

*Dedicated to Professor Dumitru Oancea
on the occasion on his 75th anniversary*

CRYSTAL STRUCTURE AND THERMAL ANALYSIS OF AN OXALATO-BASED Co(III) COMPLEX

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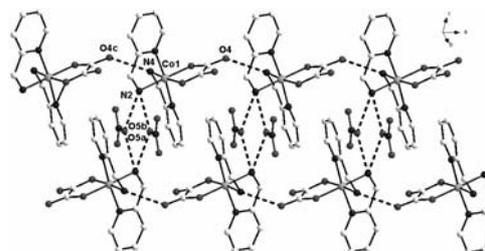
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The heteroleptic Co(III) oxalato complex, $[\text{Co}^{\text{III}}(\text{ampy})_2(\text{ox})](\text{NO}_3)$ (**1**), has been obtained from the reaction of $[\text{Co}(\text{ampy})_2(\text{NO}_3)_2]$ neutral complex with $[\text{Fe}^{\text{III}}(\text{ox})_3]^{3-}$ (ampy is 2-(aminomethyl)pyridine; ox^{2-} is the oxalate ion). The structure consists of mononuclear Co(III) complex cations, $[\text{Co}^{\text{III}}(\text{ampy})_2(\text{ox})]^+$, and nitrate counterions. The central atom, Co(III), is coordinated in a distorted octahedral geometry by one oxalato ion and two ampy molecules, which act as chelating ligands. The Co(III) units assemble into a bidimensional supramolecular network through hydrogen bonds established between each two units and each two units along a nitrate supramolecular bridge, and $\pi-\pi$ stacking interactions between the aromatic pyridine rings. According to the thermal analysis results, the compound is stable up to 200 °C and decomposes to form cobalt(III) oxide.



INTRODUCTION

Mononuclear complexes of various 3d-5d ions with oxalato ligands are very attractive as building blocks to construct polynuclear complex compounds.^{1,2} Moreover, due to the ability of the oxalato bridge to mediate magnetic coupling between paramagnetic ions, interesting magnetic

molecular materials can be obtained.^{1,2} Among the heteroleptic oxalato-based metalloligands, the bis(oxalato)chromate(III) complexes with chelating ligands, $[\text{CrAA}(\text{ox})_2]$, were extensively used against complex cations of transition metal ions to assemble coordination polymers.² Also, heteroleptic $[\text{FeAA}(\text{ox})_2]$ complexes were reported as versatile paramagnetic metalloligands.³ Mono-oxalato based

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heteroleptic Co(III) complexes are rare examples, among them being: $[\text{Co}(\text{C}_2\text{O}_4)(\text{C}_7\text{H}_{10}\text{N}_2)_2]\text{ClO}_4$, $\text{C}_7\text{H}_{10}\text{N}_2$ being 2-picoline,⁴ $[\text{Co}(\text{pypn})(\text{C}_2\text{O}_4)](\text{ClO}_4)$, where pypn is *N,N'*-bis(2-pyridylmethyl)-1,3-propanediamine,⁵ and $[\text{Co}(\text{phen})_2(\text{ox})](\text{NO}_3)\cdot 4\text{H}_2\text{O}$.⁶ Another Co(III) oxalato complex, $[\text{Co}(\text{phen})_2(\text{ox})](\text{BF}_4)$, was synthesized from $\text{K}_3[\text{Co}(\text{ox})_3]$, 1,10-phenanthroline and NaBF_4 .⁷ By reacting sodium monooxamide with Co(III) complexes of type $[\text{CoLCl}_2]\text{Cl}$, four oxalato-based complexes were obtained: $[\text{Co}(\text{en})_2(\text{ox})]\text{Cl}\cdot 4\text{H}_2\text{O}$, *cis*- β - $[\text{Co}(3,2,3\text{-tet})(\text{ox})]\text{Cl}\cdot 4\text{H}_2\text{O}$, *cis*- α - $[\text{Co}(\text{trien})(\text{ox})]\text{Cl}\cdot 2\text{H}_2\text{O}$, and $[\text{Co}(\text{tren})(\text{ox})](\text{ClO}_4)\cdot 0.5\text{H}_2\text{O}$ (en = ethylenediamine; 3,2,3-tet = 1,5,8,12-tetraazadodecane; trien = triethylenetetramine; tren = tris(2-aminoethyl)amine).⁸ Herein we report a new Co(III) heteroleptic oxalato-based structure, $[\text{Co}^{\text{III}}(\text{ampy})_2(\text{ox})](\text{NO}_3)$ (**1**), the spectral and crystal characterization, and its behavior with increasing temperature, through thermal analysis.

