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N,*N*-Dimethylethylenediamine in direct and direct template syntheses of Cu(II)/Cr(III) complexes

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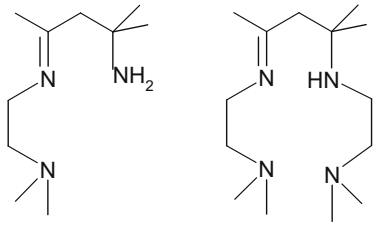
ABSTRACT

Four new heterometallic Cu(II)/Cr(III) complexes with *N*,*N*-dimethylethylenediamine (dmen) and its novel Schiff-base derivatives, *N*′-[(1*Z*)-3-amino-1,3-dimethylbutylidene]-*N*,*N*-dimethylethane-1,2-diamine (dmenac) and *N*′-((1*Z*)-3-{[2-(dimethylamino)ethyl]amino}-1,3-dimethylbutylidene)-*N*,*N*-dimethylethane-1,2-diamine ($dmen_2ac$), have been easily prepared by self-assembly and characterized by spectroscopic methods and single crystal X-ray analysis. The structures of all the complexes are assisted by numerous hydrogen bonds that provide a web of interactions and mould the supramolecular architectures of the compounds. Variable-temperature (1.8–300 K) magnetic susceptibility measurements reveal Curie-Weiss paramagnetic behavior of all the compounds, supported by EPR studies.

1. Introduction

In the recent history of coordination chemistry a great deal of attention has been devoted to heterometallic complexes. The combination of two dissimilar metal centers can lead to fascinating structures and new topological features with the promise for interesting magnetic, magneto-optical and optoelectronic properties [1–7]. In spite of the advantages of more popular and successful metalloligand strategies [8], the search and elaboration of novel approaches to the synthesis of heterometallic complexes is still of current importance. In recent years one-pot synthesis that allows all the transformations to occur without isolation of intermediates has attracted much interest [9–11] because it provides a simple and efficient route to a variety of compounds starting from commercially available and relatively simple precursors. Recently, we have shown that the use of anionic complexes as a source of metalloligands (Reineckes salt, $(NH)_4[Cr(NCS)_4(NH_3)_2 \cdot H_2O]$, was taken as a representative example) in the direct synthesis of Cu(II)/Cr(III) heterometallic compounds holds great promise in the preparation of novel supramolecular polymetallic assemblies [12–14]. To explore new possibilities of our synthetic method, we have used zerovalent copper, Reinecke's salt, ammonium thiocyanate (for **2** and **4**), acetone (for **3** and **4**) and *N*,*N*-dimethylethylenediamine (dmen) as starting reagents. These reactions produced four novel heterometallic compounds $[Cu(dmen)_2(dmf)_2][Cr(NCS)_4(NH_3)_2]_2 \cdot 6dmf$ (**1**), $[Cu(dmen)_2(NCS)][Cr(NCS)_4(NH_3)_2]$ (**2**), $[Cu(dmenac)(NCS)(\mu\text{-}SCN)Cr(NCS)_3(NH_3)_2]$ (**3**) and $[Cu(dmen_2ac)(NCS)][Cr(NCS)_4(NH_3)_2] \cdot 6dmso$ (**4**), containing new open-chain Schiff-base ligands, dmenac (*N*′-[(1*Z*)-3-amino-1,3-dimethylbutylidene]-*N*,*N*-dimethylethane-1,2-diamine) and $dmen_2ac$(*N*′-((1*Z*)-3-{[2-(dimethylamino)ethyl]amino}-1,3-dimethylbutylidene)-*N*,*N*-dimethylethane-1,2-diamine).



Herein, we describe the synthesis, spectroscopic, magnetic and structural characterization of 1–4.

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2. Experimental

2.1. General

All chemicals were of reagent grade purity and were used without further purification. All experiments were carried out in air. Elemental analyses were performed by atomic absorption spectroscopy for copper and spectrophotometrically for chromium (as chromate at λ = 370 nm) at the Department of Chemistry, National Taras Shevchenko University of Kyiv and with a vario EL III Universal CHNOS Elemental Analyzer (for C, H, N, S) at the Faculty of Chemistry, University of Wroclaw.

2.2. Preparation

Copper powder (1.26 mmol for **1**–**3**; 2.5 mmol for **4**), $NH_4[Cr(NCS)_4(NH_3)_2]\cdot H_2O$ (2.52 mmol for **1**, **3**; 1.26 mmol for **2**; 0.625 mmol for **4**), NH_4NCS (1.26 mmol for **2**; 4.375 mmol for **4**), non-aqueous solvent (20 mL, dmf for **1**, CH_3CN for **2**, CH_3OH for **3**, dmso for **4**), acetone (5 mL, for **3** and **4**) and *N*,*N*-dimethylethylenediamine (2.25 mmol for **1**–**3**; 5.0 mmol for **4**) were placed in a flask in the above order, heated to 50–60 °C and magnetically stirred until total dissolution of the copper powder was observed (10–15 min). Crystals suitable for X-ray crystallography were formed after several days (**2**), separated after several days following the successive addition of 5 ml of Pr^iOH (**1** and **4**), deposited after slowly evaporation of the solvent at room temperature (**3**). The crystals were filtered off and dried in vacuo at room temperature. The compounds are soluble in CH_3CN, dmso and dmf.

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

Yield: 1.24 g, 67% (per copper). *Anal. Calc.* for $C_{40}H_{92}N_{24}S_8O_8Cr_2Cu$: C, 32.88; H, 6.34; N, 23.00; S, 17.55; Cr, 7.12; Cu, 4.35. Found: C, 32.7; H, 6.5; N, 22.8; S, 17.7; Cr, 7.3; Cu, 4.4%. IR (KBr, cm^{-1}): 3330(w), 3250(w), 3180(w), 2950(w), 2090(vs), 1665(s), 1595 (m), 1470(m), 1400(m), 1255(s), 1150(m), 1110(m), 1060(m), 1010(m), 950(w), 790(w).

