

Syntheses, Spectral and Thermal Studies, and Crystal Structure of 1,10-Phenanthroline and Picolinamide Complexes of Cobalt(II) Squarate

Okan Zafer Yeşilel^a, Halis Ölmez^b, O. Ozan Yılan^c, Hümeysra Paşaoğlu^c, and Orhan Büyükgüngör^c

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

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

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

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

Z. Naturforsch. **61b**, 1094 – 1100 (2006); received February 7, 2006

Preparations, crystal structures, thermal properties, IR and UV/vis spectroscopic studies and magnetic moments of tris(1,10-phenanthroline)cobalt(II) squarate octahydrate, $[\text{Co}(\text{phen})_3]\text{sq} \cdot 8\text{H}_2\text{O}$ (**1**) and diaquabis(picolinamide)cobalt(II) squarate, $[\text{Co}(\text{H}_2\text{O})_2(\text{pia})_2]\text{sq}$ (**2**) are described. **1** crystallizes in the monoclinic system, space group $P2_1/c$, with $a = 10.9832(5)$, $b = 21.4569(12)$, $c = 17.0649(7)$ Å, $\beta = 98.159(3)^\circ$ and $Z = 8$, while **2** crystallizes in the triclinic system, space group $P\bar{1}$, with $a = 6.9624(9)$, $b = 7.9224(11)$, $c = 8.0501(11)$ Å, $\alpha = 107.404^\circ$, $\beta = 93.340(11)^\circ$, $\gamma = 93.266^\circ$ and $Z = 1$. Both **1** and **2** have slightly distorted octahedral coordination geometry, involving six N atoms from bidentately chelating phen ligands and *trans*- $[\text{CoN}_2\text{O}_4]$ coordination geometry, in which the Co atom is located at a center of symmetry. There are significant hydrogen-bonding interactions in the structure of **1**. The squarate dianions are linked to the eight solvent water molecules by means of hydrogen-bonding interactions. Moreover, there are links between the complex cation and the squarate dianion via C–H \cdots O hydrogen bonds. These interactions hold the crystal structure of **1** in a three-dimensional network, while O–H \cdots O, N–H \cdots O, weak $\pi\cdots\pi$ and $\pi\cdots$ ring interactions lead to a three-dimensional crystal structure for **2**. The thermal decomposition pathways of **1** and **2** have been investigated by the help of thermal analyses data (TG and DTA).

Key words: Cobalt(II) Complex, 1,10-Phenanthroline, Picolinamide, Squarate, Thermal Decomposition

Introduction

The versatility of the squarate anion ($\text{C}_4\text{O}_4^{2-}$, sq) as a ligand has been amply demonstrated. The results suggest that it may act as a monodentate [1] or a bridging ($\mu - 1,2$) [2–5], ($\mu - 1,3$) [5–14] ligand, but less has been written about the equally important complexes with squarate counter anions. Squarate and its metal complexes continue to attract attention, not only because of the coordination modes of squarate, but also because of the potential application of metal complexes to xerographic photoreceptors, organic solar cells and optical recording [15,16]. Mixed ligand complexes with 1,10-phenanthroline is also interesting due to their potential role as models for biological systems such as binding of small molecules to DNA [17]. Picolinamide (pyridine-2-carboxamide,

pia) ligands represent a promising class of bidentate ligands for complex molecules that can be used to separate trivalent actinide and/or lanthanide cations from aqueous solutions of nuclear waste obtained by dissolution of spent fuel in nitric acid. These ligands possess such functionality because they combine a moderately hard amide O- and a softer pyridine N-binding site, which can co-operatively bind hard cations with possible discrimination as a function of size and hardness [18]. On the structure of cobalt(II) complexes with pia very little has been published. We reported earlier the crystal structure determinations of the $[\text{Ni}(\text{pia})_2(\text{H}_2\text{O})_2](\text{sac})_2 \cdot 4\text{H}_2\text{O}$ (sac = saccharinate) [19], $[\text{Cu}(\text{pia})_2(\text{H}_2\text{O})_2]\text{sq}$ [20], $[\text{Ni}(\text{phen})_3]\text{sq} \cdot 8\text{H}_2\text{O}$ [21], $[\text{Cu}(\text{phen})_2]\text{sq} \cdot 3\text{H}_2\text{O}$ [1], and $[\text{Co}(\text{H}_2\text{O})_2(\text{phen})_2](\text{H}_2\text{Or})_2 \cdot 2.25\text{H}_2\text{O}$ [22] (H_2Or^- = monoanionic orotate). We have studied

Table 1. Selected IR spectral data*.

