

Potassium *trans*-[bis(oxalato)diaquacobaltate(II)] tetrahydrate: synthesis, structure, potentiometric and thermal studies

Research Article

Agnieszka Chylewska*, Artur Sikorski,
Aleksandra Dąbrowska, Lech Chmurzyński

Faculty of Chemistry, University of Gdańsk,
80-952 Gdańsk, Poland

Received 17 April 2012; Accepted 1 August 2012

Abstract: The title compound, $\text{trans-K}_2[\text{Co}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$, was synthesised, and characterised by elemental analysis. Acid dissociation constants for the complex were determined by potentiometric titration and calculated by STOIChIO program. The crystal structure of $\text{trans-K}_2[\text{Co}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ was determined by X-ray diffraction studies. The asymmetric part of the unit cell contains one symmetric anion of oxalate and water molecule bound with Co(II) ion in crystallographic special position, one potassium cation and two molecules of water. Thermal properties of the complex were examined by thermogravimetric analysis (TGA). A decomposition mechanism is proposed on the basis of the results.

Keywords: Cobalt(II) complex • Oxalate ligands • X-ray • Thermogravimetry • Potentiometry

© Versita Sp. z o.o.

1. Introduction

Metals have been used in the treatment of human diseases since ancient times. More recently, a stable metal coordination complex based on the element platinum, $\text{cis-}[\text{PtCl}_2(\text{NH}_3)_2]$ (cisplatin), has become the most well-known of all metal-based drugs and hundreds of articles have been published on the synthesis and activity of complexes derived from the parent cisplatin molecule. Gold-containing complexes, such as auranofin, are commonly used to treat rheumatoid arthritis [1], radiopharmaceuticals based on metals such as technetium and rhenium are used in imaging and radiotherapy [2], and ruthenium complexes have had some success as anticancer drugs [3]. Complexes containing gadolinium, cobalt, lithium, bismuth, iron, calcium, lanthanum, gallium, tin, arsenic, rhodium, copper, zinc, aluminum, and lutetium have all been used in medicine [4]. More recently, cobalt(III)-based ligand complexes have been found to possess both antiviral and antibacterial activities. Only a small number of cobalt(III) complexes are known

to have biochemical roles. Vitamin B12 is a cobaloxime, a cobalt complex containing a glyoxime ligand, and is one of the rare examples of a naturally occurring organometallic complex, *i.e.*, a complex possessing a metal carbon bond. Vitamin B12 is a cofactor for a number of enzymes, virtually all of which are isomerases, methyl transferases, or dehalogenases. Other examples of cobalt-containing enzymes in biology include nitrile hydratase, prolidase, glucose isomerase, methylmalonyl-CoA carboxytransferase, aldehyde decarboxylase, lysine-2,3-aminomutase, bromoperoxidase, and methionine aminopeptidase, but only nitrile hydratase possesses cobalt in an oxidation state of 3+ [5]. The simple Co^{3+} ion is unstable in water, but can be stabilized against reduction to Co^{2+} by coordination to ligands or chelators. By far, the most common ligand type used to stabilize the cobalt(III) ion in aqueous solution is the chelating N,O-donor ligand. A large number of reports on the antibacterial properties of cobalt complexes have appeared in the literature, with Co(II) complexes being the most studied ones, presumably due to their aqueous

* E-mail: lapa@chem.univ.gda.pl

stability, availability, and ease of synthesis. Surprisingly, cobalt(III) complexes derived from this group of ligands have also found applications as antibacterial or antiviral agents [6-8].

Mononuclear cobalt complexes with organic ligands are attractive, because catalytically active cobalt ions can be isolated at the atomic level and their reactivity can be controlled by changing the chemical structure of ligands as far as they are stable under highly oxidative conditions.

Oxalate as a bidentate ligand has been of great interest in coordination chemistry for many years because of its analytical, catalytic and biomedical applications [9-13]. Many bis(oxalato)diaqua compounds of iron(III) and iron(II), chromium(III), indium(III), iridium(III) or manganese(III) have been reported [14-18]. $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ oxalate complex with iron(III) as the coordination center yields a blue Fe(II) pigment upon a photochemical reduction in solution [19]. $[\text{Mn}(\text{C}_2\text{O}_4)_3]^{3-}$ ion has been applied as a catalyst in the polymerization of vinyl compounds, whereas oxalate compounds of aluminium have found an application in electropolishing [20,21]. Moreover, the metal oxalate complexes are involved in several branches of industrial blueprinting, metal cleaning, chemical and electrolytic polishing, anti-corrosion protection, polymerization of vinyl compounds, control of soil acidity, or in chrome tanning process.

Some of the oxalato complexes, such as $[\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4]^+$ and $[\text{Co}(\text{en})_2\text{C}_2\text{O}_4]^+$, have been used for the redox photolysis to investigate the formation of cobalt(III)-carbon bond [22-25]. Upon irradiation in the charge-transfer region, these cobalt(III) complexes undergo intramolecular electron transfer from ligand to metal resulting in an aminoalkanecarboxylate free radical coordinated to the cobalt(II) ion. The removal of electron from the aminoalkanecarboxylate group leads to a loss of carbon dioxide with simultaneous delocalization of the unpaired electron in the remaining ligand to give an aminoalkyl radical. In addition, the absorption spectra of the transients and the steady-state photolysis results indicate that the product formed is the cobalt(III)-alkyl complex [26].

