

Synthesis and Structure of Heterometallic Chromium(III) Complexes with Ethylenediaminetetraacetic Acid

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Abstract—The complexes $[M(\text{Tsc})_2][\text{Cr}(\text{Edta})]_2$, where M is Ni, Cu; Tsc is thiosemicarbazide; Edta^{4-} is the ethylenediaminetetraacetate anion, were synthesized and characterized by X-ray diffraction. The ionic structures are composed of the $[M(\text{Tsc})_2]^{2+}$ cations and $[\text{Cr}(\text{Edta})]^-$ anions with a component ratio of 1 : 2. The cation has a distorted *trans*-square coordination. The carboxyl groups of the H_4Edta molecule are deprotonated and the ligand is attached to the Cr atom in the hexadentate chelating mode. The cations and anions are linked by a system of hydrogen bonds.

We have studied a number of heterometallic bismuth [1] and chromium [2] complexes the interest in which stems from the design of new oxide materials. The thermal decomposition of the complexes results in the formation of ceramic materials and thin films, which can be used as superconductors [3], ionic conductors [4], and catalysts [5].

This communication reports the data on the synthesis and structure of new heterometallic Cr(III) complexes in which the ethylenediaminetetraacetate anion (Edta^{4-}) acts as a ligand and a nickel(II) or copper(II) complex with thiosemicarbazide (Tsc) is the counter-ion.

EXPERIMENTAL

Synthesis of $[\text{Ni}(\text{Tsc})_2][\text{Cr}(\text{Edta})]_2$ (I). $[\text{Cr}(\text{HEdta})(\text{H}_2\text{O})]$ (1.43 g, 4 mol), prepared by a reported procedure [6], was dissolved in 25 ml of boiling water. $(\text{NiOH})_2\text{CO}_3$ (~0.25 g, ~1 mol) was added to the solution and the mixture was heated at 95°C for 1 h. The excess of $(\text{NiOH})_2\text{CO}_3$ was filtered off. A solution of Tsc (~0.36 g, ~4 mol), prepared by dissolving Tsc with heating in 25 ml of water and 60 ml of ethanol, was added to this solution cooled to 50–60°C. The mixture was heated at reflux on a water bath for ~30 min. Cherry-colored crystals precipitated from the hot solution. The crystals were washed with ethanol and ether and dried in air. The product yield was 0.95–1.00 g (52%–54%).

For $\text{C}_{22}\text{H}_{35}\text{Cr}_2\text{N}_{10}\text{NiO}_{16}\text{S}_2$

anal. calcd. (%): Cr, 11.27; C, 28.65; H, 3.82; N, 15.18.

Found (%): Cr, 11.25; C, 28.72; H, 3.80; N, 15.14.

Synthesis of $[\text{Cu}(\text{Tsc})_2][\text{Cr}(\text{Edta})]_2$ (II). Compound **II** was prepared similarly to **I**, except that the solution was cooled on an ice bath after the addition of Tsc. The dark red crystals were filtered after 12–24 h, washed with water, ethanol, and ether, and dried at room temperature. The product yield was 1.47–1.50 g (75%).

For $\text{C}_{22}\text{H}_{35}\text{Cr}_2\text{N}_{10}\text{CuO}_{16}\text{S}_2$

anal. calcd. (%): Cr, 11.22; C, 28.50; H, 3.80; N, 15.11.

Found (%): Cr, 11.20; C, 28.44; H, 4.02; N, 14.99.

X-Ray diffraction analysis. The unit cell parameters and experimental reflections for the crystals of **I** and **II** were measured on a Stoe Imaging Plate Diffractometer System (MoK_α radiation, graphite monochromator) at room temperature. The crystal–CCD detector distance was 80 mm for **I** and 70 mm for **II**. The crystal data and experiment details for compounds **I** and **II** are summarized in Table 1.