RESULTS AND DISCUSSION

By reacting $[\text{Co}^{\text{II}}(\text{ampy})_2(\text{NO}_3)_2]$ neutral complex with $[\text{Fe}^{\text{III}}(\text{ox})_3]^{3-}$ complex ion, we obtained a mononuclear heteroleptic complex, $[\text{Co}^{\text{III}}(\text{ampy})_2(\text{ox})](\text{NO}_3)$ (**1**). The tris(oxalato) ferrate complex ion was not stable and decomposed, acting as an oxalate supplier for the $[\text{Co}(\text{ampy})_2(\text{NO}_3)_2]$ cation. The Co(III) ion has two labile sites for coordination, suitable for a bidentate oxalato ligand. Reedijk *et al.*⁵ also obtained an oxalato-based complex of Co(III) ion starting from a Co(II) salt, ammonium oxalate and a tetradentate ligand.

Furthermore, we also reacted the same mononuclear complex of Co(II), $[\text{Co}(\text{ampy})_2(\text{NO}_3)_2]$, with $[\text{Cr}(\text{ox})_3]^{3-}$ and a complex cation-complex anion was formed, $[\text{Co}(\text{ampy})_3][\text{Cr}(\text{ox})_3]$. Due to the higher stability of the Cr(III) oxalato complex compared to the Fe(III) analogue, the resulting compound contains the $\{\text{Cr}^{\text{III}}(\text{ox})_3\}$ fragment is a part of the resulting complex compound. This compound was reported in 2014, although synthesized differently.⁹

Description of structure of the compound **1**

Complex **1** crystallizes in the orthorhombic system, space group *Pbca*. The crystal structure consists of mononuclear Co(III) complex cations,

$[\text{Co}(\text{ampy})_2(\text{ox})]^+$, and nitrate counterions (Fig. 1). The most relevant bond and angle lengths are gathered in Table 1.

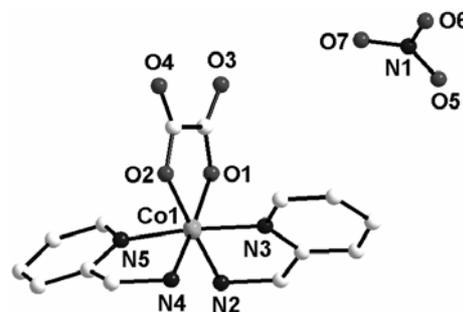


Fig. 1 – Crystal structure of complex **1**. Hydrogen atoms are omitted for clarity.

The coordination geometry of the Co(III) ion is best described as distorted octahedral, the apical position being occupied by two nitrogen-pyridine atoms from the ampy molecules and the equatorial plane, by two nitrogen-amino atoms from the ampy ligands and by two oxygen atoms from the bidentate oxalato ligand. The values of the bond lengths formed between the ampy molecule and Co(III) atom are: 1.939(3) for Co1-N2, 1.935(3) for Co1-N3, 1.944(3) for Co1-N4, and 1.928(3) Å for Co1-N5. The other two coordinate bonds, involving the oxygen atoms, Co1-O1 and Co1-O2, are of 1.918(3) and 1.901(3) Å, respectively. These values are close to those reported for similar complexes.^{4,6} The angle between the apical nitrogen atoms and the Co(III) ion, N5-Co1-N3, is 174.21(13)°, while the value of the torsion angle between the atoms forming the equatorial plane, O2-N4-N2-O1, is 0.295°.