In our previous studies, we have synthesised chromium(III) oxalate complexes with aminosugars as ligands [27]. These compounds turned out to be biologically active and, consequently, were tested as biosensors in NO_2 and SO_2 uptake reactions from biological material [28]. Here, similar small gas molecule uptake reactions have been investigated for the title complex to and their reaction mechanism has been determined. Investigations involving cobalt(II) complexes with oxalates can provide information about their interesting kinetic and acids-base properties.

The current paper is a continuation of studies on synthesis, thermal properties and the crystal structure of complexes of transition metals such as chromium(III) and cobalt(III)/(II), which are used in the kinetic studies by our research group [29].

2. Experimental procedure

2.1. Materials and methods

All substrate compounds are commercially available and were purchased from Sigma-Aldrich. The thermogravimetric data and infrared spectra were measured by a Netzsch TG209 thermogravimetric analyzer coupled with FT-IR. All experiments were carried out under argon atmosphere. The analyzer was equipped with a programmed temperature controller, automatically maintaining constant temperature during thermal events. The thermogravimetric measurements were conducted at temperatures from 25 to 1000°C at a heating rate of 15°C min⁻¹. Infrared spectra were also registered in Nujol mull using a Bruker IFS 66 spectrophotometer. Carbon and hydrogen contents were determined on a Carlo Erba MOD 1106 elemental analyzer. All measurements were verified at least twice.

2.2. Synthesis of *trans*- $\text{K}_2[\text{Co}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$

The complex was prepared according to a modified procedure [30]. Cobalt(II) chloride hexahydrate (4.0 g, 17 mmol) was dissolved in 13 mL of distilled water (A). The mixture was stirred at 50°C for about 20 minutes. 0.5 g of activated charcoal was added to a solution of potassium oxalate ($\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$, 6.3 g, 34 mmol) in 10 mL of warm water (B). The solutions (A) and (B) were mixed together and air was bubbled through the mixture for 17 hours. The activated charcoal was removed and the red-purple filtrate was evaporated under an air stream on a steam bath to a volume of 10 mL. The solution was cooled on ice. The purple crystals of *trans*- $\text{K}_2[\text{Co}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ (1.8 g) were collected. The filtrate was left standing in the refrigerator for several days and a small amount of ethanol was added to obtain 3.5 g of pink solid. The recrystallisation of this solid from warm water by cooling on ice gave 0.7 g of *trans*- $\text{K}_2[\text{Co}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$. Yield: 25%. *Anal. Calc.* for $\text{K}_2\text{CoC}_4\text{H}_{12}\text{O}_{14}$ (421.27): C, 11.40; H, 2.85. Found: C, 11.42; H, 2.86.

2.3. X-ray investigations

Diffraction data were collected at a room temperature (298 K) on a KUMA KM-4 four circle diffractometer

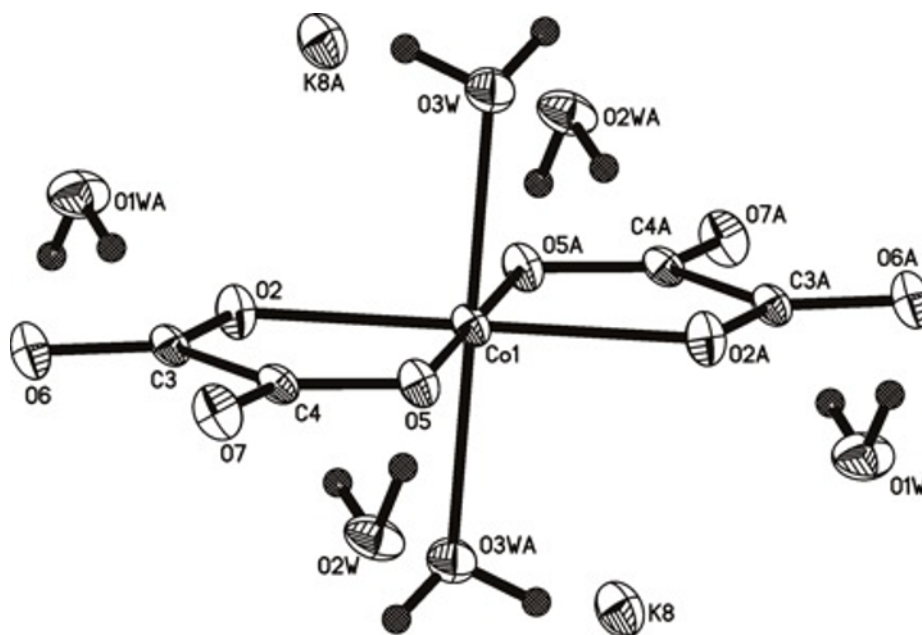


Figure 1. Structure of *trans*-K₂[Co(C₂O₄)₂(H₂O)₂]·4H₂O showing 25% probability displacements for ellipsoids. Hydrogen atoms are shown as small spheres of arbitrary radius.

with MoK α radiation ($\lambda = 0.71073$ Å) using the $2\theta/\omega$ scan mode [31]. The initial phase angle determination was performed by SHELXS software [32]. The crystal structure was refined by the full-matrix least-squares method using SHELXL [33] program based on 98 parameters. All H atoms were placed geometrically and refined using a riding model with O–H = 0.82 Å, and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$.

