

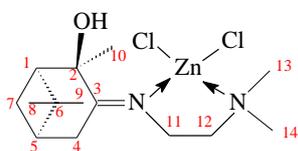
Copper(II) and zinc(II) complexes with terpene derivatives of ethylenediamine: unexpected ligand transformations

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Synthesis of copper(II) complexes A solution of $\text{CuCl}_2 \times 2\text{H}_2\text{O}$ (0.5 mmol) and the corresponding ligand **L1** or **L2** (0.5 mmol) in MeOH (10 ml) was stirred at room temperature for 8 h. Copper(II) complexes were obtained as powders after removal of the solvent and recrystallization from a mixture of acetone - diethyl ether. Slow evaporation of the solution of **1** (20 mg) in EtOH (5 ml) for 7 days at room temperature afforded the crystals mixture **4a+4b** (green prisms) and **5** (blue prisms), which were separated by hand. Slow evaporation of the solution of **2** (15 mg) in EtOH (5 ml) under the same conditions afforded crystals of complex **5**. Structure **4a+4b** and **5** was verified by X-ray diffraction data.

Synthesis of zinc(II) complexes A solution of ZnCl_2 (0.5 mmol) and ligand **L3** (0.5 mmol) in EtOH (10 ml) was stirred at room temperature for 8 h. Zinc(II) complex **3** was obtained as powder after removal of the solvent and recrystallization from a chloroform–hexane mixture. Yield 92%. Slow evaporation of the solution **3** (10 mg) in acetone (10 ml) at room temperature for 3 days afforded crystals of complex **6** as white prisms. Structure **6** was verified by X-ray diffraction data.

Dichloro{(E)-N¹,N¹-dimethyl-N²-[(1R,2R,5R)-2-hydroxy-2,6,6-trimethylbicyclo[3.1.1]heptane-3-ylidene]ethane-1,2-diamine-N¹,N²}zinc(II) **3**: yellow powder; yield 92%; m.p.: 98 °C (decomp.); $[\alpha]_D +31.6$ (*c* 0.2, acetone); selected FT-IR data, ν , cm^{-1} : 3439 (OH), 1624 (C=N), 484,436 (Zn-N). Complex **3** dissolves in EtOH, DMSO, CHCl_3 , acetone. Elemental analysis (%) calcd. for $\text{C}_{14}\text{H}_{26}\text{N}_2\text{OCl}_2\text{Zn}$ C 44.88; H 6.99; N 7.48. found: C 44.27; H 6.92; N 7.31. ¹H MR (300 MHz, CDCl_3 , δ , ppm): 0.93 (s, 3H, CH_3^8), 1.37 (s, 3H, CH_3^9), 1.55 (m, 1H, *endo*-H⁷), 1.82 (s, 3H, CH_3^{10}), 2.13 (m, 2H, H¹, H⁵), 2.42 (m, 1H, *exo*-H⁷), 2.58 (s, 3H, CH_3^{13}), 2.67 (s, 3H, CH_3^{14}), 2.76 (m, 2H, *endo*-H⁴, *exo*-H⁴), 2.84 (m, 1H, H¹²), 3.13 (m, 1H, H¹²), 3.62 (m, 2H, H¹¹), 4.31 (s, 1H, OH). ¹³C-NMR (75 MHz, CDCl_3 , δ , ppm): 23.05 (C⁸), 26.94 (C⁹), 27.91 (C¹⁰), 27.96 (C⁷), 36.66 (C⁴), 38.24 (C¹), 39.08 (C⁶), 45.23 (C^{13,14}), 46.79 (C¹¹), 52.16 (C⁵), 57.14 (C¹²), 76.63 (C²), 190.75 (C³).