The structures were solved by the direct method and refined by the full-matrix least-squares method in the anisotropic approximation for non-hydrogen atoms and in the isotropic approximation for hydrogen atoms using the SHELX97 program package [7]. The H atoms were localized objectively from difference Fourier synthesis and refined in the rigid-body model.

The final position and equivalent isotropic thermal parameters for compound **II** are presented in Table 2 (those for **I** are deposited with the Cambridge Structural Database, CCDC no. 254321). Selected interatomic distances and angles for both structures are presented in Table 3.

Table 1. Crystal data, X-ray experiment details, and refinement parameters for structures **I** and **II**

Parameter	Value	
	I	II
<i>M</i>	921.42	926.26
System	Monoclinic	Monoclinic
Space group	<i>P2₁/n</i>	<i>P2₁/n</i>
<i>a</i> , Å	8.307(2)	8.331(2)
<i>b</i> , Å	10.290(2)	10.340(2)
<i>c</i> , Å	19.093(4)	19.066(4)
β, deg	99.48(3)	99.06(3)
<i>V</i> , Å ³	1609.8(6)	1621.9(6)
<i>Z</i> ; ρ(calcd), g/cm ³	2; 1.901	2; 1.897
μ, mm ⁻¹	1.464	1.528
<i>F</i> (000)	944	946
θ range, deg	2.16–24.09	2.16–25.94
Range of indices	–9 ≤ <i>h</i> ≤ 9 –11 ≤ <i>k</i> ≤ 11 –21 ≤ <i>l</i> ≤ 21	–10 ≤ <i>h</i> ≤ 10 –12 ≤ <i>k</i> ≤ 12 –23 ≤ <i>l</i> ≤ 23
The number of measured/independent reflections	6319/1843 (<i>R</i> _{int} = 0.0890)	16758/3131 (<i>R</i> _{int} = 0.0693)
The completeness of the θ angle	71.9%	98.6%
The number of refined parameters	241	241
GOOF	0.969	0.869
<i>R</i> -factor (<i>I</i> > 2σ(<i>I</i>))	<i>R</i> ₁ = 0.0434 <i>wR</i> ₂ = 0.0980	<i>R</i> ₁ = 0.0356 <i>wR</i> ₂ = 0.0802
<i>R</i> -factor for all reflections	<i>R</i> ₁ = 0.0680 <i>wR</i> ₂ = 0.1082	<i>R</i> ₁ = 0.0521 <i>wR</i> ₂ = 0.0864
Δρ _{max} /Δρ _{min} , eÅ ⁻³	0.560/–0.473	0.458/–0.440

RESULTS AND DISCUSSION

The isostructural crystals of compounds **I** and **II** are constructed from [M(Tsc)₂]²⁺ cations (M = Ni, Cu) and [Cr(Edta)][–] anions linked by a system of hydrogen bonds. Figure 1 shows a fragment of structure **II** with numbering of independent atoms.

In the complex cation, the Ni(Cu) atoms occupy a special position at an inversion center and have a distorted square coordination formed by pairs of nitrogen atoms of the amino groups and sulfur atoms of the Tsc molecules. The M–N and M–S distances are 1.872(5) and 2.175(2) Å in **I**, and 1.946(3) and 2.276(1) Å in **II**. A similar structure of the [M(Tsc)₂]²⁺ *trans*-fragments has been found in [[Cu(Tsc)₂](NO₃)₂] (**III**) [8] and [Ni(Tsc)₂][C₆H₄(CO₂)₂-1,4] [9]. In complexes **I** and **II**, no contacts shorter than 3.9 Å occur in apical directions, whereas in compound **III**, the apical positions are

occupied by the oxygen atoms of the NO₃ groups located at Cu–O distances of 2.773 Å; therefore, copper(II) coordination can be described as 4+2.

The structure of the anion in **I**, **II** represents a rather rare example of hexadentate Edta^{4–} coordination in a Cr(III) complex giving rise to five chelate rings (Fig. 1). Only one compound with such structure is known, K[Cr(Edta)] · 2H₂O [10]. Chromium(III) complexes with a pentadentate coordination of Edta [11] or related ligands with longer diamine or carboxylate chains [12] are more stable.