2.4. Potentiometric titration

Potentiometric titrations were carried out using an automated system applying Microtitrator software. The titration system consisted of a titration cell, a magnetic stirrer and an automatic titrator with Hamilton syringe (0.5 mL). All probes used in titrations were prepared under nitrogen atmosphere to avoid CO₂ contamination and the temperature was kept at 25±0.1°C. A constant ionic strength of 0.1 M was maintained with NaClO₄. The complex was titrated with 0.0502 M aqueous NaOH solution. A combination pH electrode was bought from Mettler Toledo and calibrated using pH standard buffers [34].

2.5. Fitting model of chemical equilibria to titration curve

STOICHIO program is based on the algorithm by Kostrowicki and Liwo [35–37] and is able to handle any chemical equilibrium model (Eq. 1). The program determines the equilibrium constants as parameters of the function to be minimized:

$$\Phi = \sum_{i=1}^n \frac{1}{\sigma_E^2} [\hat{E}_i - E(V_i, V, y, x)]^2 + \frac{1}{\sigma_V^2} (V_i - V_i)^2 + \sum_{i=1}^{n_y} \frac{1}{\sigma_{y_i}^2} (\hat{y}_i - y_i)^2 \quad (1),$$

where $\hat{E}$ - the measured potential difference for the i -th titration point, $\hat{V}$ - measured volume of the solution at the i -th titration point, vector x - unknown equilibrium constants and vector y - calibration parameters, total concentrations of reagents in the stock solution, titrants, etc. [38,39]. The minimization of the sum of the squares is done using Marquardt's method [40] and it takes into account not only the errors in the emf (electromotive force) but also those in the titration volume, stock-solution preparation, electrode calibration parameters, and reagent impurities [41].

3. Results and discussion

3.1. Crystal and molecular structure

The crystallographic data and the structure refinement are summarised in Table 1. The asymmetric part of the unit cell contains one symmetric anion of oxalate and water molecule bound with Co(II) ion lying in a crystallographic special position (center of inversion), one potassium cation and two molecules of water. The structure of the compound showing the ellipsoids and atom numbering system is illustrated in Fig. 1 [42].

Table 1. Crystal data and structure refinement.

Empirical formula	CoK ₂ C ₄ H ₁₂ O ₁₄
Formula weight	421.27
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P2 ₁ /n
Unit cell dimensions	
<i>a</i> (Å)	8.652(2)
<i>b</i> (Å)	6.632(1)
<i>c</i> (Å)	12.034(2)
β (°)	101.53(3)
Volume (Å ³)	676.6(2)
<i>Z</i>	2
<i>D</i> _{calc} (g cm ⁻³)	2.068
Absorption coefficient (mm ⁻¹)	1.956
<i>F</i> (000)	426
Crystal size (mm)	0.6×0.3×0.2
θ Range for data collection (°)	2.05 to 25.02
Limiting indices	-10 ≤ <i>h</i> ≤ 10, 0 ≤ <i>k</i> ≤ 7, -14 ≤ <i>l</i> ≤ 0
Reflections collected / unique	1196 / 1143 [<i>R</i> _{int} = 0.0765]
Completeness to 2θ (%)	96.1
Data / restraints / parameters	1143 / 0 / 98
Goodness-of-fit on <i>F</i> ²	0.999
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0538, <i>wR</i> ₂ = 0.1325
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0600, <i>wR</i> ₂ = 0.1393
Extinction coefficient	0.020(6)
Largest diff. peak and hole (e Å ⁻³)	1.273 and -1.748

All water molecules are involved in the multidirectional O—H···O hydrogen bonds between water molecules and oxalate O atoms or between water molecules (Fig. 2). Selected bond lengths and angles are presented below in Table 2.

Comparison of the crystal structure of the title compound with related complexes containing Co(II) and other metals(II) with the same co-ordination sphere shows that the structure of *trans*-K₂[Co(C₂O₄)₂(H₂O)₂]·4H₂O is very similar to bis(1*H*,3*H*-Cytosinium) diaqua-bis(oxalato)-cobalt(II) [43] and dipotassium *trans*-diaqua-bis(oxalato-O,O′)-nickel(II) tetrahydrate [44]. The X—O_(water) and X—O_(oxalate) bond lengths (X = Cr(II) or Ni(II)) are very similar: 2.076 – 2.112 Å and 2.041 – 2.101 Å, respectively. However, we can observe small differences in the O_(oxalate)—X—O_(oxalate) angle. In K₂[Co(C₂O₄)₂(H₂O)₂]·4H₂O, this angle ranges from 79.6 to 100.7 ° which means that the co-ordination sphere adopts non-ideal octahedral geometry, in contrast to other discussed compounds with O_(oxalate)—X—O_(oxalate) = 88.0 – 91.80°.

