Caselli).

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2. Experimental

2.1. Materials and methods

All the reagents employed for the preparation of the ligands and their complexes were of the highest grade available and used without further purification. Copper (II) acetate monohydrate was purchased from Aldrich and used as received. All aldehydes and thiosemicarbazide were of reagent grade and used as purchased. Thiosemicarbazones, **1**–**8** and **10**–**11**, were prepared according to a slightly modified procedure with respect to what reported in the literature [27]. 2-Hydroxybenzaldehyde *N*-ethylthiosemicarbazone (**9**) was purchased from Sigma–Aldrich. Unless otherwise stated, all catalytic tests were carried out under an atmosphere of purified dinitrogen using modified Schlenk techniques. Used solvents were dried and distilled before use by standard methods. Benzene, cyclohexene and 1-octene were distilled over sodium, styrene and α-methylstyrene were distilled over calcium hydride and stored under dinitrogen. NMR spectra were recorded on an Avance 300-DRX Bruker instrument, operating at 300 MHz for ^{1}H and at 75 MHz for ^{13}C. Chemical shifts (ppm) are reported relative to TMS. The ^{1}H NMR signals of compounds described in the following have been attributed by COSY and NOESY techniques. Assignments of the resonances in ^{13}C NMR were made using the APT pulse sequence, HSQC and HMQC techniques. Elemental analyses and mass spectra were recorded in the analytical laboratories of Milan University. GC analyses were performed on a Shimadzu 2010 FAST-GC equipped with an automatic sampler AOI-20i.

Some of the ligands and their metal complexes were analysed for C, H, N and M contents at the Microanalytical Laboratory, Faculty of Science, Cairo University, Egypt. IR spectra of the ligands and their metal complexes were measured using KBr discs with a Jasco FT/IR 300E Fourier transform infrared spectrophotometer and/or on a Varian Scimitar FTS 1000 spectrophotometer covering the range 400–4000 cm^{-1} and in the 500–100 cm^{-1} region using polyethylene-sandwiched Nujol mulls on a Perkin Elmer FT-IR 1650 spectrophotometer. The electronic spectra of the ligands and their complexes were obtained in DMSO solutions using an Agilent 8453 UV–visible recording spectrophotometer. Molar conductivities of the metal complexes in DMSO (10^{-3} M) were measured using a dip cell and a Bibby conductimeter MC1 at room temperature. The resistance measured in ohms and the molar conductivities were calculated according to the equation: $\Lambda = V \times K \times Mw/g \times \Omega$, where Λ, molar conductivity (Ω^{-1} cm^2 mol^{-1}); V, volume of the complex solution (ml); K, cell constant 0.92 cm^{-1}; Mw, molecular weight of the complex; g, weight of the complex; and Ω, resistance measured in ohms. Magnetic moments at 298 K were determined using the Gouy method with $Hg[Co(SCN)_4]$ as calibrant [28]. XPS analyses were carried out using an M-probe apparatus (Surface Science Instruments).

2.2. Synthesis of the ligands

2.2.1. Typical procedure for the synthesis of the ligands

Thiosemicarbazide (202.2 mg, 2.22 mmol) was added to a hot (75 °C) solution of salicylaldehyde (271.3 mg, 2.22 mmol) in ethanol (20 ml). The reaction mixture was refluxed for 2.5 h. The reaction mixture was then concentrated to ca. 10 ml. The precipitated white product was filtered off, washed with water, methanol, recrystallized from ethanol and dried under vacuum (412.7 mg, 95%). Analytical and spectroscopical data for this compound are in agreement with those reported in the literature [29,30]. For the IR spectrum see Lobana et al. [31]. **1** (H_2L^1): ^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 11.33 (s, 1H, N*H*), 9.84 (s, 1H, O*H*), 8.34 (s, 1H, *H*(7)), 8.07 (br s, 1H, NH_2), 7.90 (br s, 1H, NH_2), 7.87 (d, J = 7.5 Hz, 1H, *H*(3)), 7.18 (pst, J = 7.5 Hz, 1H, *H*(4)), 6.83 (d, J = 7.5 Hz, 1H, *H*(6)), 6.79 (pst, J = 7.5 Hz, 1H, *H*(5)). MS (EI): m/z = 195 (M$^+$). Anal. Calcd. for $C_8H_9N_3OS$ (195.24 g/mol): C, 49.21; H, 4.65; N, 21.52. Found: C, 49.64; H, 4.55; N, 21.51. IR (KBr, ν/cm^{-1}): 3441m (ν_{OH}), 3318s–2987s (ν_{as} and ν_{sNH2}), 3172s (ν_{OH}), 1616s (δ_{NH2}), 1603s ($\nu_{C=N}$), 1539s, 1265s (ν_{CO}), 1061m ($\nu_{C=S}$), 829m (ν_{sCS}), 751s. UV/vis (10^{-5} M, DMSO (nm)): λ = 276, 340.

2 (H_2L^2): in this case, in order to separate any trace of starting thiosemicarbazide, a further purification by column chromatography was needed (eluant *n*-hexane:ethyl acetate = 7/3) (yield 80%). ^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 11.33 (s, 1H, N*H*), 9.84 (s, 1H, O*H*), 8.26 (s, 1H, *H*(7)), 8.02 (br s, 2H, NH_2), 7.29 (d, ^{4}J = 2.3 Hz, 1H, *H*(4)), 7.16 (d, ^{4}J = 2.3 Hz, 1H, *H*(6)), 1.40 (s, 9H, CH_3), 1.27 (s, 9H, CH_3). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.17 (s, 1H, N*H*), 9.93 (s, 1H, O*H*), 8.13 (s, 1H, *H*(7)), 7.44 (s, 1H, *H*(4)), 7.08 (s, 1H, *H*(6)), 6.57 (br s, 2H, NH_2), 1.45 (s, 9H, CH_3), 1.32 (s, 9H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 177.9 (C_8), 155.1 (C_2), 150.4 (C_7), 142.4 (C_q), 137.2 (C_q), 128.3 (C_4), 127.0 (C_6), 116.3 (C_q), 35.5 (C_q), 34.5 (C_q), 31.8 (*C*H$_3$), 29.8(*C*H$_3$). MS (EI): m/z = 307 (M$^+$). Anal. Calcd. for $C_{16}H_{25}N_3OS$ (307.45 g/mol): C, 62.50; H, 8.20; N, 13.67. Found: C, 62.38; H, 8.06; N, 13.60. IR (KBr, ν/cm^{-1}): 3452m (ν_{OH}), 3274–2961s (ν_{as} and ν_{sNH2}), 3166s (ν_{NH}), 1715s (δ_{NH2}), 1606s ($\nu_{C=N}$), 1579m, 1538s, 1290m, 1265m (ν_{CO}), 1108m, 1067w ($\nu_{C=S}$), 826m (ν_{sCS}), 769m. UV/vis (10^{-5} M, DMSO (nm)): λ = 274, 340.

3 (H_2L^3): (89%) ^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 11.36 (s, 1H, N*H*), 9.19 (s, 1H, O*H*), 8.39 (s, 1H, H^7), 8.05 (s, 1H, NH_2), 7.85 (s, 1H, NH_2), 7.51 (d, 1H, ^{3}J = 7.5 Hz, H^6), 6.96 (dd, 1H, ^{3}J = 7.5 Hz, ^{4}J = 1.3 Hz, H^4), 6.77 (pst, 1H, ^{3}J = 7.5 Hz, H^5), 3.80 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, DMSO-d$_6$): δ = 178.6 (C_8), 148.7 (C_2), 140.7 (C_3), 140.4 (C_7), 121.6 (C_1), 119.9 (C_6), 119.0 (C_5), 113.7 (C_4), 56.8 (*C*H$_3$). MS (EI): m/z = 225 (M$^+$). Anal. Calcd. for $C_9H_{11}N_3O_2S$ (225.27 g/mol): C, 47.99; H, 4.92; N, 18.65. Found: C, 47.93; H, 5.02; N, 18.40. IR (KBr, ν/cm^{-1}): 3461s (ν_{OH}), 3343–2975m (ν_{as} and ν_{sNH2}), 3167m (ν_{NH}), 1621m (δ_{NH2}), 1598s ($\nu_{C=N}$), 1588m, 1536s, 1281m, 1263s (ν_{CO}), 1059m ($\nu_{C=S}$), 822m (ν_{sCS}), 778m. UV/vis (10^{-5} M, DMSO (nm)): λ = 323, 390.

