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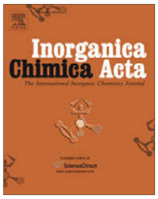

Supramolecular diversity and magnetic properties of novel heterometallic Cu(II)/Cr(III) complexes prepared from copper powder, Reineckes salt and ethylenediamine

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ABSTRACT

Three novel heterometallic complexes $[Cu(en)_2Cr(NCS)_4(NH_3)_2][Cr(NCS)_4(NH_3)_2] \cdot 6dmf$ (**1**), $[Cu(en)_2Cr(NCS)_4(NH_3)_2](OAc)$ (**2**) and $[\{Cu(en)_2\}_3\{Cr(NCS)_4(NH_3)_2\}_2(NCS)_2](NCS)_2$ (**3**) have been synthesized in a one-pot reaction from copper powder, Reineckes salt, NH_4X [$X^- = OAc^-$ (**2**), NCS^- (**3**)] in a dmf (**1**) or CH_3CN (**2**, **3**) solution of ethylenediamine (en). X-ray studies showed that **1** and **2** consist of cationic polymeric chains, formed by $Cu(en)_2{}^{2+}$ and $Cr(NCS)_4(NH_3)_2{}^-$ building blocks that bridged through thiocyanate anions. In both complexes, distinct hydrogen bonds are present and serve to increase the dimensionality of the compound from one to two (in **1**) or three (in **2**). The main structural feature of **3** is the pentanuclear Cu_3Cr_2 cation which is H-bonded with uncoordinated thiocyanate groups generating a 3D supramolecular assembly. The shortest Cu···Cr distances are 5.840(1) Å for **1**, 5.856(1) and 6.018(3) Å for **2** and 6.009(9) and 6.465(9) Å for **3**. Compounds **1** and **2** are essentially paramagnets whereas compound **3** shows a weak antiferromagnetic coupling. The magnetic properties are simulated and discussed in terms of the structural features.

1. Introduction

Significant research efforts in the design and preparation of heterometallic systems are stimulated by the ability of these compounds to reveal intriguing crystal structures and attractive magnetic properties, since the combination of two different spin carriers represents a perfect model for the studies of exchange interactions. In order to obtain such complexes with potentially interesting magnetic behavior the search of appropriate units as building blocks is highly important. It is well known that the thiocyanate anion can act as a bridge between either identical or different metal ions. Nevertheless, the thiocyanate complexes have rarely been used in the assembling of heterometallic compounds [1]. The present work is focused on the anion of the Reineckes salt, $[Cr(NCS)_4(NH_3)_2]^-$, since it presents a multi-linking function (from one to four) by joining different metal centres and it may also participate in hydrogen bonding to generate fascinating supramolecular networks. Albeit, the number of compounds based on the $[Cr(NCS)_4(NH_3)_2]^-$ anion is very limited and only a few reports devoted to this building block have been published to date. One of them is the work of P. Day and co-workers describing the use of the Reineckes salt and its derivatives to obtain a series of charge transfer salts [2]. Moreover, examples of heterometallic systems containing this building block have only been reported in five compounds: $[(HL)Cu(SCN)Cr(NCS)_3(NH_3)_2] \cdot dmf$ (H_2L = 3,3′-trimethylenedinitrilobis(2-butanoneoxime)) [3]; $[Ni_2(H_2O)_2(fsal\text{-}33)\{Cr(NCS)_4(NH_3)_2\}_2] \cdot 2H_2O$ (fsal-33 is a dianionic macrocyclic binucleating Schiff-base ligand obtained by condensation of 2,6-diformyl-4-methyl-phenol with 1,3-propylenediamine) [4]; $[In(DMSO)_4(H_2O)_2][Cr(NCS)_4(NH_3)_2]_3$ [5]; $[W_2(\mu\text{-}N_2CHN_2)(dppe)_4Br_2]^+[Cr(NH_3)_2(NCS)_4]^- \cdot {}^1/_3CH_2Cl_2$ (dppe = 1,2-bis(diphenylphosphino)-ethane) [6] and $[\{Cu(enac)\}_2Cr(NCS)_4(NH_3)_2][Cr(NCS)_4(NH_3)_2]_3 \cdot 4(CH_3)_2CO$ (enac = 4,6,6-trimethyl-3,7-diazanon-3-ene-1,9-diamine) [7]. The most popular two-step synthetic approach for the preparation of heterometallic complexes is the metalloligand strategy, based on

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the interaction between a preformed complex with free chelating sites, used as the ligand, and a complex with labile ligands, playing the role of the metal [8].

