

Synthesis, Crystal Structure, Spectral and Thermal Studies of a New Organic-Inorganic Hybrid Cobalt(II) Complex of 2,2'-Bipyridine and Nitrate with Squarate

Okan Zafer Yeşilel^a, Hümeysra Paşaoğlu^b, Gökhan Kaştaş^b, Halis Ölmez^c, and Orhan Büyükgüngör^b

^a Department of Chemistry, Faculty of Arts and Sciences, Eskişehir Osmangazi University, 26480 Eskişehir, Turkey

^b Department of Physics, Faculty of Arts and Sciences, Ondokuz Mayıs University, 55139 Kurupelit-Samsun, Turkey

^c Department of Chemistry, Faculty of Arts and Sciences, Ondokuz Mayıs University, 55139 Kurupelit-Samsun, Turkey

Reprint requests to O. Z. Yeşilel. E-mail: yesilel@ogu.edu.tr

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The $[\text{Co}(\text{NO}_3)(\text{bipy})_2](\text{sq})_{1/2} \cdot 4\text{H}_2\text{O}$ complex (**I**) (bipy: 2,2'-bipyridine, sq^{2-} : squarate) has been prepared and characterized by elemental analysis, IR, UV/vis spectra, thermal analysis, and single crystal X-ray diffraction. The title compound crystallizes in the triclinic system, space group $P\bar{1}$, with $a = 7.6302(9)$, $b = 12.0426(15)$, $c = 14.2271(14)$ Å, $\alpha = 107.252(9)^\circ$, $\beta = 98.755(9)^\circ$, $\gamma = 103.363(9)^\circ$ and $Z = 2$. The Co(II) ion in its octahedral complex is chelated by the nitrogen atoms of the two 2,2'-bipyridine, and by two oxygen atoms of the nitrate group. The anionic squarate behaves as a counter ion. Thermal analysis has shown that the title compound decomposes in three stages over the range 20 – 1000 °C on heating in a static air atmosphere. The final decomposition product is CoO.

Key words: Squarate, 2,2'-Bipyridine, Thermal Decomposition

Introduction

Squaric acid ($\text{H}_2\text{C}_4\text{O}_4$, H_2sq) has been of much interest because of its cyclic structure and possible aromaticity. In recent years, considerable progress has been made in the crystal engineering of multidimensional arrays and networks containing metal ions as nodes. From the viewpoint of crystal engineering, squaric acid is a useful tool for constructing crystalline architectures, because of its rigid, planar four membered ring framework, and its proton donating and accepting capabilities for hydrogen bonding [1–5]. Squaric acid has also been studied for potential application in xerographic photoreceptors, organic solar cells and optical recording [6, 7]. Studies of the coordination chemistry of the squarate ligand have also attracted increasing attention because it gives rise to a wide variety of complexes and adopts mono- or polydentate coordination modes when acting as a ligand towards first row transition metal ions [8–27], in which most squarates bridge metal ions *via cis*-oxygen atoms or *trans*-oxygen atoms. Only a limited number of articles have focused on squarate complexes, where

squarate acts as a counter ion [23–32]. Solid state thermal studies of several metal squarates and mixed ligand and metal squarate complexes have been reported, indicating a high thermal stability of the squarate moiety [29–32].

Research on organic–inorganic hybrid materials has attracted much attention owing to their importance for the development of new materials with unusual properties, such as nonlinear optical (NLO) response, magnetism, luminescence, and multifunctional properties [33–35].

In the present paper, we describe the synthesis, spectroscopic and thermal studies and crystal structure of an organic-inorganic hybrid Cobalt(II) complex of 2,2'-bipyridine and nitrate ligands and with a squarate counter ion.

Results and Discussion

IR spectrum

The important IR absorption bands of the title complex are listed Table 1. The spectrum shows a broad and intense band located at $3467\text{--}3332\text{ cm}^{-1}$ due to

Table 1. Selected IR spectral data* (cm^{-1}).