4 (H_2L^4): (85%) ^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 11.04 (s, 1H, N*H*), 9.52 (s, 1H, O*H*), 8.18 (s, 1H, H^7), 7.81 (s, 1H, NH_2), 7.64 (s, 1H, NH_2), 7,50 (d, 1H, ^{3}J = 8.8 Hz, H^6), 6.20 (dd, 1H, ^{3}J = 8.8 Hz, ^{4}J = 2.2 Hz, H^5), 6.08 (d, 1H, ^{4}J = 2.2 Hz, H^3), 3.30 (q, 4H, ^{3}J = 6.9 Hz, N(CH_2CH$_3$)$_2$), 1.09 (t, 6H, ^{3}J = 6.9 Hz, N(CH$_2$CH_3)$_2$). ^{13}C NMR (75 MHz, DMSO-d$_6$): δ = 177.3 (C_8), 159.0 (C_2), 151.0 (C_4), 143.3 (C_7), 129.9 (C_6), 108.2 (C_1), 104.8 (C_5), 98.2 (C_3), 44.7 (*C*H$_2$), 13.4 (*C*H$_3$). MS (EI): m/z = 266 (M$^+$). Anal. Calcd. for $C_{12}H_{18}N_4OS$ (266.36 g/mol): C, 54.11; H, 6.81; N, 21.03. Found: C, 54.52; H, 6.79; N, 21.20. IR (KBr, ν/cm^{-1}): 3409s (ν_{OH}), 3302–2960m (ν_{as} and ν_{sNH2}), 3175m (ν_{NH}), 1630s (δ_{NH2}), 1610s ($\nu_{C=N}$), 1590s, 1553s, 1286m, 1245s (ν_{CO}), 1058m ($\nu_{C=S}$), 821m (ν_{sCS}), 787w. UV/vis (10^{-5} M, DMSO (nm)): λ = 273, 364.

5 (H_2L^5): (90%) ^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 11.52 (s, 1H, N*H*), 10.06 (s, 1H, O*H*), 8.33 (s, 1H, *H*(7)), 8.22 (br s, 2H, NH_2), 8.06 (d, ^{4}J = 2.6 Hz, 1H, *H*(4)), 7.52 (d, ^{4}J = 2.6 Hz, 1H, *H*(6)). ^{13}C NMR (75 MHz, DMSO-d$_6$): δ = 179.0 (C_8), 151.4 (C_2), 138.5 (C_7), 130.5 (C_4), 126.0 (C_q), 125.1 (C_6), 125.0 (C_q), 123.5 (C_q). MS (EI): m/z = 264 (M$^+$). Anal. Calcd. for $C_8H_7Cl_2N_3OS$ (263.13 g/mol): C, 36.38; H, 2.67; N, 15.91. Found: C, 36.54; H, 2.66; N, 15.75. IR (KBr, ν/cm^{-1}): 3464s (ν_{OH}), 3347s (ν_{asNH2}), 3154m (ν_{NH}), 1612s ($\nu_{C=N}$), 1153s, 1099m ($\nu_{C=S}$), 817m (ν_{sCS}). UV/vis (10^{-5} M, DMSO (nm)): λ = 275, 346.

6 (H_2L^6): (50%) ^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 11.50 (s, 1H, N*H*), 10.04 (br s, 1H, O*H*), 8.29 (s, 1H, *H*(7)), 8.20 (br s, 2H, NH_2), 8.11 (br s, 1H, *H*(4)), 7.74 (d, ^{4}J = 2.3 Hz, 1H, *H*(6)). ^{13}C NMR (75 MHz, DMSO-d$_6$): δ = 178.9 (C_8), 152.8 (C_2), 139.3 (C_7), 136.0 (C_4), 129.9 (C_6), 126.0 (C_q), 113.8 (C_q), 112.9 (C_q). MS (EI): m/z = 353 (M$^+$). Anal. Calcd. for $C_8H_7Br_2N_3OS$ (353.03 g/mol): C, 27.22; H, 2.00; N, 11.90. Found: C, 23.34; H, 2.01; N, 11.91. IR (KBr, ν/cm^{-1}): 3468s (ν_{OH}),

3357s–3015m (ν_{as} and ν_{sNH2}), 3155m (ν_{NH}), 1611s ($\nu_{C=N}$), 1542s, 1535s, 1288s, 1265m (ν_{CO}), 1138s, 1094m ($\nu_{C=S}$), 859w, 815w, 714w. UV/vis (10^{-5} M, DMSO (nm)): λ = 321, 346, 413.

7 (H_2L^7): (84%) ^{1}H NMR (300 MHz, DMSO-d_6): δ = 11.40 (s, 1H, N*H*), 10.21 (s, 1H, O*H*), 8.29 (s, 1H, *H*(7)), 8.20 (d, ^4J = 2.6 Hz, 1H, *H*(6)), 8.14 (br s, 2H, NH_2), 7.33 (dd, ^3J = 8.7 Hz, ^4J = 2.6 Hz, 1H, *H*(4)), 6.82 (d, ^3J = 8.7 Hz, 1H, *H*(3)). ^{13}C NMR (75 MHz, DMSO-d_6): δ = 179.0 (C_8), 156.4 (C_2), 138.1 (C_7), 134.0 (C_4), 129.2 (C_6), 123.7 (C_1), 119.0 (C_3), 112.0 (C_5). MS (EI): m/z = 273 (M^+). Anal. Calcd. for $C_8H_8BrN_3OS$ (274.14 g/mol): C, 35.05; H, 2.94; N, 15.33. Found: C, 35.06; H, 2.59; N, 15.01. IR (KBr, ν/cm^{-1}): 3456s (ν_{OH}), 3250s–2997m (ν_{as} and ν_{sNH2}), 3162s (ν_{NH}), 1655s (δ_{NH2}), 1610s ($\nu_{C=N}$), 1601s, 1545s, 1294m, 1264m (ν_{CO}), 1064 ($\nu_{C=S}$), 819m (ν_{sCS}). UV/vis (10^{-5} M, DMSO (nm)): λ = 270, 347, 400.

8 (H_2L^8): (31%). ^{1}H NMR (300 MHz, DMSO-d_6): δ = 11.51 (s, 1H, N*H*), 10.05 (s, 1H, O*H*), 8.34 (s, 1H, *H*(7)), 8.19 (br s, 2H, NH_2), 7.78 (d, ^3J = 9.5 Hz, 1H, *H*(4)), 7.22 (dt, ^3J = 9.5 Hz, ^4J = 2.9 Hz, 1H, *H*(6)). ^{19}F NMR (282 MHz, DMSO-d_6): δ = −122.0 (pst, ^3J = 9.5 Hz, 1F, *F*(5)), −131.1 (d, ^3J = 9.6 Hz, 1F, *F*(3)). MS (EI): m/z = 231 (M^+). Anal. Calcd. for $C_8H_7F_2N_3OS$ (231.22 g/mol): C, 41.56; H, 3.05; N, 18.17. Found: C, 41.54; H, 3.14; N, 18.02. IR (KBr, ν/cm^{-1}): 3430s, 3324m, 3289s, 3176s, 1618s, 1588m, 1541s, 1485s, 1459s, 1378s, 1298m, 1226m, 1104m, 1011m, 987m, 832m.

10 (H_2L^{10}): (66%). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.75 (s, 1H, N*H*), 10.04 (s, 1H, N*H*Ph), 9.97 (br s, 1H, O*H*), 8.50 (s, 1H, *H*(7)), 8.08 (d, J = 7.6 Hz, 1H, *H*(6)), 7.58 (d, J = 7.8 Hz, 2H, PhH_{ortho}), 7.37 (pst, J = 7.8 Hz, 2H, PhH_{meta}), 7.24 (pst, J = 7.6 Hz, 1H, *H*(4)), 7.20 (pst, J = 7.8 Hz, 1H, PhH_{para}), 6.89 (d, J = 7.6 Hz, 1H, *H*(3)), 6.84 (pst, J = 7.6 Hz, 1H, *H*(5)). ^{13}C NMR (75 MHz, DMSO-d_6): δ = 176.6 (C_8), 157.5 (C_2), 141.0 (C_7), 140.0 (C_{Ph}), 132.2 (C_4), 128.9 ($C_{Ph\text{-}meta}$), 127.9 (C_6), 126.5 ($C_{Ph\text{-}ortho}$), 126.0 ($C_{Ph\text{-}para}$), 121.1 (C_1), 120.1 (C_3), 116.9 (C_5). MS (EI): m/z = 271 (M^+). Anal. Calcd. for $C_{14}H_{13}N_3OS$ (271.34 g/mol): C, 61.97; H, 4.83; N, 15.49. Found: C, 61.40; H, 5.15; N, 15.29. IR (KBr, ν/cm^{-1}): 3380m, 3150s, 2992m, 1621m, 1604m, 1593m, 1539s, 1509s, 1271s, 1260m, 1208s, 1151m, 1080m, 1033m, 794w, 755m, 742m, 692m. UV/vis (10^{-5} M, DMSO (nm)): λ = 283, 344.