The Cr(III) coordination polyhedron in **I** and **II** is a distorted octahedron. The equatorial plane accommodates two nitrogen atoms (Cr–N, 2.039(5) and 2.062(4) Å for **I**; 2.050(2) and 2.069(2) Å for **II**) and two oxygen atoms of the carboxyl groups of the *G*-rings (according to a reported classification [13]). The Cr–O(*G*) dis-

Table 2. Atomic coordinates ($\times 10^4$) and equivalent thermal parameters U_{eq} ($\times 10^3$) for **II**

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}, \text{\AA}^2$
Cu(1)	0	0	0	24(1)
Cr(1)	4511(1)	276(1)	2978(1)	18(1)
S(1)	2695(1)	243(1)	420(1)	33(1)
O(1)	2871(3)	1627(2)	4647(1)	44(1)
O(2)	9028(3)	357(3)	3974(2)	53(1)
O(3)	6616(3)	842(2)	1277(1)	39(1)
O(4)	143(2)	-836(3)	2062(1)	39(1)
O(5)	3227(2)	1424(2)	3517(1)	27(1)
O(6)	6358(2)	593(2)	3731(1)	26(1)
O(7)	5594(2)	1181(2)	2272(1)	28(1)
O(8)	2670(2)	-86(2)	2242(1)	27(1)
N(1)	3439(2)	-1093(2)	3547(1)	19(1)
N(2)	5909(2)	-1213(2)	2700(1)	20(1)
N(3)	233(3)	1432(3)	-638(1)	31(1)
N(4)	1749(3)	2077(3)	-521(2)	33(1)
N(5)	4391(3)	2184(3)	11(2)	42(1)
C(1)	4499(3)	-2267(3)	3573(2)	27(1)
C(2)	5076(3)	-2428(3)	2863(2)	26(1)
C(3)	3360(3)	-477(3)	4241(2)	27(1)
C(4)	3102(3)	970(3)	4135(2)	29(1)
C(5)	7567(3)	-1085(3)	3141(2)	27(1)
C(6)	7706(3)	25(3)	3651(2)	29(1)
C(7)	5985(3)	-1002(3)	1941(2)	25(1)
C(8)	6094(3)	452(3)	1802(2)	27(1)
C(9)	1774(3)	-1336(3)	3158(2)	26(1)
C(10)	1490(3)	-715(3)	2434(2)	23(1)
C(11)	2966(4)	1583(3)	-68(2)	28(1)

tances in compound **I** are 1.987(4) and 1.966(4) Å; those for **II** are 1.988(2) and 1.970(2) Å. Two oxygen atoms of the *R*-rings of the Edta ligands are arranged in the apical positions of the coordination polyhedron; the Cr–O(*R*) distances are somewhat shorter than the Cr–O(*G*) distances (1.956(4) and 1.937(5) Å in **I**; 1.960(2) and 1.945(2) Å in **II**). These data agree with the corresponding distances in Cr(III) complexes with hexadentate coordination of Edta-related ligands [10].

Table 3. Interatomic distances and bond angles in the metal coordination polyhedra in structures **I** and **II***

