

Influence of the Substituted Ethylenediamine Ligand on the Structure and Properties of $[\text{Cu}(\text{diamine})_2\text{Zn}(\text{NCS})_4]\cdot\text{Solv.}$ Compounds

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Comparison of coordination spheres in **1** and **2** with literature data

In **1** both copper(II) ion adopt 4 + 2 coordination with four short Cu–N bonds ranging from 1.993(2) to 2.031(3) Å for Cu2 and from 2.006(3) to 2.017(3) Å for Cu3 (Table S1) being similar to the Cu–N bond distances in $\text{Cu}(\text{en})_2[\text{Cd}(\text{SCN})_3]_2$ [1] (2.006(3) to 2.027(3) Å) and $[\text{Cu}(\text{en})_2(\text{SCN})_2]$ [2] (2.00 Å). In turn, those described in $[\text{Cu}(\text{en})_2\text{Cd}(\text{dca})_2(\text{SCN})_2]_n$ [3] are longer and are 2.067(3)–2.096(4) Å. The equatorial bonds of Cu–N in $\{\text{Cu}(\text{en})_2[\text{Ni}(\text{en})(\text{NCS})_2(\text{SCN})]_2\}_n$ [4] have less discrepancy than in present complex and are 2.017(2) to 2.018(2) Å. The biggest difference between Cu–N bonds was observed in **2** (from 1.980(2) to 2.085(2) Å, Table S2). Hence, for Cu–N bonds we observed significant asymmetry: shorter values were found for NH₂ groups whereas elongation by 0.1 Å occurred for groups bearing dimethyl substituents. In **1** and **2** the copper(II) coordination spheres are completed by two sulfur atoms from thiocyanato ligands occupying *trans* positions. However, for **1** these bonds are relatively short (2.9718(8) and 3.0432(9) Å for S3 and S4 atoms, respectively, Table S1) and are relatively similar to both Cu–S bond distances in $\text{Cu}(\text{en})_2[\text{Cd}(\text{SCN})_3]_2$ [1] being 3.010(1) and 3.013(1) Å. In $[\text{Cu}(\text{en})_2\text{Cd}(\text{dca})_2(\text{SCN})_2]_n$ [3] the Cu–S bonds are significantly shorter and are 2.8991(15) Å, whereas in $\{\text{Cu}(\text{en})_2[\text{Ni}(\text{en})(\text{NCS})_2(\text{SCN})]_2\}_n$ [4] the Cu–S distances are significantly longer (3.071(1) Å). All these values are substantially shorter than very long identical distances 3.3477(14) Å found in **2** which can be considered only as a semi-coordination. Such semi-coordination was observed also for $[\text{Cu}(\text{en})_2(\text{SCN})_2]$ [2] (3.27 Å) but the reported Cu–S bond lengths remains still much shorter than in **2**. In **1** Zn–N bonds are slightly shorter for non-bridging nitrogen atoms (1.950(3) and 1.965(3) Å), whereas for both bridging nitrogen atoms we found 1.969(3) Å. Contrary, in **2** these bonds are slightly shorter for nitrogen atoms from bridging thiocyanates (1.950(3) Å), whereas for nitrogen atoms from both non-bridging ligands we found 1.955(4) and 1.967(4) Å. Previously we found in the structure of $[\text{Cu}(\text{en})_2\text{Zn}(\text{NCS})_4]\cdot\text{H}_2\text{O}$ [5, 6] that the N,S-bridging activity results in the shortening of the Zn–N bonds. However, the current contradictory results for **1** and **2** proves that Zn–N bond lengths do not depend only on the bridging activity of the thiocyanate ligand but also on many subtle factors which are not fully understood.

Discussion of NCS and Zn–N–C angles

All thiocyanates are linear with N–C–S angle ranging from 177.8(3) to 179(4)° in **1** and 178.1(4) to 179.4(4)° in **2**. However, in **1** Zn–N–C angles differ significantly with the smallest values (140.9(2) and 159.7(3)° for S1 and S2 ligands, respectively) found for non-bridging ligands. The former value was found for the only ligand forming intra- and interchain hydrogen bonds. Bigger values were detected for bridging thiocyanates (171.6(4) and 165.1(3)° for S3 and S4 ligands, respectively). The latter value corresponds to anion involved in N–H...N hydrogen bond as it was observed also for S1. Hence, we can conclude that such interaction decreases Zn–N–C angle. The former angle was found for the S3 thiocyanate responsible for extended arrangement of Zn1–Cu2–Zn1[1–x, 1–y, 1–z]. In **2** the Zn–N–C angle for the bridging thiocyanate (171.9(3)°) falls into the range of terminal ligands: 161.2(4) and 178.2(4)° for N1 and N2 thiocyanates, respectively.

