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Unusual complexation of 1-phenylthiocarbamoyl-3-(pyridine-2-yl)pyrazoline with copper(II) chloride

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5-(4-Dimethylaminophenyl)-1-phenylthiocarbamoyl-3-(pyridin-2-yl)-4,5-dihydro-1*H*-pyrazole (1) was obtained in two steps according to our previously reported procedure [E. K. Beloglazkina, D. D. Korablina, N. I. Vorozhtsov, L. A. Sviridova, A. A. Moiseeva, D. A. Skvortsov, V. B. Rybakov, A. G. Majouga, N. V. Zyk, *Arabian J. Chem*. 2019, **12**, 1050].

(E)-3-(4-Dimethylaminophenyl)-1-(pyridin-2-yl)prop-2-en-1-one (step 1). To a hot solution of hydrazine hydrate (2 equiv.) in ethanol, (*E*)-3-(4-dimethylaminophenyl)-1-(pyridin-2-yl)prop-2-en-1-one (1 equiv.) was added in several portions with stirring; then AcOH (2 equiv.) was added dropwise. The resulting mixture was refluxed for 4 h to complete the reaction (TLC control), cooled, partially evaporated and poured onto ice. The precipitate was washed with water and used immediately in subsequent reaction.

*5-(4-Dimethylaminophenyl)-1-phenylthiocarbamoyl-3-(pyridin-2-yl)-4,5-dihydro-1H-pyrazole **1** (step 2).* Freshly prepared (*E*)-3-(4-dimethylaminophenyl)-1-(pyridin-2-yl)prop-2-en-1-one (1 eq.) was dissolved in benzene, and phenyl isothiocyanate (1.5 eq.) was added. The resulting mixture was stirred with a magnetic stirrer until the reaction was completed (TLC control). The reaction mixture was concentrated *in vacuo*, and the residue was dissolved in a minimum amount of ethanol, cooled, triturated with ether to form a precipitate. The precipitate was washed with ether and recrystallized from ethyl acetate.

Light yellow crystalline powder, m.p. 194 °C. Yield: 0.48 g (1.20 mmol, 53%) from 0.65 g of (*E*)-3-(4-dimethylaminophenyl)-1-(pyridin-2-yl)prop-2-en-1-one. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.85 (s, 6 H, CH_3), 3.18 (dd, J_1 =18.5, J_2 =3.1 Hz, 1 H, 4-H), 3.93 (dd, J_1=18.6, J_2=11.3 Hz, 1 H, 4-H), 5.94 (dd, J_1=11.3, J_2=3.2 Hz, 1 H, 5-H), 6.66 (d, J=8.7 Hz, 2 H, H_{Ar}), 7.02 (d, J=8.7 Hz, 2 H, H_{Ar}), 7.13 - 7.21 (m, 1 H, H_{Ar}), 7.34 (t, J=7.7 Hz, 2 H, H_{Ar}), 7.48 (dd, J_1=7.4, J_2=5.0 Hz, 1 H, H_{Ar}), 7.55 (d, J=7.9 Hz, 2 H, H_{Ar}), 7.91 - 7.99 (m, 1 H, H_{Ar}), 8.46 (d, J=7.9 Hz, 1 H, H_{Ar}), 8.63 (d, J=4.9 Hz, 1 H, H_{Ar}), 10.22 (s, 1 H, NH) ppm. $C_{23}H_{23}N_5S$: calculated C 68.80, H 5.77, N 17.44; found C 68.79, H 5.77, N 17.27.