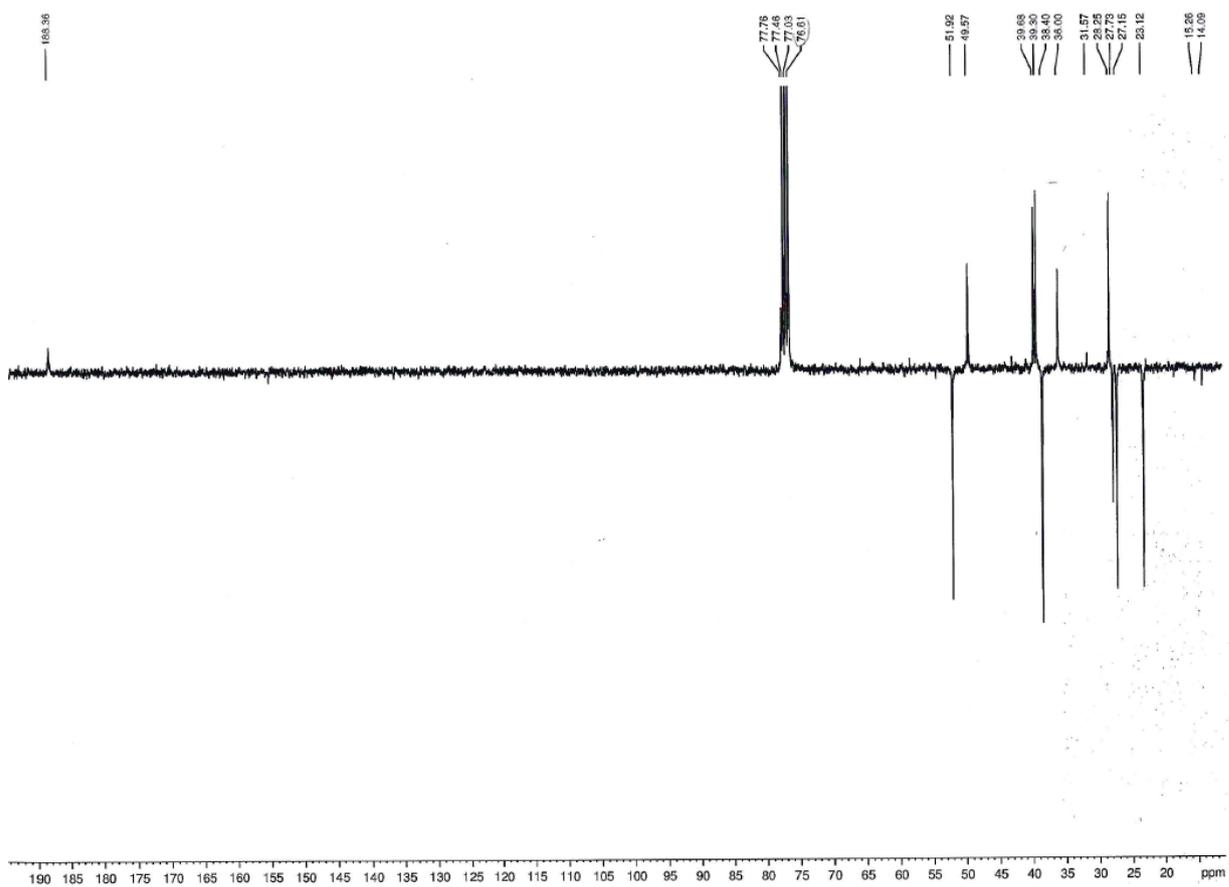


Figure S2 ^{13}C NMR spectrum (75 MHz, CDCl_3) of complex **3**.