Assignment	1	2	Squaric acid ^a
νOH	3512 m	3622 m	3462 s
νNH_2	—	3329 m, 3380 m	—
νCH	2828 vw, 2965 vw	3029 vw, 3 3075 vw	—
$\nu\text{C=O}$	—	1786 w	1822 w
$\nu\text{C=N}$	1555 m	1593 m	—
$\nu[(\text{C-O}) + (\text{C-C})]$	1520 vs, b	1527 vs, b	1530, 1516 vs
$\nu\text{Cu-O}$	512 w	631 w	—

* w = weak; vw = very weak; m = medium; s = strong; vs = very strong; b = broad. ^a Reference [26].

the synthesis, spectral and thermal properties of metal-orotate complexes with the phen ligand [23, 24]. As part of our ongoing research, in this study, the synthesis, spectral and thermal properties and crystal structures of two new Co(II) complexes with 1,10-phenanthroline and picolinamide ligands and squarate anions are described.

Results and Discussion

IR spectra

Selected IR bands of both complexes are listed in Table 1. IR spectra of squarate complexes are quite characteristic. The IR bands at *ca.* 3600 cm^{-1} are attributed to the $\nu(\text{OH})$ vibrations of coordinated and crystal water molecules in the complexes. In the IR spectrum of **2**, the νNH_2 stretching vibration appears as two split bands at 3329 and 3380 cm^{-1} . The weak peaks in the 3075–2800 cm^{-1} range are due to νCH stretching of pia and phen ligands. The IR vibration modes of the squarate anion, which are broad and very strong, were observed at 1520 and 1527 cm^{-1} for **1** and **2** complexes, respectively, and assigned to a mixture of C–C and C–O stretching vibrations. This type of absorption is characteristic of salts of $\text{C}_n\text{O}_n^{2-}$ ions and it was found at 1500 cm^{-1} in the IR spectrum of $\text{K}_2\text{C}_4\text{O}_4$ [25]. The medium bands at the 1555 and 1593 cm^{-1} are due to $\nu(\text{CN})$ stretching absorptions in **1** and **2**, respectively. The strong band at 1661 cm^{-1} is due to νCO stretching of pia ligands. The low intensity bands at *ca.* 512 and 631 cm^{-1} are attributed to $\nu(\text{Co-N})$ and $\nu(\text{Co-O})$ vibrations, respectively.

UV/vis spectra and magnetic moments of the complexes

The electronic spectra of **1** and **2** in water exhibit a band at *ca.* 235 nm in the UV region, characteristic of the squarate. The λ_{max} values of the first two