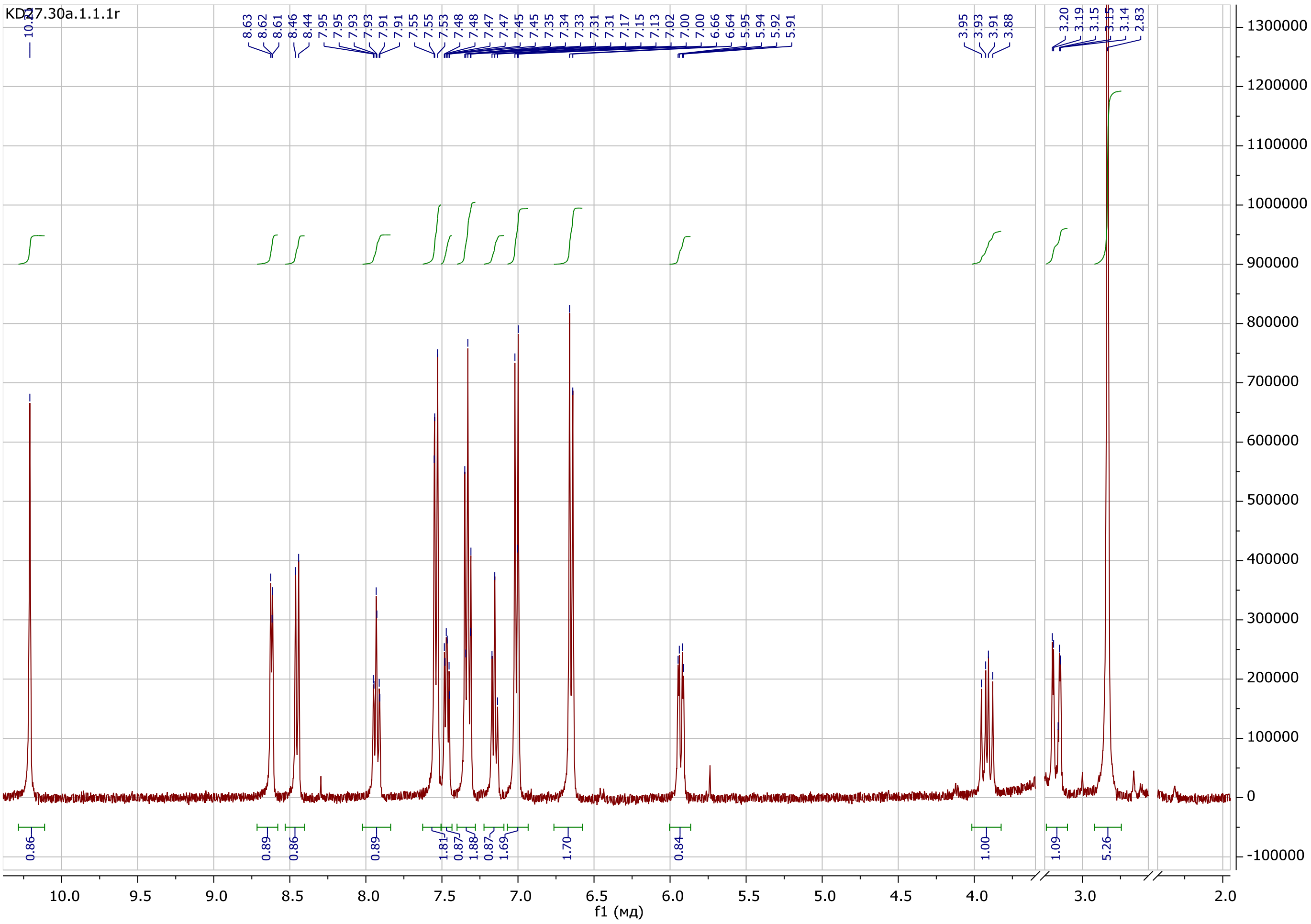

Figure S1 ^{1}H NMR spectrum of compound **1** (DMSO and water signals were removed for clarity).

Table S1. X-ray data for compound **3a**

Formula	$C_{24}H_{26}ClCuN_5OS$
Formula weight	531.55
Temperature/K	295
Wavelength/ Å	1.54186
Crystal system	monoclinic
space group	$P2_1/n$
Unit cell/Å,°	a = 8.3788(3)
	b = 11.9966(3)
	c = 23.8255(8)
	α = 90.0
	β= 96.803(3)
	γ = 90.0
Volume, $Å^3$	2378.01(13)
Z	4
Density/mg mm^{-3}	1.485
μ	3.368mm^{-1}
Size/mm^3	21 x.16 x .16
Theta range	3.73 /68.46.
Limiting indices	-9<=h<=6,
	-14<=k<=14,
	-28<=l<=28
Reflections unique	3879
Data / restraints / parameters	
3879 / 1 / 306	14297/29/1087
Goodness-of-fit on F^2	0.981
Final R indices [I>2σ(I)]	0.071
Extinction coefficient	0.0031(5)
Largest diff. peak and hole e.$Å^{-3}$	0.63 /-0.71