It has been shown that the use of a synthetic strategy named "direct synthesis of coordination compounds", based on the one-step self-assembly of building blocks formed in situ, results in a series of heterometallic complexes with complicated architectures and intriguing physico-chemical properties [9]. This approach consists in the reaction of a zerovalent metal or its oxide with a second metal center in the same reaction vessel to generate in situ a metal-containing ligand and has allowed the obtaining of a wide range of heterometallic compounds with aprotic ligands using the following system (L = amines; Solv = non-aqueous solvents) [10]:

$$\mathrm{M}^0_{(1)}/\mathrm{M}_{(1)}\mathrm{O} - \mathrm{M}_{(2)}\mathrm{O}/\mathrm{M}_{(2)}\mathrm{X}_2 - \mathrm{L} - \mathrm{NH_4X} - \mathrm{Solv} \quad \text{(in air)}$$

In this study, while developing our synthetic method, we propose to combine this strategy with the metalloligand approach by using the Reineckes salt as the source of the second metal:

$$\mathrm{M}^0 - \mathrm{NH_4[Cr(NCS)_4(NH_3)_2]} - \mathrm{L} - \mathrm{NH_4X} - \mathrm{Solv} \quad \text{(in air)}$$

In the present work we report the synthesis and crystal structure of three novel Cu(II)/Cr(III) supramolecular assemblies as well as their spectroscopic and magnetic properties.

2. Experimental

2.1. General

All chemicals were of reagent grade and used as received. All experiments were carried out in air. Elemental analyses were performed with a Vario EL III Universal CHNOS Elemental Analyzer (for C, H, N, S) in the Faculty of Chemistry, University of Wroclaw. Quantitative determinations of the metals were performed spectrophotometrically for chromium (as chromate at $\lambda = 370$ nm) and by atomic absorption spectroscopy for copper.

2.2. Preparation

2.2.1. $[Cu(en)_2Cr(NCS)_4(NH_3)_2][Cr(NCS)_4(NH_3)_2] \cdot 6dmf$ (**1**)

Copper powder (0.04 g, 0.63 mmol), $NH_4[Cr(NCS)_4(NH_3)_2] \cdot H_2O$ (0.446 g, 1.26 mmol), dmf (20 mL) and ethylenediamine (0.085 mL, 1.26 mmol) were placed in a flask in the above order, heated to 60 °C and magnetically stirred until total dissolution of the copper powder (15 min). The solution was filtered and subsequently violet crystals suitable for X-ray crystallography separated within several hours after the successive addition of 5 ml of Pr^iOH into the resulting violet solution. Crystals were filtered off, washed with dry Pr^iOH and finally dried in vacuo at room temperature. Yield: 0.47 g, 59%. *Anal.* Calc. for $C_{30}H_{70}N_{22}S_8O_6Cr_2Cu_1$: C, 28.62; H, 5.60; N, 24.47; S, 20.37; Cr, 8.26; Cu, 5.05. Found: C, 28.5; H, 5.5; N, 24.4; S, 20.3; Cr, 8.2; Cu, 5.0%. IR (KBr, cm^{-1}): 3300(m), 3244(sh), 3179(w), 2960(w), 2130(vs), 2090(vs), 1660(s), 1590(sh), 1390(m), 1410(sh), 1250(s), 1280(sh), 1140(w), 1040(m), 980(w), 720(m), 680(sh). The compound is soluble in CH_3CN, dmso and dmf.

2.2.2. $[Cu(en)_2Cr(NCS)_4(NH_3)_2](OAc)$ (**2**)