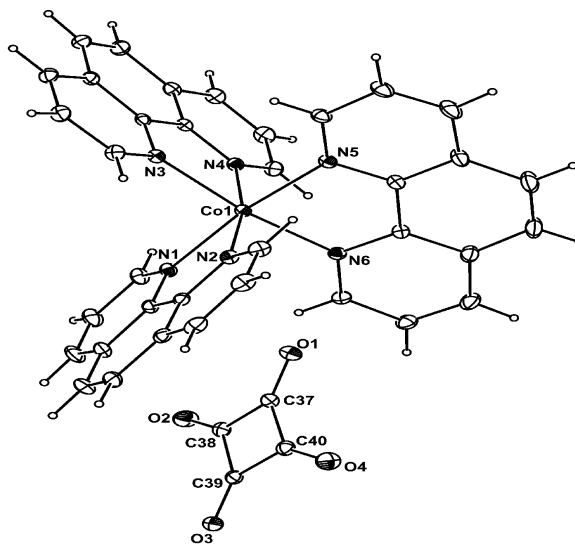


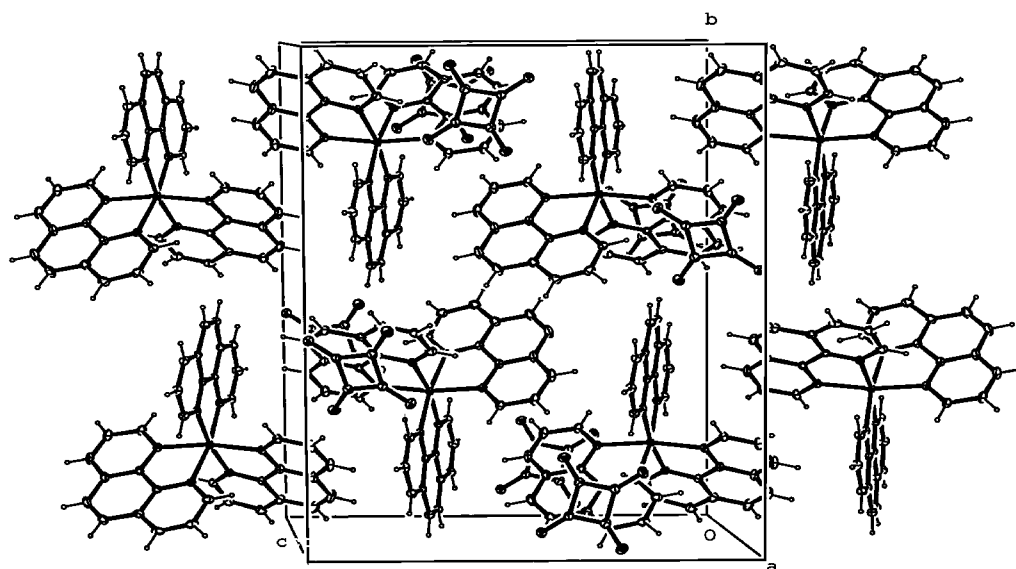
Fig. 1. The molecular structure of the title compound showing the atom labeling scheme at the % 30 probability level.

absorption bands in the spectrum of **1** are 475 ($\epsilon = 17 \text{ l mol}^{-1}\text{cm}^{-1}$) and 881 nm ($\epsilon = 32 \text{ l mol}^{-1}\text{cm}^{-1}$), while in the spectrum of **2** they are 506 ($\epsilon = 14 \text{ l mol}^{-1}\text{cm}^{-1}$) and 885 nm ($\epsilon = 24 \text{ l mol}^{-1}\text{cm}^{-1}$). These values were assigned to the d-d transitions ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{2g}$ and ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{P})$, respectively. The ${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}$ transition was not observed; it is of high energy shifted to the UV region and hidden under the intraligand transitions. **1** and **2** exhibit magnetic moment values of 4.3 and 4.1 μ_B which correspond to three unpaired electrons, respectively, consistent with a weak field octahedral geometry as expected.

Thermal studies

The thermal behaviour of the complexes was followed up to 500 $^{\circ}\text{C}$ in a static air atmosphere. The stage of in the 25–133 $^{\circ}\text{C}$ temperature range of **1** is related to endothermic removal of eight moles of crystal water, giving an endothermic contribution ($\text{DTA}_{\text{max}} = 31, 55 \text{ and } 117^{\circ}\text{C}$; found 16.08, calcd. 16.82%). The following two stages involve the exothermic oxidation of 1.5 moles of phen ($\text{DTA}_{\text{max}} = 235 \text{ and } 284^{\circ}\text{C}$; found 31.59, calcd. 31.67%). In the last stage, the strong exothermic mass loss occurs in the 295–416 $^{\circ}\text{C}$ temperature range. During this stage, the remaining organic part and squarate are abruptly burnt ($\text{DTA}_{\text{max}} = 350^{\circ}\text{C}$), leading finally to CoO .

The thermal analysis curves of **2** are similar. The first stage is related to the dehydration in the tempera-

Fig. 2. The packing of the molecule of **1**.

ture interval of 42–147 °C, the two moles of aqua ligands being released in an endothermic effect at 107 °C (DTA_{max}). The second stage in the 148–249 °C range corresponds to the endothermic elimination of pia ligands. The following stages involve the exothermic decomposition of squarate and the violently exothermic burning of organic residue. A black CoO powder remains as a final decomposition product which was identified by IR spectroscopy.

Crystallographic analysis

Description of **1**

The crystallographic data are summarized in Table 2. Tables 3 and 4 list bond lengths and angles and hydrogen-bonding geometries. The asymmetric unit of **1** contains $[\text{Co}(\text{phen})_3]^{2+}$ complex cations where phen is 1,10-phenanthroline, an uncoordinated squarate dianion and eight water molecules (Fig. 1; H_2O molecules are omitted).