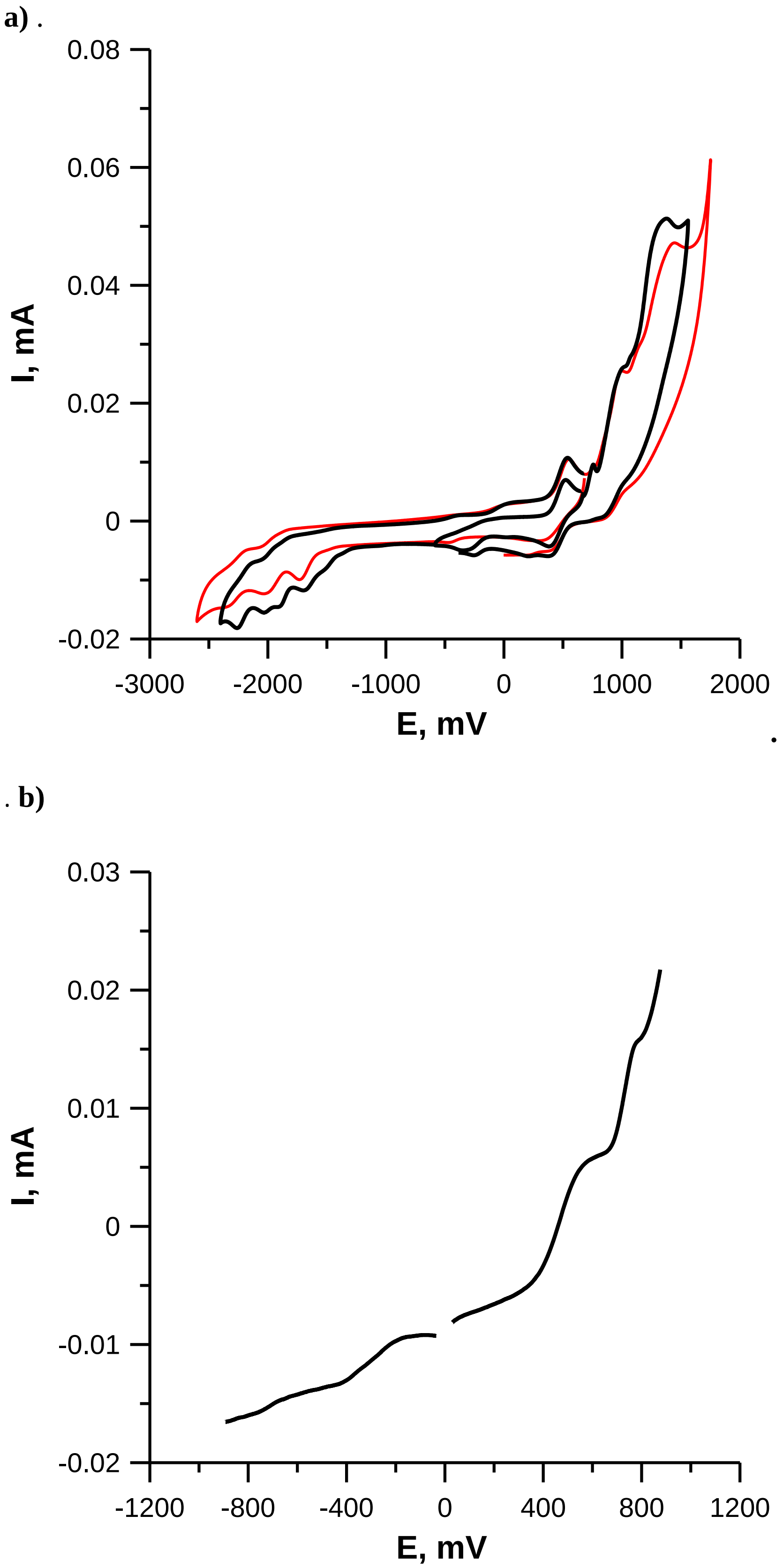

Figure S2 CVA (a) and RDE (b) for copper complex **3a** (DMF, Bu_4NClO_4) on glass carbon electrode.