3.2. Thermogravimetric measurements

The results of the thermal analysis of *trans*-K₂[Co(C₂O₄)₂(H₂O)₂]·4H₂O are shown in Fig. 3.

The first peak of the differential thermogravimetric curve indicates a phase transition rather than a sample drying. This conclusion is further supported by the absence of the characteristic vibrations

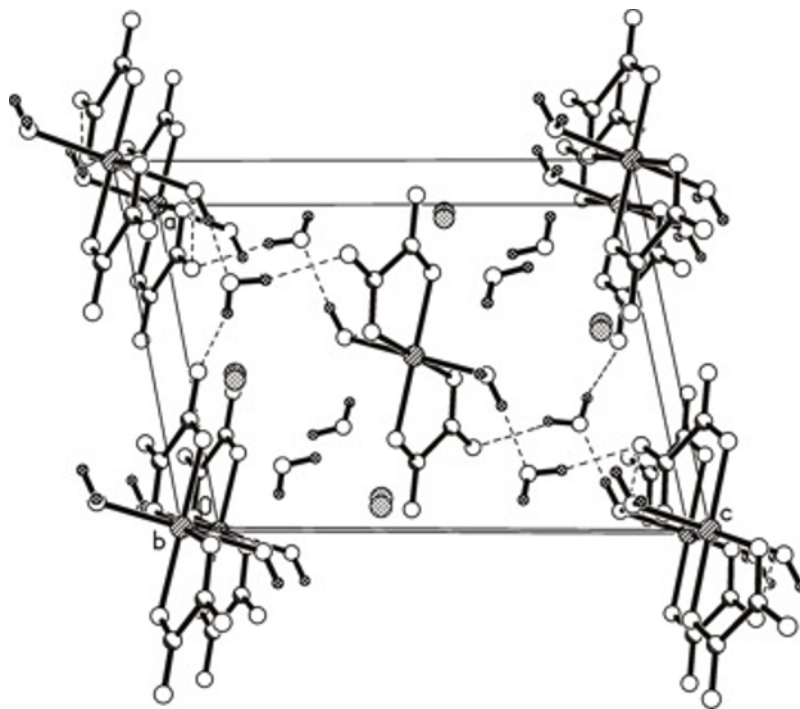
**Figure 2.** Molecular packing of *trans*-K₂[Co(C₂O₄)₂(H₂O)₂]·4H₂O (view along *b*-axis).

Table 2. Selected bond lengths (Å), angles (°), hydrogen bonding parameters (Å, °) and geometric parameters for H-bonding.

Co1-O2	2.042(2)	C4-O5-K8	118.2(2)
Co1-O5	2.076(2)	Co1-O5-K8	119.28(10)
Co1-O3W	2.101(3)	O1W-K8-O5	85.31(7)
O2-C3	1.248(4)		
C3-O6	1.224(4)	O5-Co1-O2-C3	-1.7(2)
C3-C4	1.549(4)	O3W-Co1-O2-C3	-93.1(2)
C4-O7	1.226(4)	Co1-O2-C3-O6	-177.1(3)
C4-O5	1.245(4)	Co1-O2-C3-C4	2.7(4)
O5-K8	2.995(3)	O6-C3-C4-O7	-2.9(5)
K8-O1W	2.776(4)	O2-C3-C4-O7	177.4(3)
		O6-C3-C4-O5	177.1(3)
O2-Co1-O5	79.57(9)	O2-C3-C4-O5	-2.6(5)
O2-Co1-O3W	91.66(10)	O7-C4-O5-Co1	-178.9(3)
O5-Co1-O3W	91.67(11)	C3-C4-O5-Co1	1.1(4)
C3-O2-Co1	115.1(2)	O7-C4-O5-K8	34.1(4)
O6-C3-O2	126.0(3)	C3-C4-O5-K8	-145.9(2)
O6-C3-C4	118.6(3)	O2-Co1-O5-C4	0.1(2)
O2-C3-C4	115.4(3)	O3W-Co1-O5-C4	91.5(2)
O7-C4-O5	126.3(3)	O2-Co1-O5-K8	146.83(13)
O7-C4-C3	117.4(3)	O3W-Co1-O5-K8	-121.79(12)
O5-C4-C3	116.3(3)	C4-O5-K8-O1W	-173.8(2)
C4-O5-Co1	113.6(2)	Co1-O5-K8-O1W	40.98(12)
DH...A	D-H	D...A	DH...A
O1W-H1WA...O2 ⁱ	0.82	2.740(4)	160
O1W-H1WB...O5 ⁱⁱ	0.82	2.835(4)	176
O2W-H2WA...O6 ⁱⁱⁱ	0.82	2.812(4)	166
O2W-H2WB...O7 ^{iv}	0.82	2.700(4)	162
O3W-H3WA...O6 ^v	0.82	2.962(4)	142
O3W-H3WB...O2W ⁱ	0.82	2.728(4)	162

Symmetry codes: (i) 1-x, 1-y, 1-z; (ii) 1/2-x, 1/2+y, 1/2-z; (iii) 1/2-x, 1/2+y, 3/2-z; (iv) -x, 1-y, 1-z; (v) 1-x, -y, 1-z.