Compound **1** has slightly distorted octahedral coordination geometry, involving six N atoms from bidentate chelating phen ligands. The Co–N bond distances range from 2.108 to 2.127 Å. These distances are similar to those reported for $[\text{Co}_3(\text{C}_9\text{H}_3\text{O}_6)_2(\text{C}_{12}\text{H}_8\text{N}_2)(\text{H}_2\text{O})_2]$ [27], $[\text{Co}(\text{C}_6\text{H}_6\text{NO}_3\text{S})(\text{C}_{12}\text{H}_8\text{N}_2)(\text{H}_2\text{O})_3]\text{Cl}$ [28], $[\text{Co}(\text{C}_{10}\text{H}_4\text{O}_8)(\text{C}_{12}\text{H}_8\text{N}_2)(\text{H}_2\text{O})]$ [29], $[\text{Co}(\text{C}_9\text{H}_6\text{O}_5)(\text{C}_{12}\text{H}_8\text{N}_2)(\text{H}_2\text{O})]$ [30], and $[\text{Co}_2(\text{C}_{14}\text{H}_9\text{O}_4)_4(\text{C}_{12}\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})]$ [31].

Table 2. Summary of the crystal data, details of data collection and structure determination of **1** and **2**.

Chemical formula	$\text{C}_{28}\text{H}_{20}\text{N}_4\text{O}_6\text{Co}$	$\text{C}_6\text{H}_{14}\text{N}_4\text{O}_9\text{Co}$
Molecular weight	567.41	465.24
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$
Color	orange	orange
a [Å]	10.9832(5)	6.9624(9)
b [Å]	21.4569(12)	7.9224(11)
c [Å]	17.0649(7)	8.0501(11)
α [°]		107.404(11)
β [°]	98.159(3)	93.340(11)
γ [°]		93.266(11)
V [Å ³]	3980.9(3)	421.69(10)
Z	8	1
d_{calc} [g/cm ³]	1.39	1.78
Absorption coeff. μ [mm ^{−1}]	0.93	1.09
λ (Mo- $K\alpha$) Å	0.71073	0.71073
R_{int}	0.0968	0.1074
θ_{max}	25.93	25.99
Absorption correction	By integration (X-RED32; Stoe-Cie 2002)	
h, k and l Limits	$-13 \leq h \leq 13,$ $-26 \leq k \leq 26,$ $-20 \leq l \leq 20$	$-9 \leq h \leq 9,$ $-9 \leq k \leq 10,$ $-10 \leq l \leq 10$
$R[F^2 > 2\sigma(F^2)]$	$R_1 = 0.0506,$ $R_1 = 0.097$	$R_1 = 0.0256,$ $R_1 = 0.035$
All data	0.1374	0.0689
$wR(F^2)$	where $P = (F_o^2 + 2F_c^2)/3$	
$w = 1/[\sigma^2(F_o^2) + (0.0804P)^2 + 0.0000P]$		
Goodness-of-fit on F^2	0.918	1.0470
Number of refined parameter	541	149
Largest difference peak and hole [e Å ^{−3}]	0.778, −0.707	0.342, −0.250

Table 3. Selected geometric parameters for **1**.

<i>Bond lengths (Å):</i>			
Co1–N1	2.108(3)	N4–Co1	2.112(3)
Co1–N2	2.110(3)	N5–Co1	2.123(3)
Co1–N3	2.127(3)	N6–Co1	2.120(3)
<i>Bond angles (°):</i>			
N1–Co1–N2	78.75(10)	N2–Co1–N5	93.57(10)
N1–Co1–N3	91.65(10)	N2–Co1–N6	93.98(10)
N1–Co1–N4	94.79(10)	N4–Co1–N3	78.70(9)
N1–Co1–N5	170.02(10)	N4–Co1–N5	93.70(10)
N1–Co1–N6	95.35(10)	N4–Co1–N6	94.84(10)
N2–Co1–N3	93.13(10)	N5–Co1–N3	95.14(10)
N2–Co1–N4	169.52(10)	N6–Co1–N3	170.86(10)

Table 4. Hydrogen-bonding geometry for **1** (Å, °).

D–H...A	<i>d</i> (D–H)	<i>d</i> (H...A)	<i>d</i> (D...A)	∠(DHA)
O5–H35...O8	0.85(4)	2.18(4)	2.817(5)	132(3)
O11–H36...O4 ⁱ	0.68(4)	2.20(4)	2.841(4)	157(5)

Symmetry code: ⁱ 1 – *x*, –*y*, 1 – *z*.

The angles between opposite phen ligands are 78.75(10)°, 78.70(9)° and 78.70(10)° which are similar to those observed in [Co(C₁₂H₈N₂)₃·(C₄H₂O₄)_{0.5}(C₄H₃O₄)]·1.5C₄H₄O₄ [32], [Co(C₁₂H₈N₂)₂(H₂O)₂](C₅H₃N₂O₄)₂·2.25H₂O [22] and [CoCl(C₁₂H₈N₂)₂(H₂O)]Cl·0.5C₆H₁₄N₂O₂ [33].