	This work	Squaric acid [34]
$\nu\text{O}-\text{H}$	3467–3332 m	3462 s
$\nu\text{C}-\text{H}$	3031, 3070 and 3112 w	–
$\nu\text{C}=\text{O}$	–	1822 w
$\nu\text{C}=\text{N}$	1664 s	–
$\nu\text{C}=\text{C}$	1599 w	1643 m
$\nu_{\text{asym}}\text{NO}_2$	1641 vs	–
$\nu_{\text{sym}}\text{NO}_2$	1020 w	–
$\nu[(\text{C}-\text{O}) + (\text{C}-\text{C})]$	1527 vs	1530, 1516 vs
$\nu\text{N}=\text{O}$	1227 w	–
$\nu\text{Co}-\text{O}$	507 w	–
$\nu\text{Co}-\text{N}$	411 w	–

* w = weak; s = strong; vs = very strong; m = medium.

strong hydrogen bonds including the water molecules. The weak peaks in the range 3116–3033 cm^{-1} are due to νCH stretching absorptions. The stretching vibrations of the $\text{C}=\text{N}$ group of bipy appear at 1664 cm^{-1} as a strong absorption band. The $\nu_{\text{asym}}\text{NO}_2$ and $\nu_{\text{sym}}\text{NO}_2$ modes of NO_3 are observed at 1641 and 1020 cm^{-1} , respectively. The bands with medium intensity around 1599 cm^{-1} correspond to the νCC vibrations of the phenyl ring of bipy. A very strong absorption centered at 1527 cm^{-1} is assigned to a combination of squarate $\text{C}-\text{O}$ and $\text{C}-\text{C}$ band stretching vibrations. This type of absorption is characteristic of salts of $\text{C}_n\text{O}_n^{2-}$ ions and was found at 1500 cm^{-1} in the IR spectrum of $\text{K}_2\text{C}_4\text{O}_4$ [9]. The $\nu\text{Co}-\text{O}$ and $\nu\text{Co}-\text{N}$ vibrations are observed at 507 and 411 cm^{-1} , respectively, as weak bands.

UV/vis spectrum and magnetic susceptibility

The λ_{max} values of the absorption bands in the UV/vis spectrum of **I** are 502, 835 nm and the corresponding ϵ values are 63 and 14 $\text{cm}^{-1}\text{M}^{-1}$, respectively. These values were assigned to the following $d-d$ transitions: $\nu_2: {}^4T_{1g} \rightarrow {}^4A_{2g}$; $\nu_1: {}^4T_{1g} \rightarrow {}^4T_{2g}$. The ${}^4T_{1g} \rightarrow {}^4T_{1g}(\text{P})$ transition was not observed since this band may be shifted to the UV region. The Δ_o value was calculated as 7.944 cm^{-1} and exhibits an experimental magnetic moment of 4.12 BM corresponding to three unpaired electrons.

Thermal analysis

Thermal decomposition proceeds in three stages. The broad endothermic peak ($\text{DTG}_{\text{max}} = 105^\circ\text{C}$), in the temperature range of 62–125 $^\circ\text{C}$, corresponds to the loss of crystallization water (found: 12.02, calcd.: 12.83%). The second stage, in the temperature range of 126–203 $^\circ\text{C}$, is related to the decomposition

Table 2. Crystal data and structure refinement parameters.

Empirical formula	$\text{C}_{22}\text{H}_{24}\text{CoN}_5\text{O}_9$
Formula weight	561.39
Temperature [K]	296
Wavelength [\AA]	0.71073
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a, b, c [\AA]	7.6302 (9), 12.043 (2), 14.227 (1)
α, β, γ ($^\circ$)	107.252 (9), 98.755 (9), 103.363 (9)
V [\AA^3]	1179.9 (2)
Z	2
Absorption coeff. [mm^{-1}]	0.791
D_{calc} [Mg m^{-3}]	1.580
Crystal size [mm]	
Θ Range for data coll. [$^\circ$]	1.85–27.99
Measured reflections	12611
Independent reflections	5140
Absorption correction	integration
Refinement method	full-matrix least-squares on F^2
Final R indices	$R1 = 0.0572$ $wR1 = 0.1443$
$[F^2 \geq 2\sigma(F^2)]$	
Goodness-of-fit on F^2	1.051
Largest difference peak and hole [e \AA^{-3}]	$\Delta\rho_{\text{max}} = 0.0992$, $\Delta\rho_{\text{min}} = -1.379$