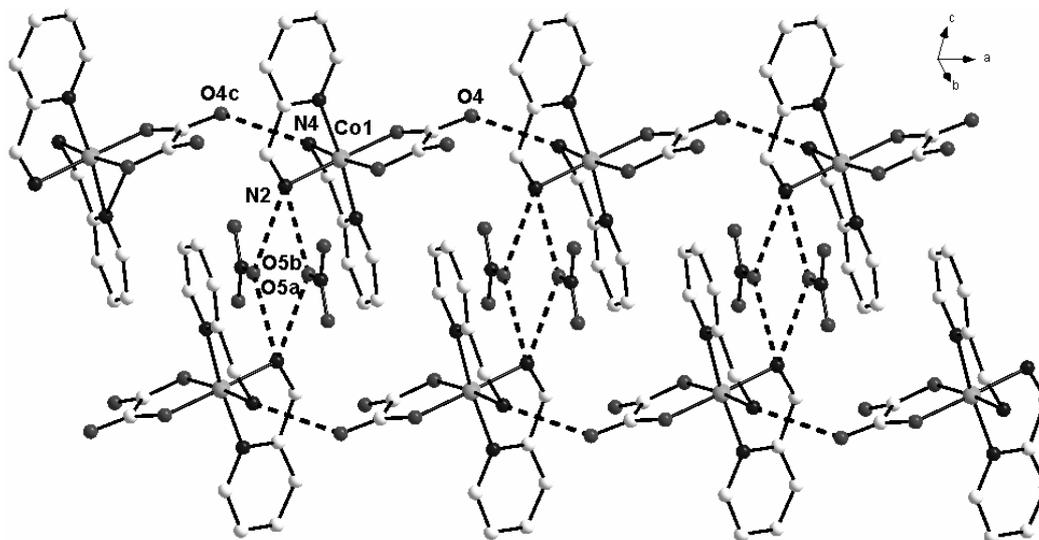
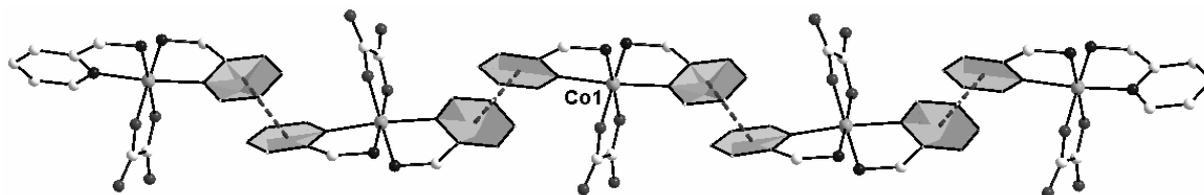
The analysis of the packing diagram reveals supramolecular double chains assembled from the Co(III) complex cations and nitrate ions through hydrogen bonds (Fig. 2). Each mononuclear unit is connected, through N4 as hydrogen donor and O4 as hydrogen acceptor (the value of the N4...O4c distance is 2.946 Å), to other two units, and to the third Co(III) moiety, through a double nitrate supramolecular bridge (the N2...O5a and N2...O5b distances are of 2.963 and 2.962 Å, respectively).