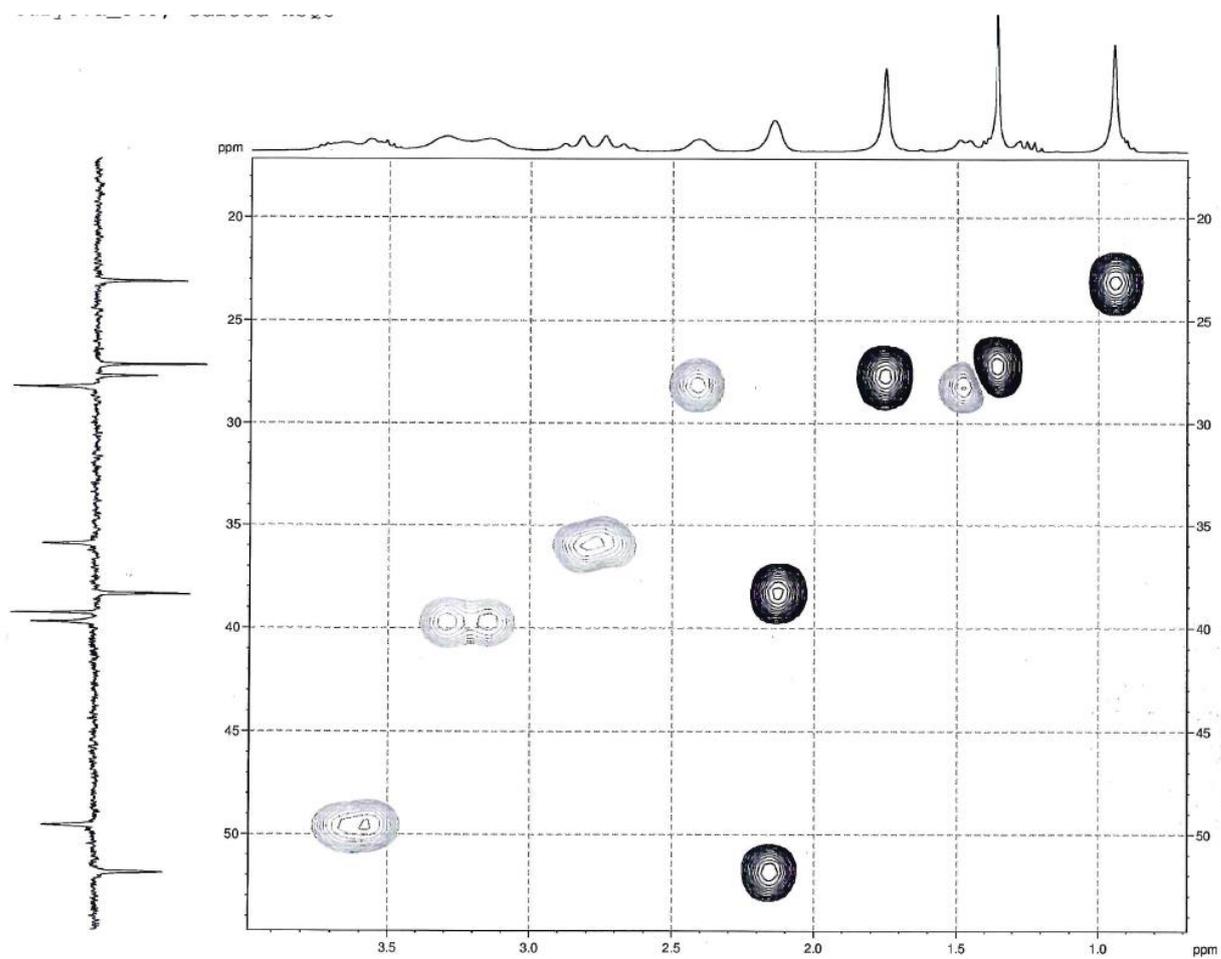


Figure S3 ^1H , ^{13}C -HSQC spectrum (300 MHz, CDCl_3) of complex **3**.

Guryeva-349, 15 mg, 30°C, CDCl₃+MeOD
NOESY, rt

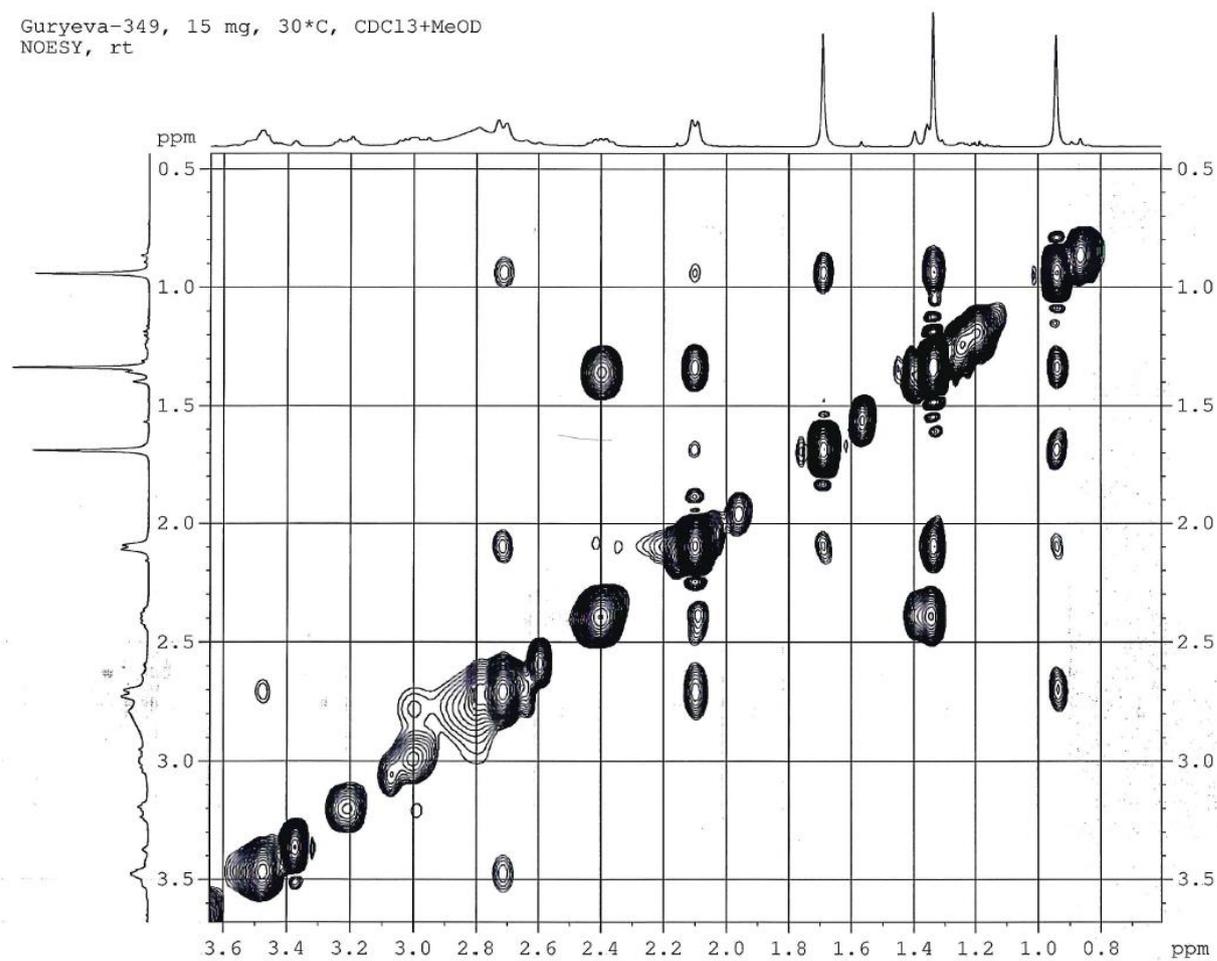


Figure S4 $^1\text{H}, ^1\text{H}$ -NOESY spectrum (300 MHz, CDCl₃) of complex **3**.