11 (H_2L^{11}): (79%). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.66 (s, 1H, N*H*), 10.15 (s, 1H, N*H*Ph), 9.98 (br s, 1H, O*H*), 8.38 (s, 1H, *H*(7)), 7.50 (d, J = 7.5 Hz, 2H, Ph*H*), 7.38 (pst, J = 7.5 Hz, 2H, Ph*H*), 7.32 (d, J = 2.1 Hz, 1H, *H*(4)), 7.20 (m, 2H, *H*(6) and Ph*H*), 1.41 (s, 9H, CH_3), 1.29 (s, 9H, CH_3). ^{13}C NMR (75 MHz, DMSO-d_6): δ = 177.1 (C_8), 154.1 (C_2), 149.1 (C_7), 141.8 (C_{Ph}), 140.2 (C_5), 136.9(C_3), 129.1 ($C_{Ph\text{-}meta}$), 126.7 ($C_{Ph\text{-}para}$), 126.6 (C_4), 126.4 ($C_{Ph\text{-}ortho}$)126.1 (C_6), 118.7 (C_1), 35.5 (C_{CMe3}), 34.8 (C_{CMe3}), 32.1 (C_{CH3}), 30.2 (C_{CH3}). MS (EI): m/z = 383 (M^+). Anal. Calcd. for $C_{22}H_{29}N_3OS$ (383.55 g/mol): C, 68.89; H, 7.62; N, 10.96. Found: C, 68.58; H, 8.00; N, 10.91. IR (KBr, ν/cm^{-1}): 3325s, 3142s, 2956s, 1560s, 1545s, 1272s, 1210s, 1087m, 803w, 747m. UV/vis (10^{-5} M, DMSO (nm)): λ = 283, 345.

2.3. Synthesis of the complexes

2.3.1. Typical procedure for the synthesis of the copper complexes

A solution of copper (II) acetate monohydrate (222 mg, 1.11 mmol) in the minimum required amount of methanol was added dropwise to a hot (75 °C) solution of H_2L^1, **1** (214 mg, 1.10 mmol) in ethanol (50 ml) (75 °C). The reaction mixture was then refluxed for 2.5 h. The brown precipitate so formed was recovered by filtration and was recrystallized from refluxing ethanol. The collected solid was suspended in cold ethanol (3 × 10 ml), separated by centrifugation, then suspended in diethyl ether (3 × 10 ml), separated by centrifugation and dried under vacuum.

[$CuHL^1$]$_n$ (**12**) was collected as a light brown powder (233 mg, 83%). MS (FAB$^+$): m/z = 258 (M^+ + 1). Anal. Calcd. for $C_8H_8CuN_3OS$ (257.78 g/mol): C, 37.27; H, 3.13; N, 16.30. Found: C, 37.66; H, 3.00; N, 16.14. IR (KBr, ν/cm^{-1}): 3467s, 3367s, 3352s, 3267s, 1599s, 1596m, 1511s, 1492s, 1317m, 1278m, 1210m, 1152w, 809m, 751s. UV/vis (10^{-5} M, DMSO (nm)): λ = 279, 329, 396. UV/vis (10^{-3} M, DMSO (nm)): λ 578. Conductance Λ_m (DMSO 10^{-3} M): 2.5 Ω^{-1} cm^2 mol^{-1}. $\mu_{eff.}$ (25 °C) = diamagnetic.

[$CuHL^2$]$_n$ (**13**) was collected as a brown powder (88%). MS (FAB$^+$): m/z = 370 (M^+ + 1), 677 [2M-Cu + 2]$^+$. Anal. Calcd. for $C_{16}H_{24}CuN_3OS$ (369.99 g/mol): C, 51.94; H, 6.54; N, 11.36. Found: C, 51.90; H, 6.31; N, 11.10. IR (KBr, ν/cm^{-1}): 3472s, 3294s, 2960s, 1600s, 1596m, 1528m, 1432s, 1332s, 1301m, 1172s, 1026w, 839w, 784m. UV/vis (10^{-5} M, DMSO (nm)): λ = 275, 335, 407. UV/vis (10^{-3} M, DMSO (nm)): λ = 583. Conductance Λ_m (DMSO 10^{-3} M): 8.8 Ω^{-1} cm^2 mol^{-1}. $\mu_{eff.}$ (25 °C) = diamagnetic.

[$CuHL^3$]$_n$ (**14**) was collected as a green powder (58%). MS (FAB$^+$): m/z = 288 (M^+ + 1), 513 [2M − Cu + 2]$^+$. Anal. Calcd. for $C_9H_{10}CuN_3O_2S$ (287.81 g/mol): C, 37.56; H, 3.50; N, 14.60. Found: C, 37.42; H, 3.39; N, 14.20. IR (KBr, ν/cm^{-1}): 3449s, 3347m, 3303s, 3200m, 1618m, 1602s, 1336m, 1307m, 1246s, 1218s, 1085w, 968w, 857w, 775m, 734m. UV/vis (10^{-5} M, DMSO (nm)): λ = 260, 329, 398. UV/vis (10^{-3} M, DMSO (nm)): λ = 577. Conductance Λ_m (DMSO 10^{-3} M): 3.5 Ω^{-1} cm^2 mol^{-1}. $\mu_{eff.}$ (25 °C) = diamagnetic.

[$CuHL^4$]$_n$ (**15**) was collected as a light brown powder (90%). MS (FAB$^+$): m/z = 329 (M^+ + 1), 595 [2M-Cu + 2]$^+$. Anal. Calcd. for $C_{12}H_{17}CuN_4OS$ (328.9 g/mol): C, 43.82; H, 5.21; N, 17.03. Found: C, 44,24; H, 5.07; N, 16.75. IR (KBr, ν/cm^{-1}): 3409s, 3291m, 3103s, 2967m, 1637m, 1610s, 1587s, 1354s, 1297m, 1244s, 1134s, 1051w, 829w, 785m. UV/vis (10^{-5} M, DMSO (nm)): λ = 270, 388. UV/vis (10^{-3} M, DMSO (nm)): λ = 573. Conductance Λ_m (DMSO 10^{-3} M): 1.2 Ω^{-1} cm^2 mol^{-1}.

[$CuHL^5$]$_n$ (**16a**) was collected as a brown powder (73.2%). MS (FAB$^+$): m/z = 326 (M^+ + 1). Anal. Calcd. for $C_8H_6Cl_2CuN_3OS$ (326.67 g/mol): C, 29.41; H, 1.85; N, 12.86. Found: C, 29.32; H, 1.80; N, 12.82. IR (KBr, ν/cm^{-1}): 3439s, 3247m, 3154s, 1617s, 1613s, 1477s, 1441s, 1342m, 1319m, 1213m, 1182s, 866w, 772m, 760m. UV/vis (10^{-5} M, DMSO (nm)): λ = 274, 331, 418. UV/vis (10^{-3} M, DMSO (nm)): λ = 591. Conductance Λ_m (DMSO 10^{-3} M): 8.0 Ω^{-1} cm^2 mol^{-1}.

[$CuHL^6$]$_n$ (**17**) was collected as a brown powder (51%). MS (FAB$^+$): m/z = 414 (M^+ + 1), 766 [2M-Cu + 2]$^+$, 829 [2M + 2]$^+$. Anal. Calcd. for $C_8H_6Br_2CuN_3OS$ (415.57 g/mol): C, 23.12; H, 1.46; N, 10.11. Found: C, 23.18; H, 1.50; N, 9.98. IR (KBr, ν/cm^{-1}): 3468s, 3232m, 3135m, 3066m, 1618s, 1608m, 1596m, 1474s, 1435s, 1410m, 1340m, 1308m, 1218m, 1167m, 867w, 730m. UV/vis (10^{-5} M, DMSO (nm)): λ = 276, 341, 410. UV/vis (10^{-3} M, DMSO (nm)): λ = 585. Conductance Λ_m (DMSO 10^{-3} M): 4.2 Ω^{-1} cm^2 mol^{-1}.