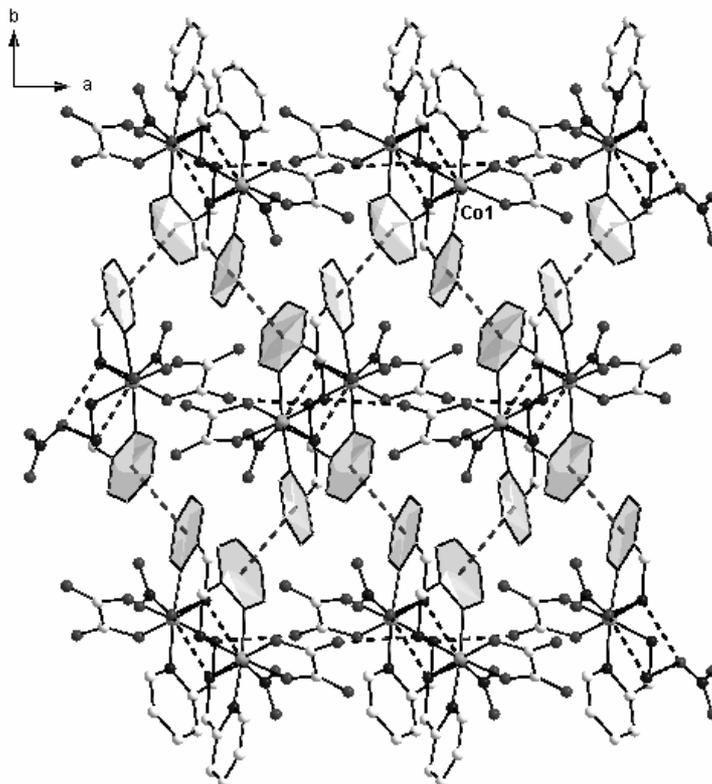
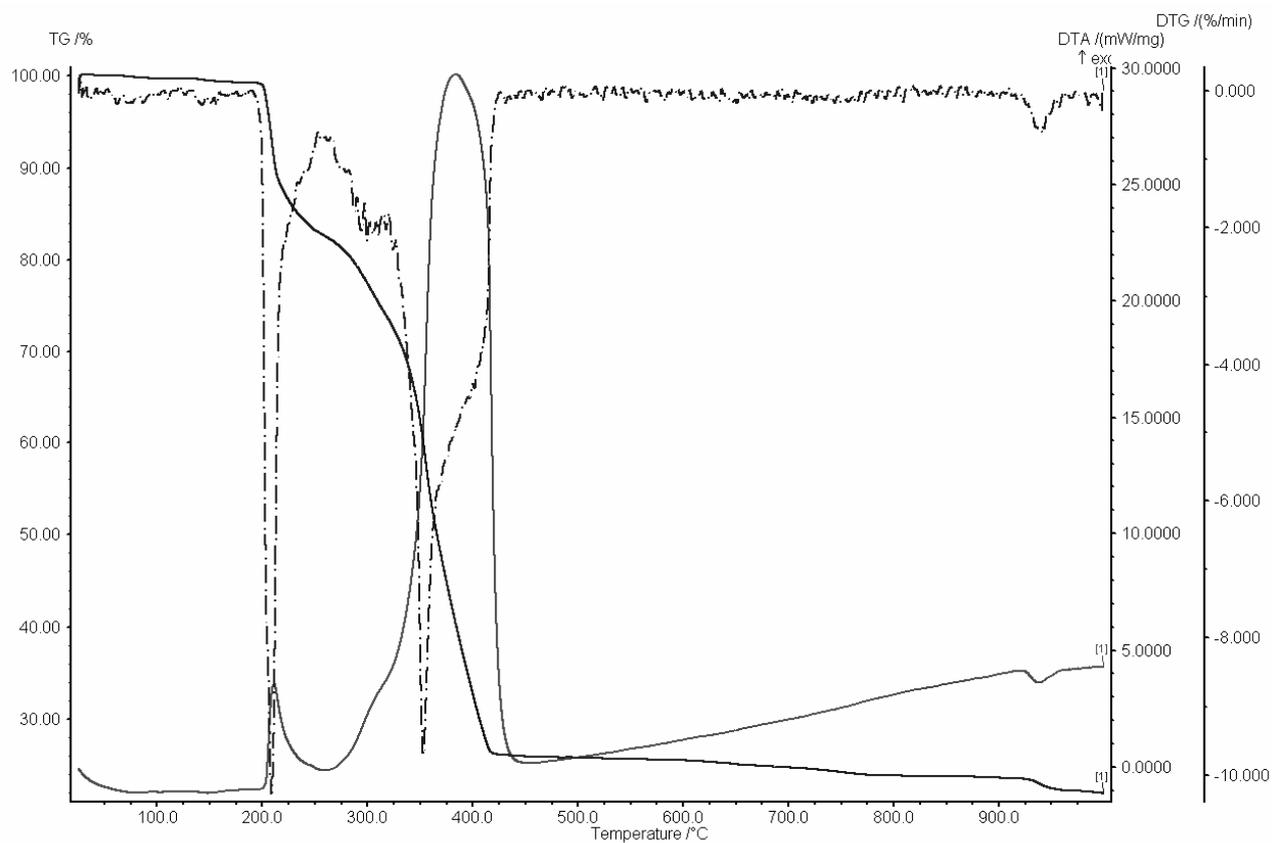
Also, at supramolecular level, π - π stacking interactions are established between the aromatic pyridine rings from the adjacent Co(III) complex cations, leading to a supramolecular waving chain (Fig. 3). The centroid-centroid distance is of 4.05 Å. Together with the hydrogen bonds, the dimensionality of the supramolecular network is 2-D (Fig. 4).