Table S1. Selected bonds lengths [Å] and angles [°] for 1.

Bond length					
Zn1–N2	1.950(3)	Cu2–N14 ⁱ	1.993(2)	Cu3–N24	2.006(3)
Zn1–N1	1.963(3)	Cu2–N14	1.993(2)	Cu3–N24 ⁱⁱ	2.006(3)
Zn1–N3	1.969(3)	Cu2–N11 ⁱ	2.031(3)	Cu3–N21	2.017(3)
Zn1–N4	1.969(3)	Cu2–N11	2.031(3)	Cu3–N21 ⁱⁱ	2.017(3)
		Cu2–S3 ⁱ	2.9718(8)	Cu3–S4 ⁱⁱ	3.0432(9)
		Cu2–S3	2.9718(8)	Cu3–S4	3.0432(9)
Angles					
N2–Zn1–N1	111.90(12)	N14 ⁱ –Cu2–N14	180.0	N24–Cu3–N24 ⁱⁱ	180.0
N2–Zn1–N3	114.19(12)	N14 ⁱ –Cu2–N11 ⁱ	84.92(10)	N24–Cu3–N21	84.73(13)
N1–Zn1–N3	103.74(13)	N14–Cu2–N11 ⁱ	95.08(10)	N24 ⁱⁱ –Cu3–N21	95.27(13)
N2–Zn1–N4	111.89(12)	N14 ⁱ –Cu2–N11	95.08(10)	N24–Cu3–N21 ⁱⁱ	95.27(13)
N1–Zn1–N4	109.04(12)	N14–Cu2–N11	84.92(10)	N24 ⁱⁱ –Cu3–N21 ⁱⁱ	84.73(13)
N3–Zn1–N4	105.56(15)	N11 ⁱ –Cu2–N11	180.0	N21–Cu3–N21 ⁱⁱ	180.0
		N14 ⁱ –Cu2–S3 ⁱ	87.54(8)	N24–Cu3–S4 ⁱⁱ	89.39(9)
N1–C1–S1	178.8(3)	N14–Cu2–S3 ⁱ	92.46(8)	N24 ⁱⁱ –Cu3–S4 ⁱⁱ	90.61(9)
C1–N1–Zn1	140.9(2)	N11 ⁱ –Cu2–S3 ⁱ	85.47(8)	N21–Cu3–S4 ⁱⁱ	92.00(8)
N2–C2–S2	179.4(3)	N11–Cu2–S3 ⁱ	94.53(8)	N21 ⁱⁱ –Cu3–S4 ⁱⁱ	88.00(8)
C2–N2–Zn1	159.7(3)	N14 ⁱ –Cu2–S3	92.46(8)	N24–Cu3–S4	90.61(9)
C3–S3–Cu2	110.38(12)	N14–Cu2–S3	87.54(8)	N24 ⁱⁱ –Cu3–S4	89.39(9)
N3–C3–S3	178.0(3)	N11 ⁱ –Cu2–S3	94.53(8)	N21–Cu3–S4	88.00(8)
C3–N3–Zn1	171.6(4)	N11–Cu2–S3	85.47(8)	N21 ⁱⁱ –Cu3–S4	92.00(8)
C4–S4–Cu3	85.00(11)	S3 ⁱ –Cu2–S3	180.0	S4 ⁱⁱ –Cu3–S4	180.0
N4–C4–S4	177.8(3)				
C4–N4–Zn1	165.1(3)				

ⁱ –x+1, –y+1, –z+1; ⁱⁱ –x, –y+1, –z+2.**Table S2.** Selected bonds lengths [Å] and angles [°] for 2.