[$CuHL^7$]$_n$ (**18**) was collected as a brown powder (67%). MS (FAB$^+$): m/z = 336 (M^+ + 1). Anal. Calcd. for $C_8H_7BrCuN_3OS$ (336.68 g/mol): C, 28.54; H, 2.10; N, 12.48. Found: C, 28.77; H, 2.09; N, 11.99. IR (KBr, ν/cm^{-1}): 3418s, 3268m, 2999s, 1637s, 1600s, 1496s, 1464s, 1341m, 1294m, 1187s, 1038m, 869w, 809m, 751w. UV/vis (10^{-5} M, DMSO (nm)): λ = 271, 335, 406. UV/vis (10^{-3} M, DMSO (nm)): λ = 578. Conductance Λ_m (DMSO 10^{-3} M): 5.2 Ω^{-1} cm^2 mol^{-1}. $\mu_{eff.}$ (25 °C) = 1.18 B.M.

[$CuHL^8$]$_n$ (**19**) was collected as a dark green powder (33%). MS (FAB$^+$): m/z = 294 (M^+ + 1). Anal. Calcd. for $C_8H_6CuF_2N_3OS$ (293.76 g/mol): C, 32.71; H, 2.06; N, 14.30. Found: C, 33.11; H, 1.74; N, 14.40. IR (KBr, ν/cm^{-1}): 3430m, 3301s, 3154m, 2874m, 1587s, 1561m, 1465s, 1300m, 1267s, 1125s, 1069w, 997m, 849w, 832s, 745w. Conductance Λ_m (DMSO 10^{-3} M): 1.0 Ω^{-1} cm^2 mol^{-1}.

[$CuHL^9$]$_n$ (**20**) was collected as a light brown powder (85%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 11.75 (br s, 1H, C*H*), 11,00 (br s, 1H, O*H* or N*H*), 8.00–7.80 (br s, 2H, Ar*H*), 5.98 (br, 2H, Ar*H*), 4.11 (br s, 1H, N*H*), 1.75 (br, 2H, CH_2), 1.58 (br, 2H, CH_3). MS (FAB$^+$): m/z = 286 (M^+ + 1). Anal. Calcd. for $C_{10}H_{12}CuN_3OS$ (285.83 g/mol): C, 42.02; H, 4.23; N, 14.70. Found: C, 41.67; H, 4.13; N, 14.92. IR (KBr, ν/cm^{-1}):

3369s, 2968m, 1596s, 1555m, 1506s, 1474s, 1438m, 1320m, 1280m, 1204s, 1156w, 1073w, 835w, 745m. UV/vis (10^{-5} M, DMSO (nm)): $\lambda = 275, 332, 397$. UV/vis (10^{-3} M, DMSO (nm)): λ 577. Conductance Λ_m (DMSO 10^{-3} M): 3.1 Ω^{-1} cm^2 mol^{-1}.

[CuHL^{10}]$_n$ (**21**) was collected as a light brown powder (62%). MS (FAB$^+$): m/z = 334 ($M^+ + 1$), 605 [2M-Cu + 2]$^+$. Anal. Calcd. for $C_{14}H_{12}CuN_3OS$ (333.88 g/mol): C, 50.36; H, 3.62; N, 12.59. Found: C, 50.25; H, 3.72; N, 12.28. IR (KBr, ν/cm^{-1}): 3404w, 3235m, 3024m, 2937m, 1595m, 1508m, 1498m, 1458s, 1431s, 1314m, 1251w, 1210m, 1178m, 1088w, 866w, 769m, 747m. UV/vis (10^{-5} M, DMSO (nm)): $\lambda = 287, 323, 408$. UV/vis (10^{-3} M, DMSO (nm)): *no d–d band was detected*. Conductance Λ_m (DMSO 10^{-3} M): 3.5 Ω^{-1} cm^2 mol^{-1}.

[CuHL^{11}]$_n$ (**22**) was collected as a dark green powder (77%). MS (FAB$^+$): m/z = 446 ($M^+ + 1$), 829 [2M-Cu + 2]$^+$. Anal. Calcd. for $C_{22}H_{28}CuN_3OS$ (446.09 g/mol): C, 59.23; H, 6.33; N, 9.42. Found: C, 58.92; H, 6.46; N, 9.33. IR (KBr, ν/cm^{-1}): 3421m, 3221m, 2955s, 2904m, 2868m, 1592s, 1541s, 1498s, 1548s, 1438s, 1314m, 1299m, 1256s, 1167s, 1065w, 832w, 745m. UV/vis (10^{-5} M, DMSO (nm)): $\lambda = 324, 417$. UV/vis (10^{-3} M, DMSO (nm)): λ 592. Conductance Λ_m (DMSO 10^{-3} M): 2.5 Ω^{-1} cm^2 mol^{-1}.

2.3.2. Alternative synthesis of the copper complex **16b**

A solution of copper (II) acetate monohydrate (200.0 mg, 1.00 mmol) in the minimum required amount of methanol was added dropwise to a hot (60 °C) solution of H_2L^5, **5** (191.0 mg, 0.723 mmol) in methanol (50 ml). The reaction mixture was refluxed for 3 h and then concentrated to half volume. The dark green precipitate so formed was recovered by filtration, it was washed with ethanol, then with diethyl ether and dried under vacuum over anhydrous $CaCl_2$. [$CuL^5 \cdot 2H_2O$] (**16b**) was collected as a dark green powder (204.9 mg, 78.4%). Anal. Calcd. for $C_8H_9Cl_2CuN_3O_3S$ (361.69 g/mol): C, 26.57; H, 2.51; N, 11.91; Cu 17.57. Found: C, 26.42; H, 2.63; N, 11.74; Cu 17.44. IR (KBr, ν/cm^{-1}): 3480s, 3464s, 3277s, 3182s, 1748w, 1620s, 1610m, 1601s, 1473s, 1439s, 1314s, 1212s, 1164w, 950m, 867m, 630w, 520w, 431w, 364w. $\mu_{eff.}$ (25 °C) = 1.79 B.M.

2.3.3. Detection of acetic aldehyde in the synthesis of complex **20**

A solution of copper (II) acetate monohydrate (14.9 mg, 0.076 mmol) in the minimum required amount of water was added to a hot (70 °C) solution of H_2L^9, **9** (15.2 mg, 0.068 mmol) in ethanol (5 ml) in a pressure tube. The reaction mixture was heated to 80 °C for 2.5 h and then cooled to 0 °C. After centrifugation, a sample of the supernatant solution was withdrawn and analysed by GC. Acetic aldehyde was detected [32].

2.4. Typical procedure for the catalytic cyclopropanation of olefins

CuHL^1 (**12**) (1.3 mg, $5.1 \cdot 10^{-3}$ mmol) and α-methylstyrene (0.660 ml, 5.1 mmol) were suspended in distilled dichloroethane (9 ml) and the reaction mixture was heated under stirring at 70 °C. Then dichloroethane solution (1 ml) of EDA (0.266 ml, 2.53 mmol) was slowly added by a syringe pump during 100 min. The end of the reaction was checked by IR, following the disappearance of the band due to the stretching of N_2 moiety at 2114 cm^{-1}. After the addition of EDA, a complete conversion of EDA (IR absorbance <0.025) was observed; the solution was analysed by GC after the addition of 2,4-dinitrotoluene (230 mg, 1.27 mmol) as internal standard. Yields were confirmed by ^{1}H NMR analysis of the crude and, in selected cases, products were isolated and purified by column chromatography. The collected analytical data for *cis* and *trans* ethyl-2-phenylcyclopropanecarboxylate [33], *cis* and *trans* ethyl-2-*p*-tolylcyclopropanecarboxylate [33], *cis* and *trans* ethyl-2-methyl-2-phenylcyclopropanecarboxylate [34], ethyl-2,2-dphenylcyclopropane carboxylate [33], *cis* and *trans* ethyl-2-(4-chlorophenyl)-2-methyl cyclopropanecarboxylate [35], *cis* and *trans* ethyl-2-naphthylcy clopropanecarboxylate [36], *cis* and *trans* ethyl-2-hexylcyclopropane carboxylate [37], *cis* and *trans* bicyclo[4.1.0]heptane-7-carboxylic acid ethyl ester [37], and *cis* and *trans* ethyl chrysantemate [37] are in agreement to those reported in the literature.