Table 1

Selected bond lengths (Å) and angles (°) for compound 1

Co1-N2	1.939(3)
Co1-N3	1.935(3)
Co1-N4	1.944(3)
Co1-N5	1.928(3)
Co1-O1	1.918(3)
Co1-O2	1.901(3)
N2-Co1-N3	84.95(13)
N4-Co1-N5	85.28(14)
N3-Co1-N5	174.21(13)
N2-Co1-N5	90.66(13)
N3-Co1-N4	91.33(14)
N2-Co1-N4	95.01(15)
O1-Co1-O2	85.90(12)
O1-Co1-N2	91.04(14)
O1-Co1-N3	88.45(13)
O1-Co1-N4	173.91(14)
O1-Co1-N5	95.41(13)
O2-Co1-N2	176.92(14)
O2-Co1-N3	94.67(13)
O2-Co1-N4	88.05(13)
O2-Co1-N5	89.92(13)

Fig. 2 – A view of the supramolecular double chains running along a axis; $a = \frac{1}{2}-x, \frac{1}{2}+y, z$; $b = -1/2+x, \frac{1}{2}-y, -z$; $c = -1+x, y, z$.Fig. 3 – Representation of the supramolecular chain developed through the π - π stacking interactions involving the pyridine rings.

Fig. 4 – Supramolecular 2-D network of **1**.Fig. 5 – TG, DTG and DTA curves for compound **1**.

Thermal studies

The TG analysis is shown in Fig. 5. Complex **1** is thermally stable up to 200 °C, when it starts to decompose. The mass loss, which occurs between 210 °C and 290 °C, corresponds to the decomposition of the nitrate anions and is accompanied by a minimum on the DTG curve at 209 °C and an exothermic DTA peak at 212 °C (mass loss: found 15%, calcd. 14.6%). The second decomposition process involves the ammonia molecules released from the ampy ligands (mass loss: found 8.5%, calcd. 8%).¹¹ The continuous mass loss up to 400 °C is due to the combustion of the rest of the ampy ligands and the oxalate ions, and is characterized by several minima in DTG (a shoulder at 300 °C and a sharp one at 353 °C) and an intense exothermic peak in DTA (at 383 °C). Complete decomposition is achieved at about 940 °C, when Co₂O₃ is formed (found 21%, calcd. 19.7%).

EXPERIMENTAL SECTION

Materials

The chemicals used as well as the solvents were of reagent grade and they were purchased from commercial sources. The starting compound, K₃[Fe(ox)₃]-3H₂O, was synthesized by following the literature procedure.¹¹

[Co(ampy)₂(NO₃)₂] was obtained by using a similar procedure as in reference 13, reacting Co(NO₃)₂·6H₂O (instead of Ni(NO₃)₂·6H₂O) with 2-(aminomethyl)pyridine. A pale pink precipitate was formed. Yield: *ca.* 65%. Anal. Calcd for C₁₂H₁₆CoN₆O₆: C, 36.09; H, 4.01; N, 21.05. Found: C, 35.41; H, 3.91; N, 21.57%. IR (KBr, cm⁻¹): 3424m (ν(NH₂)), 3225s, 3123, 1384m (ν(NO₃)), 1662, 1611, 804m, 775m. The UV-Vis spectrum shows bands at 480, 1000 nm, which can be attributed to the d-d electron transition ⁴T_{1g} → ⁴T_{1g}(P);

⁴T_{1g} → ⁴T_{2g}, characteristic for a Co(II) ion in an octahedral environment, while the band at 330 may be generated by the π-π* intraligand transitions.