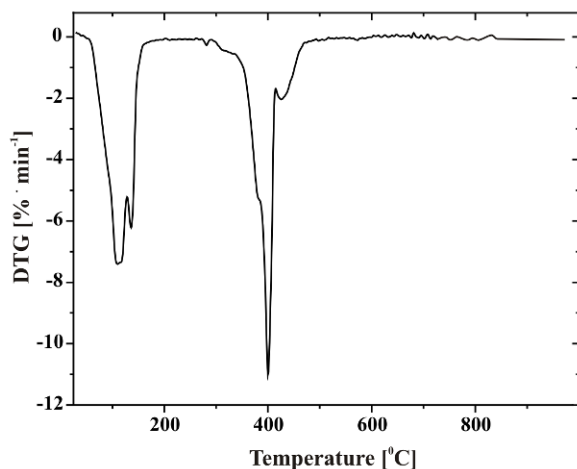


Figure 3. Differential thermogravimetric (DTG) curve of *trans*-K₂[Co(C₂O₄)₂(H₂O)₂]•4H₂O.

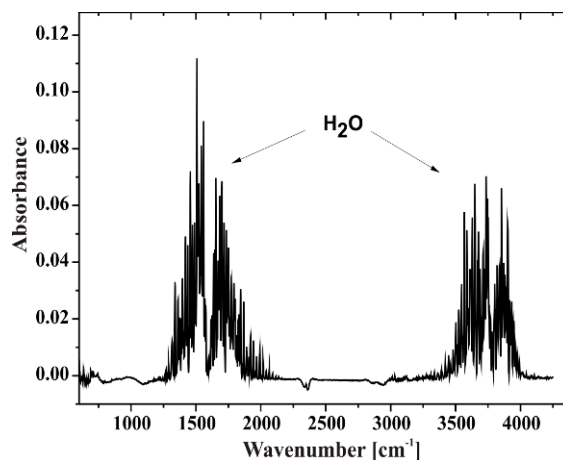


Figure 4. IR spectrum of *trans*-K₂[Co(C₂O₄)₂(H₂O)₂]•4H₂O after the first thermogravimetric decomposition step under argon (112°C).

of H₂O (1495; 1740; 3756; 3657 cm⁻¹) in the IR spectrum of the volatiles at 25 – 130°C (Fig. 4) [45].

When potassium *trans*-[bis(oxalato)diaquacobaltate(II)] tetrahydrate is heated above 100°C under argon, the weight loss is 26% (Fig. 5), which

proves that at this stage, the studied compound loses all its water molecules.

Futhermore, the thermogravimetric curve suggests that in the first step *trans*-K₂[Co(C₂O₄)₂(H₂O)₂]•4H₂O undergoes dehydration, then loses two water molecules from its coordination sphere, and finally undergoes a

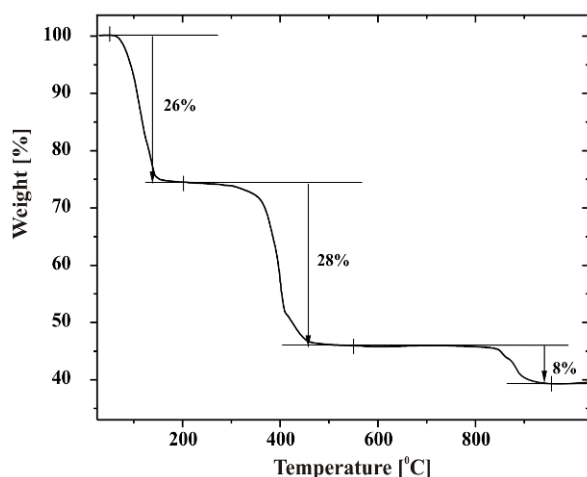


Figure 5. Thermogravimetric curve of thermal decomposition of *trans*-K₂[Co(C₂O₄)₂(H₂O)₂]·4H₂O under argon.

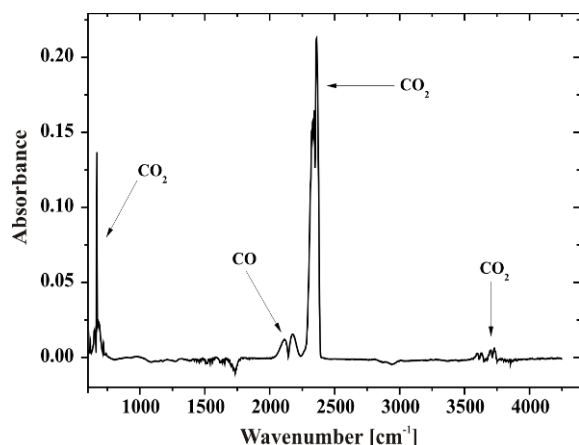


Figure 6. IR spectrum of gaseous products from the second step of decomposition of *trans*-K₂[Co(C₂O₄)₂(H₂O)₂]·4H₂O recorded at 400°C.