Cr coordination polyhedron		
Bond	<i>d</i> , Å	
	I	II
Cr(1)–O(8)	1.937(5)	1.945(2)
Cr(1)–O(6)	1.956(4)	1.960(2)
Cr(1)–O(7)	1.966(4)	1.970(2)
Cr(1)–O(5)	1.987(4)	1.988(2)
Cr(1)–N(2)	2.039(5)	2.050(2)
Cr(1)–N(1)	2.062(4)	2.069(2)
Angle	ω , deg	
	I	II
O(5)Cr(1)N(1)	80.3(2)	80.98(9)
O(5)Cr(1)N(2)	162.8(2)	162.86(10)
O(6)Cr(1)O(7)	91.7(2)	91.68(9)
O(6)Cr(1)O(5)	86.6(2)	86.87(8)
O(6)Cr(1)N(2)	84.6(2)	84.41(8)
O(6)Cr(1)N(1)	95.1(2)	94.82(9)
O(7)Cr(1)O(5)	113.9(2)	114.22(9)
O(7)Cr(1)N(2)	81.1(2)	80.82(9)
O(7)Cr(1)N(1)	164.6(2)	164.73(9)
O(8)Cr(1)O(6)	178.6(2)	178.43(9)
O(8)Cr(1)O(7)	89.3(2)	89.57(9)
O(8)Cr(1)O(5)	94.0(2)	93.48(9)
O(8)Cr(1)N(2)	94.5(2)	94.86(9)
O(8)Cr(1)N(1)	83.7(2)	83.74(9)
N(2)Cr(1)N(1)	85.8(2)	86.07(9)
Ni(I), Cu(II) coordination polyhedron		
Bond	<i>d</i> , Å	
	I	II
M(1)–N(3)	1.872(5)	1.946(3)
M(1)–S(1)	2.175(2)	2.276(1)
Angle	ω , deg	
	I	II
N(3)M(1)S(1)	88.7(2)	86.89(8)
N(3) ¹ M(1)S(1)	91.3(2)	93.11(8)

* Symmetry transformations of equivalent atoms: ¹ $-x, -y, -z$.

The Cr bond angles deviating most essentially from the ideal value of 90° are those in the equatorial plane: the O(5)CrO(7) angle is 113.9(2)° in **I** and 114.22(9)° in **II**. The other angles at Cr are in the range of 80.3(2)°–94.5(2)° in **I** and 79.98(9)°–94.86(9)° in **II** (Table 3). The chelate rings are deformed to different extents. The greatest deviation (Δ) of atoms from the mean plane is found in the *E*-rings ($\Delta_{aver} = 0.23$ Å for **I** and **II**); the sum of the intracyclic angles (Σ) is 515.12° in **I** and