Synthesis of complex **1**: 15 ml aqueous solution of 0.0496 g K₃[Fe(ox)₃]-3H₂O (0.1 mmol) was poured into 15 ml methanol solution of [Co(ampy)₂(NO₃)₂]. Red good-quality crystals were formed after 2 weeks. Yield: *ca.* 65 %. Anal. Calcd for C₁₄H₁₆CoN₅O₇: C, 39.53; H, 3.76; N, 16.47. Found: C, 39.46; H, 3.69; N, 16.61%. IR (KBr, cm⁻¹): 3414m (ν(NH₂)), 3214s, 3180m, 1704s (ν(COO)_{asym}), 1685s, 1670s, 1486 (ν(COO)_{sym}), 1386vs (ν(NO₃)), 804m, 774m.

Physical Measurements

The IR spectra of the [Co(ampy)₂(NO₃)₂] precursor and of the compound **1** were recorded on a FTIR Bruker Tensor V-37 spectrophotometer as KBr pellets in the 4000-400 cm⁻¹ range at room temperature. Elemental analyses (C, H, N) were performed on EuroVector EA3000 CHNS-O Elemental Analyzer. The UV-Vis spectra were measured on a JASCO V-670 spectrophotometer. The TG/DTG/DTA measurements were performed on a Netzsch STA 409 PC thermal analyzer. A sample weighting approx. 10 mg was placed in a cylindrical platinum holder and heated in synthetic air flow (100 ml min⁻¹, purity 99.999%), from room temperature to 1000 °C, at a heating rate of 10 °C min⁻¹.

Crystallographic Data Collection and Structure Determination

Suitable single crystals of compound **1** were mounted on an IPDS II STOE diffractometer. Diffraction data were collected at 293(2) K using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods using SHELXS-1997 and refined by means of least-squares procedures using SHELXL-1997. Atomic scattering factors were taken from the international tables for X-ray crystallography. The hydrogen atoms of the organic ligand were refined using a riding model (geometrical restraints were used for the refinement of some of them). Drawings of the molecule were performed with the program Diamond 4. A summary of the crystallographic data and the structure refinement parameters is given in Table 2. CCDC reference number: 1471485.

Table 2

Crystal data and details of the crystal determination for compound **1**

Empirical formula	C ₁₄ H ₁₆ CoN ₅ O ₇
<i>M</i> (g mol ⁻¹)	425.22
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	<i>Pbca</i>
<i>a</i> (Å)	7.5959(3)
<i>b</i> (Å)	16.6319(7)
<i>c</i> (Å)	25.7380(11)
<i>V</i> (Å ³)	3251.6(2)
<i>Z</i>	8
<i>D_c</i> (g cm ⁻³)	1.721

Table 2 (continued)

μ (mm ⁻¹)	1.108
$F(000)$	1164
Refinement on F^2	
Goodness of fit	0.983
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0528$ $wR_2 = 0.1575$
R indices (all data)	$R_1 = 0.0594$ $wR_2 = 0.1636$

CONCLUSIONS

The reaction between $[\text{Co}(\text{ampy})_2(\text{NO}_3)_2]$ and $\text{K}_3[\text{Fe}^{\text{III}}(\text{ox})_3]$ resulted in the formation of a mononuclear Co(III) heteroleptic oxalato-based complex, $[\text{Co}^{\text{III}}(\text{ampy})_2(\text{ox})](\text{NO}_3)$. The central atom, Co(III), is coordinated in an octahedral geometry by nitrogen atoms from the chelating ampy molecule and by oxygen atoms belonging to the bidentate oxalato ligand. The packing diagram reveals a 2-D supramolecular network assembled by hydrogen bonds, which involves the amino groups from the ampy molecules and the oxalato and nitrate oxygen atoms, and by π - π stacking interactions between the pyridine fragments. The thermal analysis indicates the formation of Co_2O_3 as the final compound of the complex **1** decomposition.

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