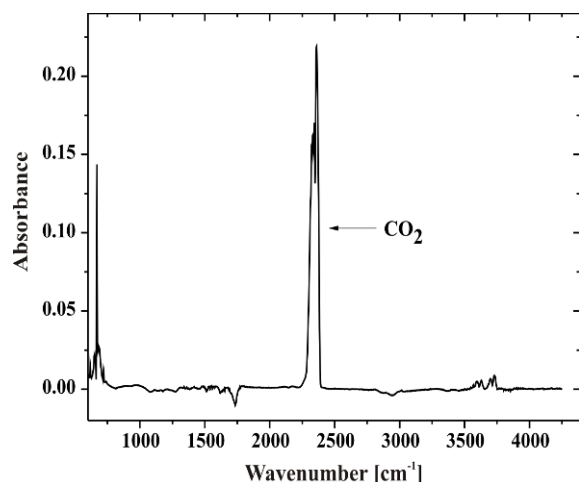
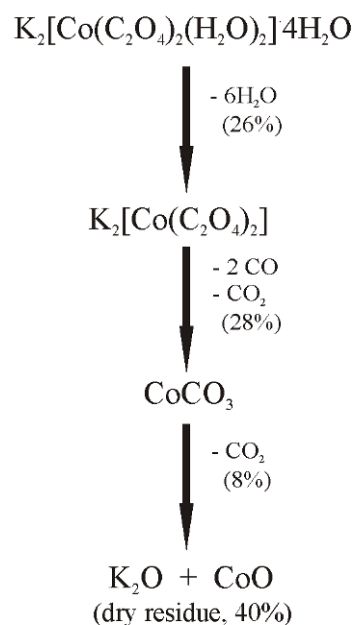


Figure 7. IR spectrum of carbon dioxide removed from *trans*-K₂[Co(C₂O₄)₂(H₂O)₂]·4H₂O during heating under argon (855°C).



Scheme 1. Proposed thermal decomposition mechanism of *trans*-K₂[Co(C₂O₄)₂(H₂O)₂]·4H₂O.

further decomposition. The second decrease in mass is 28%, and the IR spectrum of the volatiles at this decomposition step (Fig. 6) shows the presence of two carbon oxides: CO (2170 cm⁻¹) and CO₂ (667; 2349; 3740 cm⁻¹) [46].

Finally, the third weight-loss (8%) and the IR spectrum at this stage (Fig. 7) clearly indicate the release of carbon dioxide (2349 cm⁻¹).

Proposed mechanism of the thermal decomposition of the complex is presented in Scheme 1. The stoichiometry of the mechanism corresponds to the data from thermal analysis.

3.3. Determination of equilibrium models

Potentiometry is the most accurate technique for the evaluation of complex equilibrium constants. Spectrophotometric method would be useful when the former method cannot be employed, e.g. when insoluble species are formed at the concentrations typical for potentiometric titrations [47].

In the present study, the following acid-base equilibria (Eqs. 2,3) have been investigated in aqueous solutions:

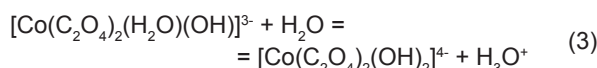
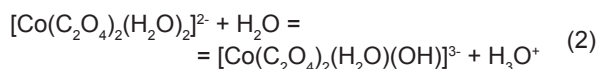


Table 3. The values of acid dissociation constants determined from potentiometric titrations at 25°C (I = 1.0 M NaClO₄).

Model of equilibria	value of pK
$[\text{Co}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^{2-} + \text{H}_2\text{O} = [\text{Co}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})(\text{OH})]^{3-} + \text{H}_3\text{O}^+$	$\text{pK}_1 = 6.04 (\pm 0.21)$
$[\text{Co}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})(\text{OH})]^{3-} + \text{H}_2\text{O} = [\text{Co}(\text{C}_2\text{O}_4)_2(\text{OH})_2]^{4-} + \text{H}_3\text{O}^+$	$\text{pK}_2 = 9.32 (\pm 0.16)$

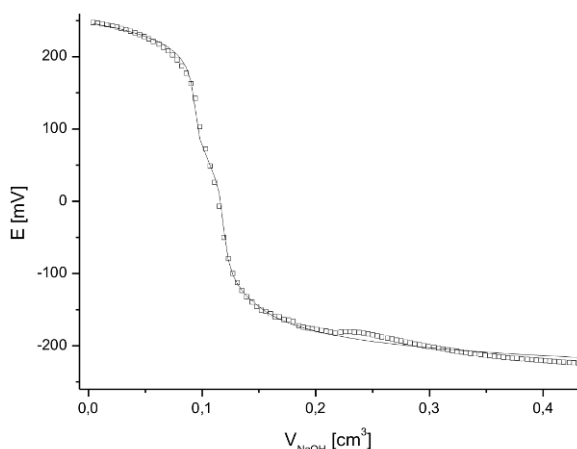


Figure 8. The relationship between the potential and the volume of titrant NaOH during the potentiometric titration of *trans*-K₂[Co(C₂O₄)₂(H₂O)₂]•4H₂O; [complex] = 0.0050 M, [NaOH] = 0.0502 M.