of the nitrato ligand (found 10.54, calcd. 11.04%). In the last stage, the strong exothermic peak ($\text{DTG}_{\text{max}} = 274^\circ\text{C}$) is related to the consecutive decomposition of the bipy and squarate moieties in the temperature range of 204–327 $^\circ\text{C}$, finally leading to Co_3O_4 . The endothermic peak at 887 $^\circ\text{C}$ is related to the conversion of Co_3O_4 to CoO . The overall weight loss (found 86.04, calcd. 86.65%) agrees with the proposed assignments. The final decomposition product, CoO , was identified by IR spectroscopy.

Crystal structure of the complex

Details of the crystal structure are given in Table 2. The compound consists of $[\text{Co}(\text{NO}_3)(\text{bipy})_2]^+$ complex cations, squarate anions, $\text{C}_4\text{O}_4^{2-}$, and water molecules (Fig. 1). The $\text{Co}(\text{II})$ ion is coordinated by four N atoms of two bipy ligands and two O atoms of one bidentate nitrato ligand. The $\text{Co}-\text{N}$ distances are different from each other and lie in a wide range [1.917(3)–1.941(3) \AA]. The nitrato ligand is symmetrically coordinated to the metal centre [$\text{Co}-\text{O}1 = 1.891(3)$ \AA , $\text{Co}-\text{O}2 = 1.897(3)$ \AA , $\text{N}5-\text{O}1 = 1.318(5)$ \AA , $\text{N}5-\text{O}2 = 1.316$ \AA , $\text{N}5-\text{O}3 = 1.230(5)$ \AA]. The bipy ligands and the chelate rings are almost planar. The angle $\text{N}3-\text{Co}1-\text{N}1$ is virtually linear, whereas $\text{O}2-\text{Co}1-\text{N}4$ and $\text{O}1-\text{Co}1-\text{N}2$ deviate much from linearity. On this basis, atoms $\text{N}2$, $\text{N}4$, $\text{O}1$ and $\text{O}2$ can

Table 3. Selected bond lengths and hydrogen bonding geometry.

<i>Bond lengths (Å) and angles (°)</i>				
Co1–O1	1.891 (3)	O1–N5	1.318 (5)	
Co1–O2	1.897 (3)	O2–N5	1.316 (5)	
Co1–N1	1.924 (3)	O3–N5	1.230 (5)	
Co1–N2	1.933 (3)	C21–O4	1.255 (5)	
Co1–N3	1.917 (3)	C21–C22	1.461 (6)	
N4–Co1	1.941 (3)	C22–O5	1.259 (5)	
O1–Co1–O2	69.34 (13)	O2–Co1–N1	88.63 (15)	
O1–Co1–N3	90.62 (13)	N3–Co1–N1	177.73 (15)	
O2–Co1–N3	92.02 (14)	O1–Co1–N2	165.65 (14)	
O1–Co1–N1	91.65 (14)	O2–Co1–N2	97.10 (13)	
N3–Co1–N2	94.66 (13)	N1–Co1–N2	83.11 (14)	
O1–Co1–N4	95.42 (13)	O2–Co1–N4	164.02 (13)	
N3–Co1–N4	83.09 (14)	N1–Co1–N4	96.85 (14)	
N2–Co1–N4	98.46 (14)			
<i>Hydrogen bonds</i>				
D–H...A	d(D–H)	d(H...A)	d(D...A)	<(DHA)
O6–H22...O5 ⁱ	0.910	1.958	2.822	157.9
O8–H25...O3 ⁱⁱ	0.894	2.003	2.877	165.7
O9–H28...O5 ⁱⁱⁱ	0.916	1.904	2.814	171.7
O8–H26...O7 ⁱⁱⁱ	0.920	1.931	2.828	164.2
O7–H23...O6 ⁱⁱⁱ	0.888	2.037	2.823	147.1
O6–H21...O4	0.906	1.966	2.860	169.1
O7–H24...O9	0.900	1.886	2.748	159.8
O9–H27...O8	0.924	1.922	2.776	152.7