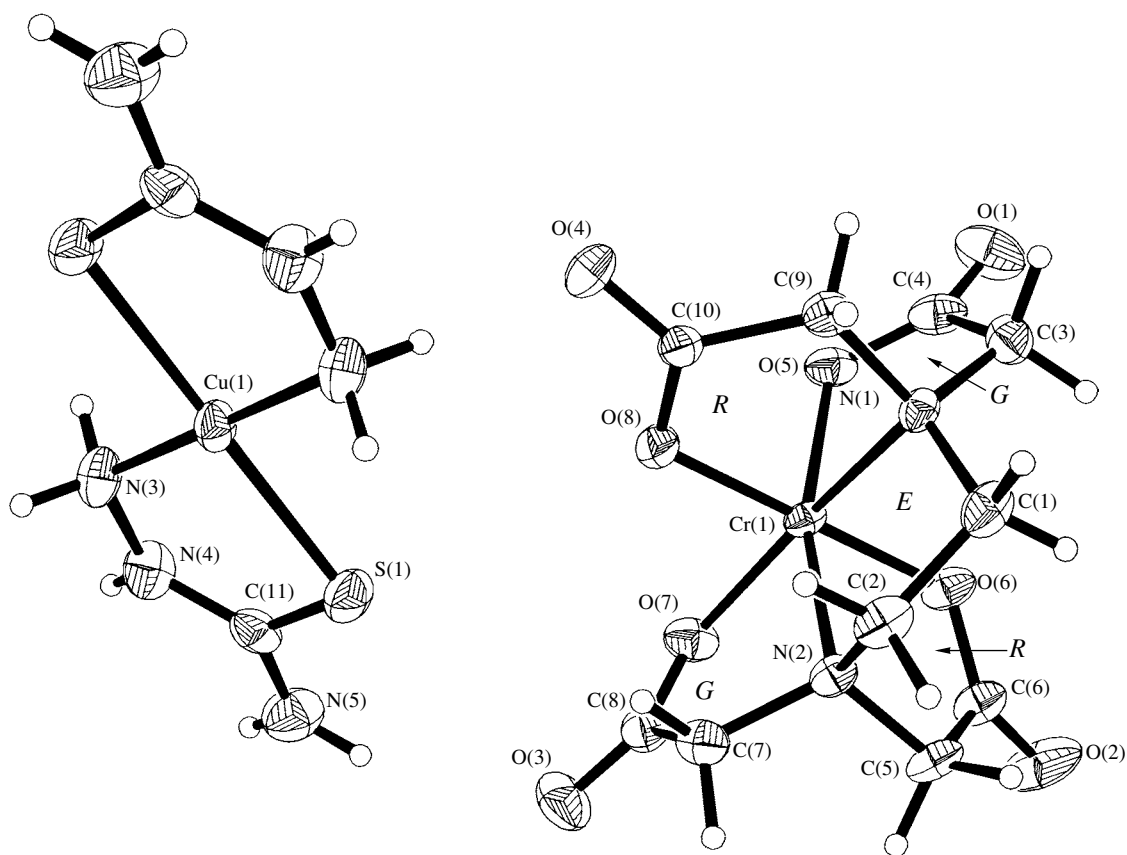


Fig. 1. Structure of complex ions in the crystal of II.

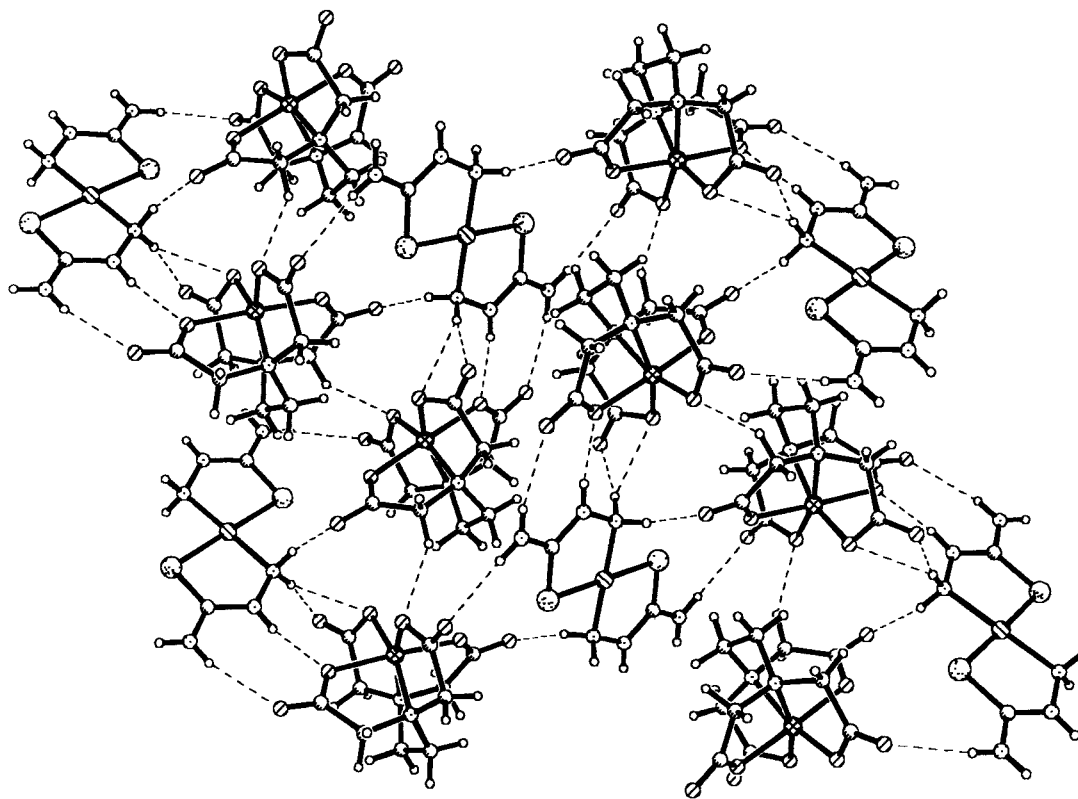


Fig. 2. Fragment of the layer formed through N-H...O interactions in structure II.