Bond length			
Zn1–N3	1.950(3)	Cu2–N4	1.980(2)
Zn1–N3 ⁱ	1.950(3)	Cu2–N4 ⁱⁱ	1.980(2)
Zn1–N1	1.955(4)	Cu2–N7 ⁱⁱ	2.085(2)
Zn1–N2	1.967(4)	Cu2–N7	2.085(2)
		Cu2–S3 ⁱⁱ	3.3477(14)
		Cu2–S3	3.3477(14)
Angles			
N3–Zn1–N3 ⁱ	116.30(15)	N4–Cu2–N4 ⁱⁱ	180.0
N3–Zn1–N1	109.81(10)	N4–Cu2–N7 ⁱⁱ	95.21(9)
N3 ⁱ –Zn1–N1	109.81(10)	N4 ⁱⁱ –Cu2–N7 ⁱⁱ	84.79(9)
N3–Zn1–N2	108.22(9)	N4–Cu2–N7	84.79(9)
N3 ⁱ –Zn1–N2	108.22(9)	N4 ⁱⁱ –Cu2–N7	95.21(9)
N1–Zn1–N2	103.70(17)	N7 ⁱⁱ –Cu2–N7	180.0
		N4–Cu2–S3 ⁱⁱ	90.20(8)
N1–C1–S1	178.1(4)	N4 ⁱⁱ –Cu2–S3 ⁱⁱ	89.80(8)
C1–N1–Zn1	161.2(4)	N7 ⁱⁱ –Cu2–S3 ⁱⁱ	86.86(7)
N2–C2–S2	179.4(4)	N7–Cu2–S3 ⁱⁱ	93.14(7)
C2–N2–Zn1	178.2(4)	N4–Cu2–S3	89.80(8)
C3–S3–Cu2	113.30(12)	N4 ⁱⁱ –Cu2–S3	90.20(8)
N3–C3–S3	179.3(3)	N7 ⁱⁱ –Cu2–S3	93.14(7)
C3–N3–Zn1	171.9(3)	N7–Cu2–S3	86.86(7)
		S3 ⁱⁱ –Cu2–S3	180.0

ⁱ x, –y–1/2, z ⁱⁱ –x, –y, –z+1.

Structure of compound 3

The crystal structure of the compound **3** is unknown (see Experimental). The diagnostic criteria, which comes from infrared spectroscopy and allow to distinguish the type of NCS group (N-bonded, S-bonded or bridging) in metal complexes, should be used with extreme caution. So, considering the data given above, we can propose at least a two possible structures for that compound with the formulas $[\text{Cu}(\text{N-Me-en})_2\text{Zn}(\text{NCS})_4] \cdot \frac{1}{2}\text{H}_2\text{O}$ (1D) or $[\text{Cu}(\text{N-Me-en})_2] \cdot [\text{Zn}(\text{NCS})_4] \cdot \frac{1}{2}\text{H}_2\text{O}$ (ionic-pair).

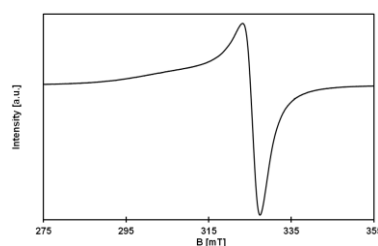


Figure S1. EPR spectrum of **3**. Some experimental conditions: powder sample, room temperature, X-band (9.32434 GHz). The simulated g -values, $g_{\parallel} = 2.190$ and $g_{\perp} = 2.045$, and calculated $G = 4.2$, correspond to $d^x^2-y^2$ ground state of copper(II) ion.

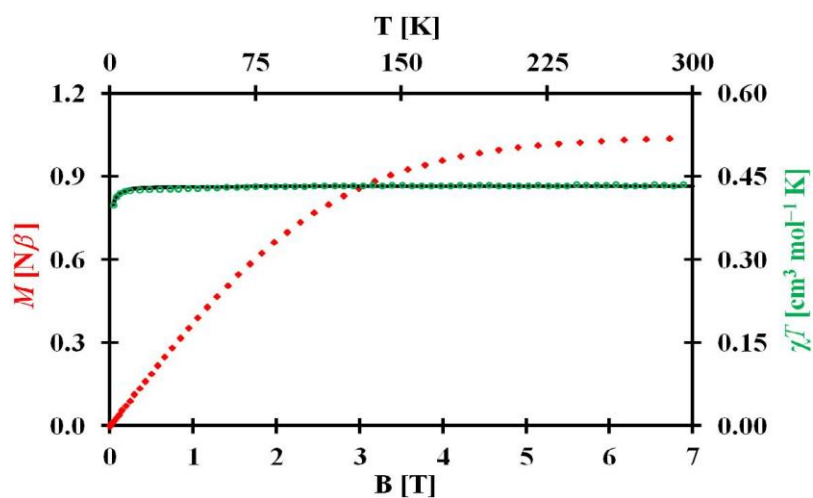


Figure S2. Magnetic properties of **3**: $\chi T(T)$ at $H_{ac} = 1$ kOe and $M(\mu_0 H)$ at $T = 1.8$ K. The solid black line is the best fit for $\chi T(T)$ to the Curie-Weiss ($C = 0.433$ cm³ mol⁻¹, $\theta = -0.15$ K, $g = 2.148$, $z' = -0.211$ cm⁻¹ and $R = 3.63 \cdot 10^{-6}$). The solid black line is the best fit to the Curie-Weiss model for $\chi T(T)$.

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[The numbers in brackets indicate the position of the citation in the main text.]

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