Symmetry operations: ⁱ $x-1, y, z$; ⁱⁱ $2-x, 1-y, 1-z$; ⁱⁱⁱ $2-x, -y, 1-z$.

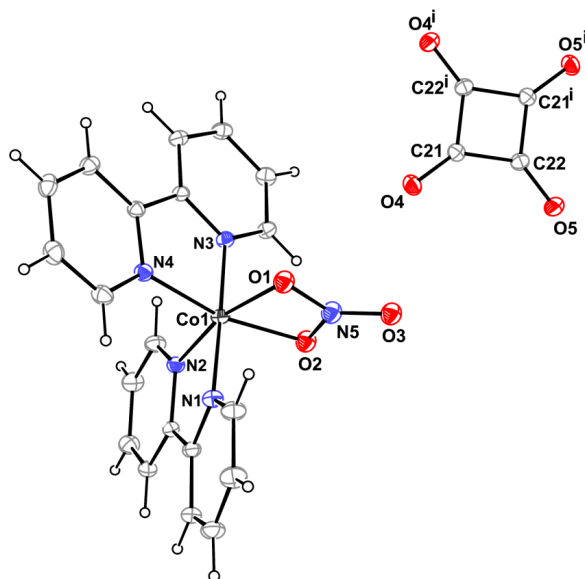


Fig. 1. The molecular structure, together with the atomic numbering system. Displacement ellipsoids are drawn at the 40% probability level. Water molecules are omitted for clarity (i: $2-x, -y, -z$).

be chosen to form the basal plane of the octahedron,

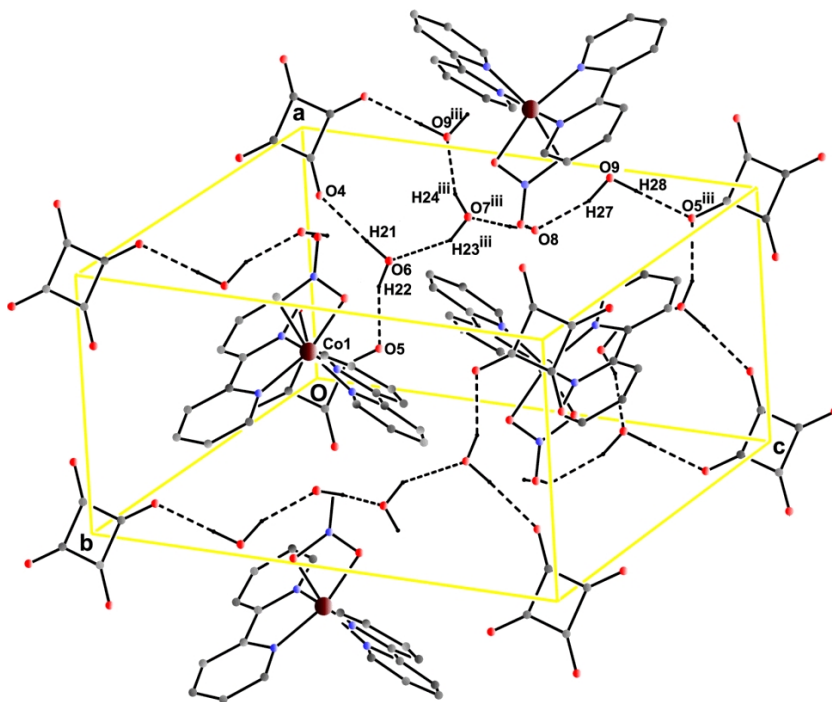


Fig. 2. The hydrogen bonding geometry. Symmetry operations: (i) $x-1, y, z$; (ii) $2-x, 1-y, 1-z$; (iii) $2-x, -y, 1-z$.