Table 4. Geometric parameters of hydrogen bonds in structures **I** and **II***

D–H...A	Distance, Å			The DHA angle, deg
	D–H	H...A	D...A	
I				
N(3)–H(31B)...O(4) ¹	0.90	1.87	2.746(7)	163
N(3)–H(31A)...O(1) ²	0.90	2.00	2.887(7)	170
N(3)–H(31A)...O(5) ²	0.90	2.48	3.093(6)	126
N(4)–H(41)...O(6) ²	0.86	1.95	2.795(6)	165
N(5)–H(51B)...O(2) ²	0.86	2.36	3.199(8)	164
N(5)–H(51A)...O(3)	0.86	2.27	3.088(7)	159
C(9)–H(9A)...O(7) ³	0.97	2.460	3.263(3)	140
C(5)–H(5B)...O(3) ⁴	0.97	2.459	3.399(4)	163
C(5)–H(5B)...O(4) ⁵	0.97	2.239	3.207(4)	176
II				
N(3)–H(31B)...O(4) ¹	0.90	1.87	2.753(4)	167
N(3)–H(31A)...O(1) ²	0.90	2.03	2.921(4)	170
N(3)–H(31A)...O(5) ²	0.90	2.44	3.075(5)	128
N(4)–H(41)...O(6) ²	0.86	1.97	2.793(3)	160
N(5)–H(51B)...O(2) ²	0.86	2.37	3.206(4)	163
N(5)–H(51A)...O(3)	0.86	2.31	3.126(4)	160
C(9)–H(9A)...O(7) ³	0.97	2.44	3.243(7)	140
C(5)–H(5B)...O(3) ⁴	0.97	2.49	3.432(7)	164
C(5)–H(5B)...O(4) ⁵	0.97	2.24	3.210(8)	176

* Symmetry transformations of equivalent atoms: ¹ $-x, -y, -z$; ² $x - 1/2, -y + 1/2, z - 1/2$; ³ $1/2 - x, y - 1/2, 1/2 - z$; ⁴ $1/2 - x, y - 1/2, 0.5 - z$; ⁵ $x + 1, y, z$.

515.48° in **II**. The *R*-angles are essentially planar (Σ is 537.50° and 537.51° for **I**; 537.36° and 537.68° for **II**). In the two *G*-rings, the Δ_{aver} values are 0.08 and 0.04 Å for both structures, $\Sigma = 523.13^\circ$ and 525.18° for **I**; and 523.48° and 525.02° for **II**. Comparison of the sums of the bond angles in the chelate rings in the Cr(III) complexes in structures **I** and **II** with the data reported in [12] for other Cr(III) complexes with Edta and its analogs shows the closest resemblance to the sum of the bond angles in $\text{K}[\text{Cr}(\text{Edta})] \cdot 2\text{H}_2\text{O}$.

All the hydrogen atoms of the Tsc molecules coordinated to nickel (copper) atoms are involved in hydrogen bonds with the oxygen atoms of the $[\text{Cr}(\text{Edta})]^-$

anion (Table 4). The hydrogen atom (H(31A)) attached to N(3) forms a bifurcated hydrogen bond with the O(1) and O(5) atoms of the *G* ring carboxyl group. The N–H...O hydrogen bonds are responsible for the formation of layers parallel to the (010) plane in the crystals of **I** and **II** (Fig. 2). The weak C–H...O interactions combine neighboring layers into a three-dimensional framework.

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