3. Results and discussion

3.1. Synthesis

Ligands were synthesized by reacting hydrazinecarbothioamide with substituted salicylaldehydes in refluxing ethanol. Pure ligands could be obtained by simple recrystallization from ethanol. Only in the case of ligand **2** it was necessary to perform a column chromatography over silica in order to obtain a compound free from traces of hydrazinecarbothioamide. The copper complexes were synthesized by treating the ligands in refluxing ethanol with copper (II) acetate monohydrate dissolved in the minimum required amount of methanol. In all cases the formation of a dark green or brown precipitate was observed at the very beginning of the addition of the copper acetate. The reaction mixture was then refluxed and the product collected upon filtration after cooling at room temperature. A recrystallization step from hot ethanol was needed to obtain a crystalline powder. Traces of water could be removed only after repeated washing with ethanol and diethyl ether. Both ligands and complexes were obtained in good yields.

3.2. Spectroscopy

The mass spectra (EI) of the Schiff base ligands **1**–**8** and **10**–**11** revealed molecular ion peaks which are coincident with the formula weights for these ligands and support the identity of their structures. Although numerous reports in the literature on the use of thiosemicarbazide derived Schiff bases have been published in the last years [29–31,38–41], reported spectroscopical and analytical data are often scant; ^{13}C NMR spectra are seldom described and in some cases, especially concerning IR spectra, reported data are not in good relative agreement (see later). The ^{1}H and ^{13}C NMR spectra of the ligands are in agreement with the proposed structure. Enol and keto tautomers are very close in energy for Schiff bases and may compete for stability. As expected for phenol Schiff bases derivatives, the enol form prevails and we never observed any keto-enol tautomerism in DMSO-d_6 (nor in $CDCl_3$) solutions [42] (see Experimental section). The IR spectra of powders show the characteristic intense bands in the range 1618–1590 cm^{-1} associated with the $\nu_{(C=N)}$ frequencies. The $\nu_{(OH)}$ band of the phenolic oxygen is found almost at the same frequencies for all ligands, in the range 3468–3409 cm^{-1}, whilst the medium to intense band in the region 3300–2900 cm^{-1} have been attributed to $\nu_{(NH2)}$ and $\nu_{(NH)}$. The free ligands exhibit medium intensity bands in the region 1099–1011 cm^{-1} and 859–793 cm^{-1}, attributed respectively to $\nu_{(C=S)}$ and to $\nu_{s(CS)}$. There is no general agreement in the literature data in the identification of $\nu_{s(CS)}$, that for some authors is at lower frequencies (see for example Ref. [30]); however, reported data in the experimental section are in accordance with those reported by Campbell in his review [43]. This band is particularly diagnostic for transition metal complexes of thiosemicarbazide and thiosemicarbazones, since upon coordination could be shifted almost 100 cm^{-1} to lower frequencies. A shift of this order would indicate a considerable change in the bond order, such as would result from the formation of a strong metal-sulfur bond. As expected, for all the synthesized copper complexes, the frequencies corresponding to $\nu_{s(CS)}$ were found in the range 809–730 cm^{-1}, therefore indicating the coordination of the copper ion to the S atom. This fact is supported even by the

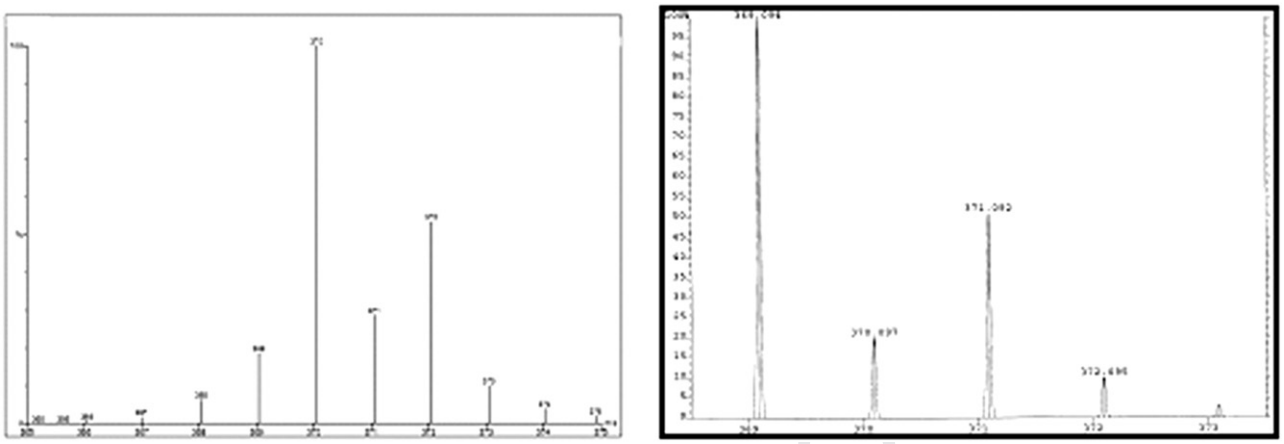


Fig. 1. FAB mass spectrum of complex **13** (left) compared with the simulated spectra for the cluster $[CuHL^2]^+$.

disappearance of the $\nu_{(C=S)}$ band at around 1050 cm^{-1}. The complexation of the metal ion is accompanied also by a negative shift of the frequencies corresponding to $\nu_{(C=N)}$ (from the spectral region 1618–1590 cm^{-1} to lower wave numbers) and to $\nu_{amideII}$ (from 1550 to 1537 cm^{-1} to 1527–1465 cm^{-1}) and a positive shift of the $\nu_{(CO)}$ (from 1271–1245 cm^{-1} to 1318–1278 cm^{-1}) [40]. All these data support that the ligand donor atoms, O, N, S, chelate the copper atom in a tridentate manner. Noteworthy, we observed for all metal complexes the persistence of a sharp band in the region 3484–3404 cm^{-1}. Normally absorption bands assigned to the $\nu_{(OH)}$ modes of lattice water appear as broad and rather intense bands in the spectral region of 3550–3200 cm^{-1} (antisymmetric and symmetric OH stretchings) and are accompanied by $\delta_{(OH)}$ in the region 1630–1600 cm^{-1}, which are not observed in the present case. It should be pointed out, however, that also the OH group in hydroxo complexes lacks the HOH bending mode near 1600 cm^{-1} [44]. The absence of coordinated water molecules within the coordination sphere of these complexes (with the exception of complex **16b**, see experimental section) is further supported by the absence of bands in the 950–930 cm^{-1} and 635–615 cm^{-1} regions, due to H_2O rocking and wagging, respectively. On the other hand, the existence of coordinated water molecules within the coordination sphere of complex $[CuL^5 \cdot 2H_2O]$ (**16b**) is supported by the presence of bands at 3480, 1610, 950 and 630 cm^{-1}, due to OH stretching, HOH deformation, H_2O rocking and H_2O wagging respectively. The complexes under study did not show any band which may be attributed to acetate ligand coordinated to the central metal atom [44].

The molar conductivities Λ_m of the metal complexes **12**–**22** dissolved in DMSO at 10^{-3} M were found to be in the range 1–8 Ω^{-1} cm^2 mol^{-1}. These low values indicate that these complexes are non-electrolytes due to the absence of any counter ion in their structures [45].

The absence of water, as well as of coordinate acetate ions, in the metal complexes is also indicated by the elemental analyses, which are in perfect agreement with a 1:1 ratio metal/ligand of general formula $[CuHL]_n$ (with the exception of complex **16b**, which is in agreement with the formula $CuL^5 \cdot 2H_2O$, see below). This general formula is supported also by the result of the FAB mass analysis of the metal complexes. In general the fast atom bombardment (FAB) gives rise to molecular ions of the type $[M^+ + 1]$ and, to the best of our knowledge, very seldom $[M^+ + 2]$ peaks are observed. For all copper complexes (with the exception of **16b**) we observed a clean base peak corresponding to a general formula $[CuHL^+ + 1]$, which seems to indicate that the ligand has just lost one hydrogen atom in the complexation reaction and thus cannot behave as a dianionic ligand, as would be expected. The mass spectra of complex **13** is reported in Fig. 1 and compared with the spectrum simulated for the cluster $[CuHL^2]^+$.