Copper powder (0.16 g, 2.5 mmol), $NH_4[Cr(NCS)_4(NH_3)_2] \cdot H_2O$ (0.22 g, 0.62 mmol), NH_4OAc (0.34 g, 4.41 mmol), CH_3CN (20 mL) and ethylenediamine (0.34 mL, 5.1 mmol) were placed in a flask in the above order, heated to 60 °C and magnetically stirred until total dissolution of the copper powder (15 min). In the course of the reaction a dark-blue precipitate, later found to be $Cu(en)_2(OAc)_2$, precipitated. The resulting reaction mixture was filtered and this solution was left in air to evaporate and dark-violet crystals of **2** suitable for X-ray crystallography appeared after several days. The crystals were filtered off and dried in vacuo at room temperature. Yield: 0.22 g, 63%. *Anal.* Calc. for $C_{10}H_{25}N_{10}S_4O_2CrCu$: C, 21.40; H, 4.49; N, 24.96; S, 22.86; Cr, 9.27; Cu, 11.32. Found: C, 21.3; H, 4.5; N, 25.0; S, 22.9; Cr, 9.3; Cu, 11.3%. IR (KBr, cm^{-1}): 3300(w), 2120(vs), 2090(sh), 1590(s), 1560(sh), 1400(s), 1310(m), 1270(m), 1100(m), 1050(s), 1020(sh), 980(w), 710(m), 670(sh) cm^{-1}. The compound is soluble in CH_3CN, dmso and dmf.

2.2.3. $[\{Cu(en)_2\}_3\{Cr(NCS)_4(NH_3)_2\}_2(NCS)_2](NCS)_2$ (**3**)

Copper powder (0.16 g, 2.5 mmol), $NH_4[Cr(NCS)_4(NH_3)_2] \cdot H_2O$ (0.223 g, 0.63 mmol), NH_4NCS (0.335 g, 4.4 mmol), CH_3CN (20 mL) and ethylenediamine (0.34 mL, 5.1 mmol) were placed in a flask in the above order, heated to 60 °C and magnetically stirred until total dissolution of the copper metal was observed (20 min). The solution was filtered and dark-violet crystals of **3** suitable for X-ray crystallography were formed immediately after filtration. The crystals were filtered off and dried in vacuo at room temperature. Yield: 0.37 g, 82%. *Anal.* Calc. for $C_{24}H_{60}N_{28}S_{12}Cr_2Cu_3$: C, 20.30; H, 4.26; N, 27.61; S, 27.09; Cr, 7.32; Cu, 13.42. Found: C, 20.2; H, 4.2; N, 27.5; S, 27.1; Cr, 7.5; Cu, 13.5%. IR (KBr, cm^{-1}): 3290(m), 3160(m), 2970(w), 2910(w), 2100(vs), 2070(sh), 1590(s), 1470(w), 1370(w), 1330(w), 1280(m), 1160(w), 1100(m), 1050(vs), 980(m), 760(sh), 730(sh), 710(m), 630(w) cm^{-1}. The compound is soluble in CH_3CN, dmso, dmf and H_2O.

2.3. Crystal structure determination

Well-shaped crystals of **1**–**3** were suitable for X-ray analysis. Crystal data and details of structure solutions are summarized in Table 1. X-ray diffraction data were collected on a Rigaku AFC7 diffractometer (for **1**), on an XCalibur 3 diffractometer (for **2**) and on a Siemens P3/PC diffractometer (for **3**), all equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Data sets were corrected for Lorentz and polarization effects and for the effects of absorption. The structures were solved by direct methods and refined by full-matrix least-squares methods using the SHELXTL package [11]. All non-hydrogen atoms were refined within anisotropic approximation. The H atoms were located from the difference map of electron density and refined with a riding model with $U_{iso} = nU_{eq}$ of carrier non-hydrogen atom ($n = 1.5$ for methyl and 1.2 for other H-atoms).

2.4. Physical measurements

Infrared spectra were recorded as KBr pellets on a UR-10 spectrophotometer in the 4000–400 cm^{-1} region using conventional techniques. UV/Vis spectra were recorded on a Perkin–Elmer Lambda 900 spectrophotometer using the diffuse-reflectance technique. The EPR spectra were recorded on a Bruker ESP 300E (Bruker, Germany) spectrometer operating at X-band and equipped with the Bruker NMR gaussmeter ER 035 M and the Hewlett-Packard microwave frequency counter HP 5350B. Magnetic susceptibility data were measured on polycrystalline samples with a SQUID magnetometer (Quantum Design MPMS XL-5) in the temperature range 1.8–300 K with an applied magnetic field of 0.5 T. Diamagnetic corrections for the samples were calculated with the Pascal's constants tables [12]. Experimental susceptibilities were also corrected for the sample holders previously measured in the same conditions. Isothermal magnetizations were measured at 2 K with magnetic fields up to 5 T on the same samples.

3. Results and discussion

3.1. Synthesis and spectroscopic characterization

The reaction of copper powder, Reineckes salt and NH_4X [X = OAc (**2**), NCS (**3**)] with ethylenediamine in dmf (**1**) or CH_3CN