The squarate dianions are linked to the eight solvent water molecules by means of hydrogen-bonding interactions. Moreover, links exist between the complex cations and squarate dianions *via* C–H...O hydrogen bonds. These interactions hold the crystal structure of **1** in a three dimensional network as represented in Fig. 2.

Description of **2**

The crystallographic data are summarized in Table 1. Tables 5 and 6 list bond lengths and angles and hydrogen-bonding geometries. The structure consists of centrosymmetric complex cations and a squarate dianions (Fig 3). The complex shows an octahedral *trans*–[CoN₂O₄] coordination geometry, in which the Co1 atom is located at a center of symmetry. The pyridine N atoms of the chelating pia ligands and the amide O atoms constitute the equatorial plane of the octahedron. The axial positions are occupied by water molecules. The Co1–O1 distance is slightly longer than the Co1–O2 distance. The Co1–O1 and Co1–N1 bond lengths are 2.1015(15) and 2.0908(14) Å, respectively. The former are in agreement with the values reported for the related structures [Co(C₄O₄)(C₆H₆N₂O)₂·2H₂O [34], [Co(C₇H₄O₆S)(C₁₂H₈N₂)(H₂O)₂] [35], [Co(C₁₀H₄O₈)₂–

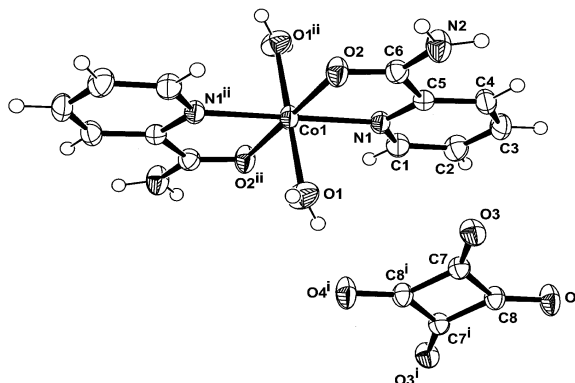


Fig. 3. The molecular structure of the title compound showing the atom-labeling scheme at the % 50 probability level.

(C₁₂H₈N₂)(H₂O)₃·H₂O [36], [Co(C₄H₄O₄S)(C₁₂H₈N₂)(H₂O)] [37], [Co(C₁₂H₈N₂)₂(H₂O)₂](C₅H₃N₂O₄)₂·2.25H₂O [22], and [Co(C₈H₄NO)₂(C₁₂H₈N₂)(H₂O)₂] [38].

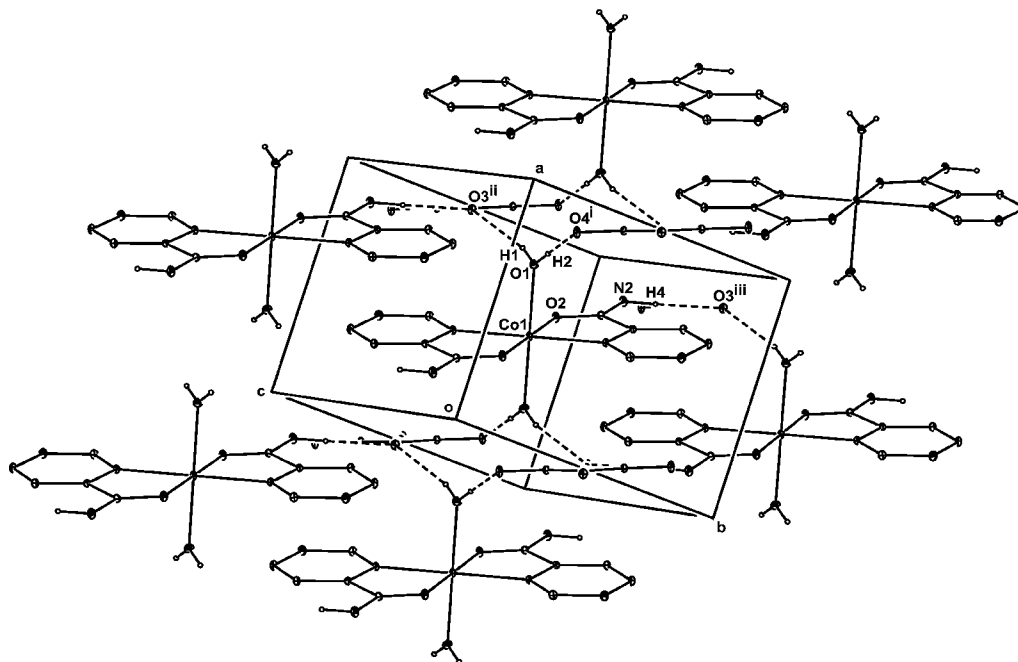
The pia ligands are almost planar with an r.m.s. deviation of 0.0023 Å and the maximum deviation from the mean plane of –0.0039(19) Å for atom C1. This deviation in the pia ligand is caused by the coordination to the Co atom. The torsion angle between the carboxamide group and the pyridine ring is C4–C5–C6–N2 = –1.3(3)°.