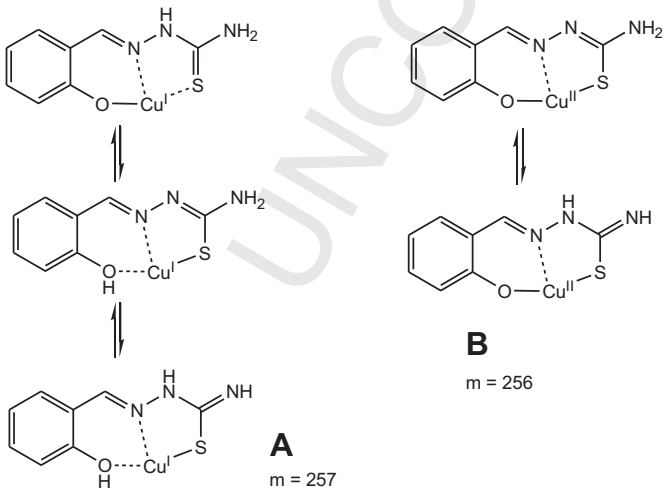


Fig. 2. Possible molecular formulae (sketched as monomers) for complex 12: A (monoanionic ligand); B (dianionic ligand).

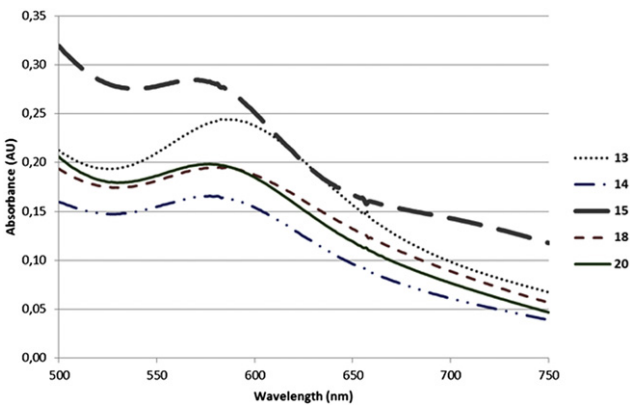


Fig. 3. UV–vis spectra for complexes **13**–**15**, **18** and **20** (see legend) in the region 500–700 nm; 10^{-3} M solutions in DMSO.

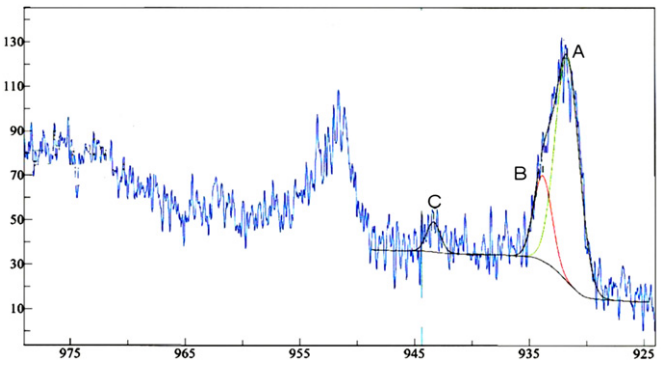


Fig. 4. The Cu_{2p} spin-orbit doublets obtained for complex **12**.

It can be seen that, even if with low intensity, an ion peak corresponding to the molecular formula [CuL^+ + 1] (369 *m*/*e*) is present. The same pattern is found in all the mass spectra of the metal complexes (see experimental section).

If we assume, as all analytical and spectroscopical data support, that the metal to ligand ratio is 1:1 and that we do not have any other ancillary ligand present in the metal complexes, we must conclude that the copper complexes are not monomeric in the solid state and that dimeric (or oligomeric) structures are formed. If the ligand behaves as monoanionic (**A**, Fig. 2), then, to balance charges, the copper atom must have been reduced to a formal I oxidation state. On the other hand, if the ligand behave as dianionic (**B**, Fig. 2), the metal ion should be formally described as copper (II).

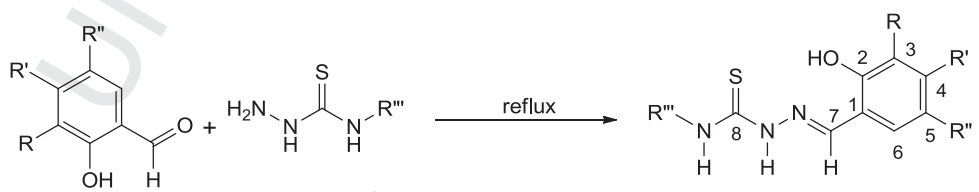
The two structures **A** and **B** differ only for one proton, and for the copper oxidation state. In the absence of coordinating solvents, we must assume that these molecules are not monomers, but must aggregate. Actually, all these metal complexes are almost insoluble in most organic solvents, and a good solubility is observed only in DMSO and DMF. Unfortunately, any attempt to grow crystals suitable for X-ray structural determination from these solvents met with failure. When we tried to record NMR spectra in deuterated DMSO, we observed broad signals that prevented any attribution of the chemical shifts. The only complex that showed a good solubility even in chlorinated solvents was **20**. In this case, it was possible to record a ^1H NMR spectrum in $CDCl_3$, that is in agreement with a diamagnetic complex (see experimental section).

The solid copper complexes **12**–**14** are diamagnetic at room temperature. The typical magnetic momentum value for mononuclear copper (II) compounds with a $S = ½$ spin state are expected in the range 1.79–1.95 B.M [46]. Only in the case of complex **18** we measured a room temperature magnetic moment of 1.18 B.M. which seems to indicate a partial antiferromagnetic coupling of spins at this temperature [47]. Further studies on the magnetism of these molecules at low temperature will be the subject of a study in the next future.

The UV–vis spectra of the thiosemicarbazone ligands in DMSO (10^{-5} M) showed broad bands in the range 270–275 nm assignable to the phenyl ring $\pi \rightarrow \pi^*$ transitions. This band is not affected to a major extent upon coordination of the copper atom. The $n \rightarrow \pi^*$ transitions associated with the C=N group [48] around 350 nm in the spectra of the free ligands are generally shifted to higher energy on complexation. In the spectra of some complexes this latter band shifts to higher energies. The shifts of these bands with respect to those of the free ligand indicate coordination of phenolic oxygen and azomethine thioenol moieties to the metal ions. There are also charge-transfer transitions partially responsible for the intense colours of some of the complexes. The absorption bands with high intensity observed at 420–430 nm are assigned to charge-transfer transitions. The UV–vis spectra of the complexes (10^{-3} M in DMSO) showed broad single band at 570–590 nm (ε in the range 200–300 M^{-1} cm^{-1}, Fig. 3) which is consistent with a distorted square pyramidal geometry at a Cu (II) metal atom [41].

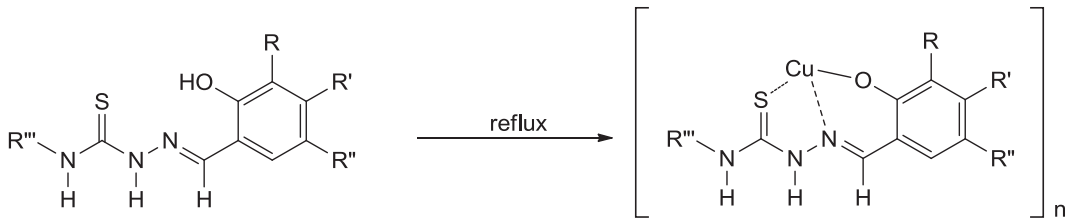
These experimental data provide grounds for suggesting a polynuclear structure for the metal complexes **12**–**22** with a spin–spin interaction between the paramagnetic copper ions. This polymeric chain would break upon dissolution in strongly coordinating solvents such as DMSO or DMF. It should be pointed out that Cu (I) complexes are not stable towards oxidation and that the experimental conditions used in the present work and the high dilutions needed to record an UV–vis spectrum in DMSO hampers the characterization of copper (I) in solution. On the other hand, only the presence of copper in the oxidation state (I) would explain the ion peaks of general formula [$CuHL^+$ + 1] observed in the mass spectra. To gain a better insight to the oxidation state of the central metal atom, we decided to carry out an X-ray photoelectron spectroscopy (XPS) analysis of selected complexes. XPS analysis, in fact, is helpful in identifying the oxidation states of elements in various compounds because the binding energy (BE) measured for the core electrons undergoes a "chemical shift" as a result of changes in the chemical environment of the atoms [49]. The Cu2p spin-orbit doublets ($2p_{1/2}$ and $2p_{3/2}$) obtained from complex **12** are illustrated in Fig. 4. A characteristic feature of the Cu^{2+} ($3d^9$) is a shift in the Cu2p photoelectron peak doublet to higher BE side compared to Cu^+ ($3d^{10}$). This can be appreciated in the $Cu2p_{3/2}$ peak that is actually split in two components: one major peak at −932 eV (**A**, Fig. 4) that can be ascribed to copper (I), and a smaller peak at −935 eV (**B**, Fig. 4), in the typical range for a copper (II) atom. A small shake-up satellite (**C** Fig. 4) can be seen on the lower kinetic energy (KE) (higher BE), which is normally associated with copper (II). Similar spectra were obtained for complexes **13** and **20**.