The equations of acid dissociation constants (Eqs. 4 and 5) are:

$$K_{a1} = \frac{[\{\text{Co}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})(\text{OH})\}^{3-}] \cdot [\text{H}_3\text{O}^+]}{[\{\text{Co}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2\}^{2-}]} \quad (4)$$

$$K_{a2} = \frac{[\{\text{Co}(\text{C}_2\text{O}_4)_2(\text{OH})_2\}^{4-}] \cdot [\text{H}_3\text{O}^+]}{[\{\text{Co}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})(\text{OH})\}^{3-}]} \quad (5)$$

The potentiometric technique requires constant ionic strength of the medium to ensure that the activity coefficients remain constant for all the species within the experiments. The titration curves obtained for *trans*-K₂[Co(C₂O₄)₂(H₂O)₂] in aqueous solution (Fig. 8) show two jumps in the potential. Fig. 8 shows the comparison of experimental data (black squares) and the data calculated by STOICHIO software (solid line). The values of acidity constants of the Co(II) complex are summarized in Table 3.

4. Conclusions

On the basis of potentiometric results and the results calculated by STOICHIO software, we have determined pK₁ and pK₂ values for *trans*-K₂[Co(C₂O₄)₂(H₂O)₂]

in aqueous solution (Table 3). The values indicate that the Co(II) complex is a weak acidic compound. The automated potentiometric technique combined with the calculations is a reliable, accurate and easily applicable method, well suitable for the determination of dissociation constants of the studied system.

The crystal structure of *trans*-K₂[Co(C₂O₄)₂(H₂O)₂]•4H₂O has been obtained by X-ray diffraction studies. Finally, the thermal analysis results allow us to propose a possible mechanism of the thermal decomposition of potassium *trans*-[bis(oxalato)diaquacobaltate(II)] tetrahydrate.

Acknowledgements

This work was financially supported by the Polish Ministry of Science and Higher Education NN 204 1362 38, DS/8232-4-0088-12. The publication is financed from European Social Fund in as a part of the project “Educators for the elite - integrated training program for PhD students, post-docs and professors as academic teachers at University of Gdansk” within the framework of Human Capital Operational Programme, Action 4.1.1, Improving the quality of educational offer of tertiary education institutions. This publication reflects the views only of the author, and the funder cannot be held responsible for any use, which may be made of the information contained therein.

EUROPEAN
SOCIAL FUND



HUMAN CAPITAL
NATIONAL COHESION STRATEGY

Supplementary material

Supplementary crystallographic data are available from the CCDC, Union Road, Cambridge CB2 1EZ, UK on request quoting the deposition number CCDC 671320 (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