2.2.2. $[Cu(dmen)_2(NCS)][Cr(NCS)_4(NH_3)_2]$ (**2**)

Yield: 0.61 g, 78% (per copper). *Anal. Calc.* for $C_{13}H_{30}N_{11}S_5CrCu$: C, 25.33; H, 4.91; N, 25.00; S, 26.01; Cr, 8.44; Cu, 10.31. Found: C, 25.1; H, 5.1; N, 24.8; S, 26.2; Cr, 8.6; Cu, 10.2%. IR (KBr, cm^{-1}): 3330(w), 3240(w), 3150(w), 2980(w), 2100(vs), 2070(vs), 1660(w), 1590(s), 1465(s), 1410(w), 1260(s), 1190(m), 1140(s), 1120(s), 1060(m), 1030(w), 1010(s), 950(w), 860(w), 840(w), 790(s).

2.2.3. $[Cu(dmenac)(NCS)(\mu\text{-}SCN)Cr(NCS)_3(NH_3)_2]$ (**3**)

Yield: 0.51 g, 65% (per copper). *Anal. Calc.* for $C_{15}H_{29}N_{10}S_5CrCu$: C, 28.81; H, 4.67; N, 22.40; S, 25.64; Cr, 8.32; Cu, 10.16. Found: C, 28.6; H, 4.8; N, 22.2; S, 25.8; Cr, 8.5; Cu, 10.1%. IR (KBr, cm^{-1}): 3300(w), 3240(w), 3160(w), 2980(w), 2140(vs), 2120–2070 (vs), 1660(s), 1600(s), 1480(m), 1415(w), 1380(m), 1260(s), 1195(m), 1130(w), 1110(m), 1030(m), 1020(s), 980(w), 960(m), 910(w), 790(w), 775(w).

2.2.4. $[Cu(dmen_2ac)(NCS)][Cr(NCS)_4(NH_3)_2] \cdot 6dmso$ (**4**)

Yield: 0.52 g, 71% (per copper). *Anal. Calc.* for $C_{31}H_{74}N_{11}S_{11}O_6CrCu$: C, 31.95; H, 6.40; N, 13.22; S, 30.27; Cr, 4.46; Cu, 5.45. Found: C, 31.8; H, 6.6; N, 13.0; S, 30.4; Cr, 4.6; Cu, 5.5%. IR (KBr, cm^{-1}): 3320(w), 3230(w), 3160(w), 2980(w), 2100(vs), 1650(s), 1590(m), 1550(w), 1480(w), 1280(s), 1230(w), 1170(w), 1080(w), 1030(s), 960(w), 845(w), 790(w).

2.3. Physical measurements

Infrared spectra were recorded as KBr discs 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.

Table 1
Crystal data and structure refinement for **1**–**4**.

	1	**2**	**3**	**4**
Empirical formula	$C_{40}H_{92}N_{24}S_8O_8Cr_2Cu$	$C_{13}H_{30}N_{11}S_5CrCu$	$C_{15}H_{29}N_{10}S_5CrCu$	$C_{31}H_{74}N_{11}S_{11}O_6CrCu$
M	1461.40	616.32	625.32	1165.26
Crystal system	triclinic	orthorhombic	orthorhombic	monoclinic
Space group	$P\bar{1}$	$Pna2_1$	*Pbca*	$P2_1/c$
a (Å)	13.9396(8)	16.166(3)	15.4491(6)	17.983(2)
b (Å)	13.9485(8)	12.290(4)	13.3876(4)	14.8012(15)
c (Å)	19.9961(7)	13.952(3)	26.9866(10)	22.371(3)
α (°)	90.635(4)	90.000	90.000	90.000
β (°)	90.167(4)	90.000	90.000	102.532(12)
γ (°)	113.099(3)	90.000	90.000	90.000
V (Å^3)	3575.9(3)	2772.0(12)	5581.5(3)	5812.5(13)
Z	2	4	8	4
D_{calc} (g cm^{-3})	1.357	1.477	1.488	1.332
μ (mm^{-1})	0.886	1.559	1.549	0.993
F(000)	1538	1272	2576	2456
Data collection				
T (K)	294(2)	294(2)	294(2)	294(2)
2θ scan range (°)	2.57–25.00	3.02–30.00	2.52–27.50	2.70–27.50
h, *k*, *l* ranges	−16 + 13, ±16, −23 + 20	−14 + 22, −11 + 17, −17 + 19	−20 + 11, −17 + 9, ±35	±23, −15 + 19, −27 + 29
Reflections collected	24900	10826	21888	29296
Independent reflections [R_{int}]	7366 [0.052]	4847 [0.017]	4342 [0.099]	5546 [0.071]
Refinement				
Final *R* indices	R_1 = 0.0915	R_1 = 0.0334	R_1 = 0.0718	R_1 = 0.0537
[$I > 2\sigma(I)$]	wR_2 = 0.2482	wR_2 = 0.0795	wR_2 = 0.1251	wR_2 = 0.0999
R indices	R_1 = 0.1442	R_1 = 0.0512	R_1 = 0.1172	R_1 = 0.1460
(all data)	wR_2 = 0.2814	wR_2 = 0.0852	wR_2 = 0.1456	wR_2 = 0.1208
Goodness-of-fit (GOF) (*F*)	1.063	0.917	1.103	0.804
$\Delta(\rho)$ (e Å^{-3})	+2.171, −0.750	+0.473, −0.250	+0.513, −0.558	+0.916, −0.540