These data suggest that copper is present as copper (I) in the complexes. The fact that small peaks due to the presence of some



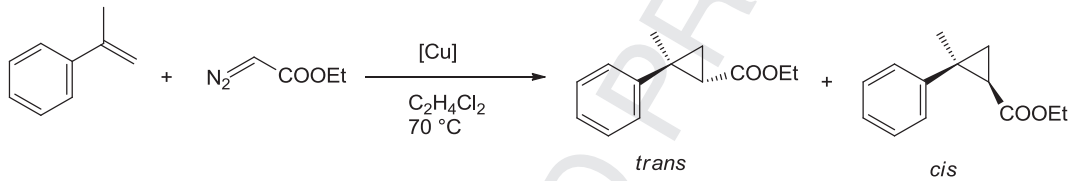
1 R = R' = R'' = R''' = H
2 R = R'' = t-Bu; R' = R''' = H
3 R = OMe; R' = R'' = R''' = H
4 R = R'' = R''' = H; R' = NEt_2
5 R = R'' = Cl; R' = R''' = H
6 R = R'' = Br; R' = R''' = H
7 R = R' = R''' = H; R'' = Br
8 R = R'' = F; R' = R''' = H
9 R = R' = R'' = H ; R''' = Et
10 R = R' = R'' = H ; R''' = Ph
11 R = R'' = t-Bu; R' = H; R''' = Ph

Scheme 1. . Formation of the thiosemicarbazone ligands H_2L (**1**–**11**) and numbering scheme adopted.



12 R = R' = R" = R"' = H
13 R = R" = t-Bu; R' = R"' = H
14 R = OMe; R' = R" = R"' = H
15 R = R" = R"' = H; R' = NEt_2
16a R = R" = Cl; R' = R"' = H
17 R = R" = Br; R' = R"' = H
18 R = R' = R"' = H; R" = Br
19 R = R" = F; R' = R"' = H
20 R = R' = R" = H ; R"' = Et
21 R = R' = R" = H ; R"' = Ph
22 R = R" = t-Bu; R' = H; R"' = Ph

Scheme 2. Formation of the copper complexes $[CuHL]_n$ (**12**–**22**).



Scheme 3.

Cu (II) are present suggests that the surface of the particles was easily oxidized. We must underline that XPS analysis is a surface technique and that a partial oxidation of the surface may always occur [49].

To investigate if the employed solvent (ethanol) in the reaction may be responsible for the reduction of copper during the complexation, complex **16b** was synthesized in methanol instead. In this case we isolated a paramagnetic complex of copper (II) ($\mu_{eff.}$ (25 °C) = 1.79 B.M.) corresponding to the molecular formula $[CuL^5 \cdot 2H_2O]$. When the reaction was repeated in isopropanol (a better reducing agent than ethanol) a less pure product but with a chemical composition similar to **16a** was obtained instead (see experimental). The fact that copper (II) is reduced to copper (I) in reaction with thioylcarbamoyl ligand [50] and with thiosemicarbazones [51] is not unprecedented. However, in reported cases, reduction took place in the absence of alcohols. To clarify the role played by the alcohol in the reduction from Cu (II) to Cu (I), we have conducted a GC analysis of the reaction mixture to detect if an oxidation product from ethanol was observed. In order to do this, we had to run the reaction in the absence of methanol, that under our experimental conditions interfere with the detection of acetic aldehyde, by dissolving the copper acetate in the minimum of water and performing the reaction in a pressure tube to avoid any possible evaporation of the formed volatile products. Under these conditions, we were able to detect a reasonable amount of acetic aldehyde after the reaction took place (see experimental).

3.3. Catalytic activity

The catalytic activity of complexes **12**–**22** in cyclopropanation reactions has been investigated. As a model reaction we choose the cyclopropanation of α-methylstyrene by EDA (EDA = ethyldia

Table 1
Catalytic cyclopropanation of α-methylstyrene by EDA.[a]

Entry	Catalyst	Conversion (%)[b]	Yield (%)[c]	*trans*/*cis*[c]
1	**12**	>99%	79	56:44
2	**13**	>99%	78	56:44
3	**14**	>99%	58	55:44
4	**15**	>99%	62	56:44
5	**16a**	>99%	97 (68)[d]	57:43
6	**16b**	>99%	97	57:43
7	**17**	>99%	93	55:45
8	**18**	>99%	92	56:44
9	**19**	>99%	54	54:46
10	**20**	>99%	81	56:44
11	**21**	>99%	87	57:43
12	**22**	>99%	88	55:45

[a] Experimental conditions: EDA (2.52 mmol) dissolved in $C_2H_4Cl_2$ (1 ml) was slowly added (100 min) to a hot (70 °C) solution of cat (5.1×10^{-3} mmol) and α-methylstyrene (5.1 mmol) in dichloroethane (9 ml).
[b] Conversion of the starting EDA.
[c] Determined by GC (yield based on EDA).
[d] Isolated yield.

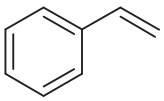
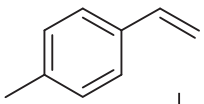
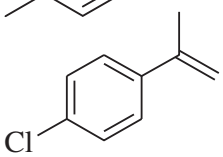
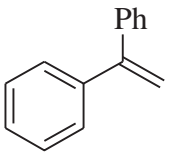
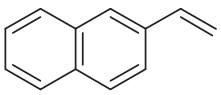
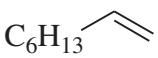
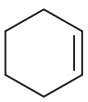
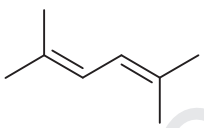
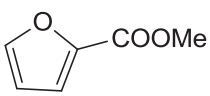
Table 2
Cyclopropanation of α-methylstyrene with EDA catalysed by complex **16b**, $CuL^5(H_2O)_2$.[a]

Entry	Cat/EDA/olefin	Time (min)	Conversion(%)[b]	Yield (%)[c]	*trans*/*cis*[c]
1	1/500/1000	7/5/5[d]	> 99	87	57:43
2[e]	1/1000/1500	100/100/100[d]	> 99	95	57:43
3[f]	1/10000/20000	380	92	77	56:44
4[g]	1/20000/40000	420	92	74	55:45

[a] Experimental conditions: EDA was added to a solution of **16b** (2.73 mg, 7.5×10^{-3} mmol) and α-methylstyrene in dichloroethane (10 ml) at 70 °C.
[b] Conversion of the starting EDA.
[c] Determined by GC (yield based on EDA).
[d] After complete consumption of the starting EDA, the catalytic cycle was restored twice by addition of EDA and α-methylstyrene; global yield is reported.
[e] **16b** (1.35 mg, 3.7×10^{-3} mmol) in 9 ml of dichloroethane was used; EDA dissolved in $C_2H_4Cl_2$ (1 ml) was slowly added.
[f] This solution was prepared by dissolving **16b** (1.35 mg, 3.7×10^{-3} mmol) in dichloroethane (10 ml); 1 ml of this solution was added to the solution of α-methylstyrene in 9 ml of dichloroethane.
[g] This solution was prepared by dissolving **16b** (1.35 mg, 3.7×10^{-3} mmol) in dichloroethane (10 ml); 0.5 ml of this solution were added to the solution of α-methylstyrene in 9.5 ml of dichloroethane.

zoacetate) (Schemes 1–3). Catalytic reactions were run by slow addition of EDA by syringe pump (100 min) to a stirred solution containing the olefin and the metal complex in dichloroethane under dinitrogen (Cu/EDA/α-methylstyrene ratio 1:500:1000) at 70 °C. In all cases a quantitative conversion of the starting EDA was observed at the end of the addition, as judged by IR spectroscopy, checking the disappearance of the band due to the stretching of the N_2 moiety ($\nu = 2114\ cm^{-1}$).