and the equatorial positions are occupied by atoms N1 and N3. The maximum deviation from the basal plane is 0.0782 (18) Å for atom O2. There are also considerable differences between N–Co–N angles in the cationic complex. Considering these differences in bond lengths and deviations, it can be said that the coordination environment of the cationic complex is a distorted octahedron (Table 3), similar to related structures [36–38]. The dihedral angle between the bipy ligands is 71.83(4)°. The uncoordinated squarate anions are at the unit-cell corners. The dihedral angle between the squarate anion and a pyridine ring is 27.13(10)°. The O–C bond lengths [1.255(5) and 1.259(5) Å], and the C–C bond length [1.461(6) Å] in the squarate anion are in agreement with related structures [23, 39].

The crystal packing is mainly stabilized by intra- and inter-molecular hydrogen bonding between the squarate anion and water molecules. The cationic complex is involved in inter-molecular hydrogen bonding, O8–H25...O3ⁱⁱⁱ, via its nitrato ligand whereas the bipy ligands are not involved in hydrogen bonding. These interactions are depicted in Fig. 2 and are included in Table 3.

Experimental Section

Materials and measurements

All chemicals used were analytical reagent products. Elemental analysis for C, H, and N was carried out at the TÜBİTAK Marmara Research Centre in Turkey. The magnetic susceptibility measurement was performed at r.t. using a Sherwood Scientific MXI model Gouy magnetic balance. The UV/vis spectrum was obtained from the aqueous solution (10^{-3} M) of the title complex with a Unicam UV2 spectrometer in the range of 900–190 nm. The IR spectrum was recorded in the 4000–200 cm^{-1} region with a Mattson 1000 FT-IR spectrometer using KBr pellets. A Rigaku TG8110 thermal analyzer was used to record TG, DTG and DTA curves in static air atmosphere at a heating rate of 10 Kmin^{-1} in the temperature range of 20–1000 °C using platinum crucibles. Highly sintered α - Al_2O_3 was used as a reference, and the DTG sensitivity was 0.05 mgs^{-1} .

Preparation

A solution of 2,2'-bipyridine (0.63 g, 4 mmol) in ethanol (10 cm^3) was added dropwise with stirring to a mixture of $\text{Co(NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (0.58 g, 2 mmol) and squaric acid (0.23 g, 2 mmol) in distilled water (20 cm^3). The solution was heated to 60 °C in a temperature-controlled bath and stirred for 5 h at 60 °C. The reaction mixture was then slowly cooled to r.t. The red crystals were filtered and washed with 10 cm^3 of cold distilled water and ethanol and dried in air. $[\text{Co}(\text{NO}_3)(\text{bipy})_2](\text{sq})_{0.5} \cdot 4\text{H}_2\text{O}$ Yield *ca.* 0.75 g, 67%. – $\text{C}_{22}\text{H}_{24}\text{N}_5\text{O}_9\text{Co}$ (561.39): calcd. C 47.07, H 4.31, N 12.47; found C 47.15, H 4.91, N 12.46.

Crystallographic analysis

Diffraction experiments were carried out at 296 K on a Stoe IPDS diffractometer. The structure was solved by Direct Methods using the program SHELXS97 [40]. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods [40]. The hydrogen atoms of bipy ligands were placed in geometrically idealized positions and refined as riding atoms. The hydrogen atoms of the water molecules were treated with constraints. The relevant crystal data and experimental conditions along with the final parameters are summarized in Table 2. Data collection: X-Area, cell refinement: X-Area, data reduction: X-RED [41]; program(s) used to refine structure: SHELXL97 [40]; molecular graphics: ORTEP-3 for Windows [42]; software used to prepare material for publication: WinGX [43].

Supplementary Material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 286118. Copies of this information may be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

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