References

- [1] P.J. Sadler, *Struct. Bond.* 29, 171 (1984)
- [2] J.A. Cowan, *Inorganic Biochemistry*, 2nd edition (Wiley-VCH: New York, 1997)
- [3] M.J.E. Clark, *Ruthenium and Other Metal Complexes in Cancer Chemotherapy* (Springer-Verlag, Heidelberg, Germany, 1989)
- [4] I. Bertini, H.B. Gray, E.I. Stiefel, J.S. Valentine, *Biological Inorganic Chemistry: Structure and Reactivity* (University Science Books, Sausalito, USA, 2007)
- [5] M. Kobayashi, S. Shimizu, *Eur. J. Biochem.* 261, 1 (1999)
- [6] T. Takeuchi, A. Böttcher, C.M. Quezada, T.J. Meade, H.B. Gray, *Bioorg. Med. Chem.* 7, 815 (1999)
- [7] J.A. Schwartz, E.K. Lium, S.J. Silverstein, *J. Virol.* 75, 4117 (2001)
- [8] S.P. Epstein, Y.Y. Pashinsky, D. Gershon, I. Winicov, C. Srivilasa, K.J. Kristic, P.A. Asbell, *BMC Ophthalmol.* 6, 22 (2006)
- [9] R. Selvam, K. Kannabiran, *J. Urology* 156, 237 (1996)
- [10] M. Yashiro, M. Komiyama, K. Kuroda, S. Miura, S. Yoshikawa, S. Yano, *Bull. Chem. Soc. Jpn.* 67, 3276 (1994)
- [11] J. Glerup, P.A. Goodson, D.J. Hodgson, K. Michelsen, *Inorg. Chem.* 34, 6255 (1995)
- [12] V. Jordanovska, R. Trojko, *Thermochim. Acta* 258, 205 (1995)
- [13] M.R. Ullah, P.K. Bhattacharya, K. Venkatasubramanian, *Polyhedron* 22, 4025 (1996)
- [14] V. Vallet, H. Moll, U. Wahlgren, Z. Szabó, I. Grenthe, *Inorg. Chem.* 25, 8598 (2003)
- [15] V. Vallet, H. Moll, U. Wahlgren, Z. Szabó, I. Grenthe, *Inorg. Chem.* 6, 1982 (2003)
- [16] H.Z. Kou, O. Sato, *Inorg. Chem.* 23, 9513 (2007)
- [17] M. Clemente-León, E. Coronado, M. López-Jordà, J. C. Waerenborgh, *Inorg. Chem.* 18, 9122 (2011)
- [18] Clare E. Rowland and Christopher L. Cahill, *Inorg. Chem.* 14, 6716 (2010)
- [19] G.T. Webster, D. McNaughton, B.R. Wood, *J. Phys. Chem. Sec. B* 113, 6910 (2009)
- [20] J.J.G. Icki, U.S. patent 2,748,069 (May 29, 1956)
- [21] K.V. Krishnamurty, G.M. Harris, *Chem. Rev.* 61, 213 (1961)
- [22] D.D. Campano, E.R. Kantrowitz, M.Z. Hoffman, M.S. Weinberk, *J. Phys. Chem.* 78, 686 (1974)
- [23] J.C. Scaiano, W.J. Leigh, G. Ferraudi, *Can. J. Chem.* 62, 2355 (1984)
- [24] E.R. Kantrowitz, M.Z. Hoffman, J.F. Endicott, *J. Phys. Chem.* 75, 1914 (1971)
- [25] A.F. Vaudo, E.R. Kantrowitz, M.Z. Hoffman, *J. Am. Chem. Soc.* 93, 6698 (1971)
- [26] A.L. Poznyak, V.I. Pavlovski, E.B. Chuklannova, T.N. Polynova, M.A. Porai-Koshits, *Monatsh. Chem.* 113, 561 (1982)
- [27] A. Dąbrowska, D. Jacewicz, A. Łapińska, B. Banecki, A. Figarski, M. Szkatuła, L. Lehman, J. Krajewski, J. Kubasik-Juraniec, M. Woźniak, L. Chmurzyński, *Biochem. Biophys. Res. Comm.* 326, 313 (2005)
- [28] D. Jacewicz, A. Dąbrowska, A. Łapińska, A. Figarski, M. Woźniak, L. Chmurzyński *Anal. Biochem.* 350, 256 (2006)
- [29] D. Jacewicz, A. Dąbrowska, A. Łapińska, M. Woźniak, L. Chmurzyński, *Trans. Met. Chem.* 31, 1045 (2006)
- [30] H. Okazaki, Y. Kushi, H. Yoneda, *J. Am. Chem. Soc.* 107, 4183 (1985)
- [31] Kuma KM-4 Software User's Guide, Version 3.1. (Kuma Diffraction, Wrocław, Poland, 1989)
- [32] G.M. Sheldrick, *Acta Cryst. A* 64, 112 (2008)
- [33] G.M. Sheldrick, *SHELXL*, Program for crystal structure refinement (University of Göttingen, Germany, 1997)
- [34] A.I. Vogel, *Vogel's textbook of quantitative inorganic analysis*, 4th edition (Longman, London, 1978)
- [35] J. Kostrowicki, A. Liwo, *Comp. Chem.* 8, 91 (1984)
- [36] J. Kostrowicki, A. Liwo, *Comp. Chem.* 11, 195 (1987)
- [37] J. Kostrowicki, A. Liwo, *Talanta* 37, 645 (1990)
- [38] Ł. Gurzyński, A. Puszek, M. Makowski, J. Makowska, L. Chmurzyński, *J. Chem. Thermodyn.* 38, 554 (2006)
- [39] Ł. Gurzyński, A. Puszek, M. Makowski, L. Chmurzyński, *J. Chem. Thermodyn.* 39, 1272 (2007)
- [40] D.W. Marquard, *J. Applied Math.* 11, 431 (1963)
- [41] E. Kaczmarczyk, K. Maj, L. Chmurzyński, *J. Chem. Thermodyn.* 32, 901 (2000)
- [42] C.K. Johnson, *ORTEP II*; Report ORNL-5138 (Oak Ridge National Laboratory, Oak Ridge, USA, 1976)
- [43] J.P. Garcia-Teran, O. Castillo, A. Luque, U. Garcia-Couceiro, G. Beobide, P. Roman, *Cryst. Growth Des.* 7, 2594 (2007)
- [44] P. Roman, C. Guzman-Mirallas, A. Luque, *Acta Crystallogr., Cryst. Struct. Comm.* C49, 1336 (1993)
- [45] W.S. Benedict, N. Gailar, E.K. Plyler, *J. Chem. Phys.* 24, 1139 (1956)
- [46] J.H. Taylor, W.S. Benedict, J. Strong, *J. Chem. Phys.* 20, 1884 (1952)
- [47] A.E. Martell, R.J. Motekaitis, *The determination and use of stability constants*, 2nd edition (VCH, New York, 1992) chapter 3