Table 3
Cyclopropanation of olefins with EDA.[a]

Entry	Olefin	Cat	Time (min)	Conversion(%)[b]	Yield(%)[c]	*trans*/*cis*[c]
1		**16b**	12	>99	68	72:28
2[d]		**16b**	100[d]	>99	99 (90)	92:8
3[d]		**16b**	100[d]	>99	82 (68)	57:43
4		**16b**	100[d]	>99	90 (63)	–
5		**16b**	31	>99	76	71:29
6		**12**	100[d]	>99	63	68:32
		16b	19	>99	65	69:31
		16a	100[d]	>99	75	80:20
		21	100[d]	>99	76	73:27
		22	100[d]	>99	78	66:44
7		**16b**	11	>99	67	91:9
		16a	100[d]	>99	92	91:9
8		**16b**	32	>99	82	64:36
		16a	100[d]	>99	98	50:50
9[e]		**16b**	100[d]	>99	85 (51)	58:41:1:0
10[f]		**16b**	100[d]	>99	90 (84)	>99
11		**21**	100[d]	>99	15	>99

[a] Experimental conditions: EDA was added to a solution of cat (5.1×10^{-3} mmol) and olefin in dichloroethane (10 ml) at 70 °C.
[b] Conversion of the starting EDA.
[c] Determined by GC; isolated yield in parenthesis (yield based on EDA).
[d] EDA dissolved in $C_2H_4Cl_2$ (1 ml) was slowly added to the solution containing the catalyst and the olefin in dichloroethane (9 ml).
[e] The two major products were determined to be (1*R*,2*R*,2′*R*) and (1*R*,2*R*,2′*S*) by comparison with literature data [52]. The fourth possible diastereoisomer was not detected.
[f] Only one diasteroeisomer (1*R*,2*R*, 2′*R*) was isolated [52].

All tested copper complexes exhibited a remarkable catalytic activity towards the decomposition of ethyldiazoacetate, and the subsequent transfer of the carbene moiety to the C=C double bond. In Table 1 are collected all the obtained results in the cyclopropanation reaction of α-methylstyrene with the different catalysts. In all cases cyclopropanes were obtained in yields from good to excellent. Fumarate and maleate, the homo-coupling product of EDA, were the only other product detected and accounted for the missing mass balance of the reactions. The diastereoselective outcome of the reaction is rather poor in all cases (almost equimolar amount of *trans* and *cis* cyclopropanes) and does not seem to be influenced by the steric and/or electronic requirement of the thiosemicarbazone ligand.

Remarkably, almost no difference in the chemical yield was observed employing a catalyst where copper is present as Cu (I) or complex **16b**, the only monomeric copper (II) catalyst tested. This finding, however, is not surprising, since it is commonly accepted that EDA reduces Cu (II) to Cu (I). We next optimised the reaction conditions and catalyst loadings, employing complex **16b**. The results are summarised in Table 2.

When EDA was added in one portion to the reaction mixture (entries 1, 3 and 4, Table 2), an induction period was observed, that, in the case of complex **16b**, can be necessary to reduce copper (II) to copper (I). In fact, this induction period is not observed upon the second and third additions (entry 1, Table 2). Noteworthy, the copper complex does not lose its catalytic activity after 3 consecutive runs. In contrast to the prolonged EDA addition time generally required to reduce the formation of homo-coupling products in cyclopropanation, we found complex **16b** to be rather insensitive to this: if we compare entry 1, Table 2 with entry 6, Table 1, a decrease only from 97% to 87% in cyclopropane yield is observed. At a **16b**/EDA/α-methylstyrene ratio of 1/1000/1500 with slow addition of EDA products are obtained with excellent yields (entry 2, Table 2). A 1.5 fold excess of olefin with respect to EDA is however necessary to reduce the formation of homo-coupling products. We were able to further reduce the catalyst loading and TON up to 18,400 have been obtained (entry 4, Table 2). Even if a poor diastereoselection was observed, to the best of our knowledge, this is the higher TON reported for a single site copper catalyst in homogeneous catalytic cyclopropanation [23]. A TON of 100,000 has been recently reported by us with a dinuclear copper polyoxometalate catalyst [26].

To determine the general applicability of copper thiosemicarbazone complexes, cyclopropanation reactions of a series of styrene derivatives with varied electronic and steric properties were carried out, using EDA as carbene source (Table 3). At a cat/EDA/olefin ratio of 1/500/1000 at 70 °C, the complexes catalysed the cyclopropanation of a range of substrates with a quantitative conversion and with selectivities ranging from good to excellent. The results are summarised in Table 3.

When styrene was employed as substrate, we observed a decrease in the reaction rate and in cyclopropane products with respect to the case of α-methylstyrene (compare entry 1, Table 3 and entry 6, Table 1). However, in this case the diastereoselectivity is improved (*trans*/*cis* = 2.6). Better yields in cyclopropane products and higher diastereoselectivities (*trans*/*cis* = 11.5) were obtained when electron donating substituents are present in the *para* position of the aromatic ring (entry 2, Table 3). If 4-chloro-α-methylstyrene was employed as substrate, a slight decrease in the yield was observed instead (entry 3, Table 3). It can be seen that in the absence of an α-substituent on the styrene derivative the formation of the *trans* cyclopropane is always favoured (entries 1, 2 and 5, Table 3). Steric hindrance at the α position does not hamper the reaction and good yields were obtained with 1,1-diphenyl ethylene (entry 4, Table 3).

Even aliphatic alkenes that are generally less reactive in cyclopropanation reactions, gave excellent results. Though the time of the cyclopropanation reaction for these substrates increased slightly if compared to what observed for styrene derivatives (compare entries 6, 7 and 8, Table 3, with entry 6, Table 1) yields ranging from good to excellent were always obtained. Even in these cases *trans* cyclopropane compounds were obtained as major products and a remarkable diastereoselectivity (*trans*/*cis* = 10.1) was observed for cyclohexene (entry 7, Table 3). With 2,5-dimethyl-2,4-hexadiene, an important precursor to chrysanthemic acid [53], the catalytic reaction yielded the desired cyclopropanes (cyclopropanation of only one double bond was observed, [37]) in very good yields (98%) (entry 8, Table 3), without the need for a large excess of the olefin. Out of the four possible diastereoisomers that could be obtained in the cyclopropanation of (−)β-pinene, two major isomers were obtained. The two major isomers are those deriving from a formal attack of the carbene moiety on the less sterically hindered side of the olefin [52]. On the other hand, when (−)α-pinene was used as the substrate, only one diastereoisomer (1*R*,2*R*,2′*R*, Ref. [52]) was isolated as a clean product in good yield (entry 10, Table 3). The only substrate that failed to give good yields in the present study was methylfuroate, (entry 11, Table 3). However, in this case, even if in low yield, only the trans isomer (attack only at the non-substituted double bond) was detected [54].

4. Conclusions

The straightforward synthesis of several thiosemicarbazide derived Schiff base copper complexes has been reported. The presence of N, S, O donor atoms of thiosemicarbazones renders the study their coordination to transition metals very interesting. Spectral and analytical collected data in this study suggested that, at least in part, reduction to copper (I) has occurred. Further studies in determining the crystal structure of these complexes in the absence of strong coordinating solvents are on-going in our lab. However, all synthesized complexes showed excellent catalytic activities in cyclopropanation reactions and TON up to 18,400 could be obtained. In contrast to the prolonged EDA addition time generally required to reduce the formation of homo-coupling products in cyclopropanation, we found those complexes very selective. Furthermore, a single addition of EDA is required to yield the desired cyclopropanes in excellent yields. Moreover, the catalysts are very robust and no decrease in yield was observed even after three catalytic runs. Several cyclopropanes have been obtained in good to excellent yields even from non-activated olefins. In the case of the cyclopropanation of (−)α-pinene, out of four possible diastereoisomers, only one product was formed that could be isolated pure in 84% yield.

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[32] The GC analysis was performed on a HP 5890 series II CG equipped with a TCD detector and with a HP-plotQ (divinylbenzene/styrene polymer) capillary column under He flux. Acetic aldehyde (compared with a pure sample) was eluted in 2.7 min; ethanol in 3.4 min; acetic acid in 8.1 min. A blank test with the same solvent used for the reaction was performed: in this case, a small amount of acetic aldehyde (or methanol, that has the same retention time under these conditions) was also observed in traces, but the intensity of this peak, with respect to that of ethanol, was 1/4 than in the analysis of the reaction mixture.
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