The chelate ring is essentially planar with a r.m.s. deviation of 0.0234 Å and the maximum deviation from the mean plane is 0.0280(14) Å for atom O2.

The pyridine ring and the carboxamide group are approximately coplanar with a dihedral angle 1.93°.

The uncoordinated squarate anion shows exact planarity with a r.m.s. deviation of 0.0158 Å. The dihedral angle between the squarate anion and the pyridine ring is 17.63°. In the squarate anion, the C–O bond distances are 1.254(2) and 1.251(2) Å, while the C–C distances are 1.460(2) and 1.470(2) Å. These distances agree with those in [Cu(C₆H₆N₂O)₂(H₂O)₂](C₄O₄) [20]. Each squarate anion is surrounded by four [Co(pia)₂(H₂O)₂]²⁺ cations. The squarate anion's O atoms take part in hydrogen bonds with amide and water H atoms.

The hydrogen bondings stabilizing the crystal structure are shown in Fig. 4. O1–H1...O3ⁱⁱ hydrogen bonding occurs between the O atom of an aqua ligand and the O atom of a squarate anion. On the other hand, the amide group of pia is involved in hydrogen bonding N2–H4...O3ⁱⁱⁱ, with the O atom of neighboring water molecule.

Fig. 4. The packing of the molecule of **2**.Table 5. Selected geometric parameters for **2**.

Bond lengths (Å)		Bond angles (°)	
Co1–O1	2.101(1)	N1–Co1–O1	89.03(6)
Co1–O2	2.081(1)	N1–Co1–O2	78.48(5)
Co1–N1	2.090(1)	O1–Co1–O2	87.30(6)

Table 6. Hydrogen-bonding geometry for **2** (Å, °).

D–H...A	d(D–H)	d(H...A)	d(D...A)	∠(DHA)
O1–H2...O4 ⁱ	0.76(3)	1.97(3)	2.732(2)	172(3)
O1–H1...O3 ⁱⁱⁱ	0.71(3)	2.08(3)	2.772(2)	165(3)
N2–H4...O3 ⁱⁱⁱ	0.89(3)	1.98(3)	2.858(2)	168(2)

Symmetry codes: ⁱ 2 – x, 1 – y, –z; ⁱⁱ 2 – x, 1 – y, 1 – z; ⁱⁱⁱ 2 – x, 2 – y, 1 – z.

There are weak intermolecular $\pi \cdots$ ring interactions between pyridine rings and neighboring pyridine molecules. The perpendicular distance from ring A to A^{iv} is 3.417 Å [symmetry code: (iv) 1 – x, –y, 1 – z]. The distance between the ring centroids is 4.2103(12) Å for ring A, with another weak $\pi \cdots \pi$ interaction between the ring A and the squarate ring (ring B). The distance between the ring centroids is 4.987 Å for ring B. And also, ring B is involved in weak intermolecular C–H $\cdots\pi$ interaction with the pyridine C1 atom.

These weak $\pi \cdots \pi$ and $\pi \cdots$ ring interactions support the three-dimensional crystal structure.

Experimental Section

Materials and instrumentation

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. Magnetic susceptibility measurement at r.t. was performed using a Sherwood Scientific MXI model Gouy magnetic balance. The UV/vis spectrum was obtained from the aqueous solution of the complex with a Unicam UV2 spectrometer in the range 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 simultaneous TG, DTG and DTA data in static air atmosphere at a heating rate of 10 K min^{–1} in the temperature range 20–500 °C using platinum crucibles. Highly sintered α -Al₂O₃ was used as a reference.

A suitable single crystal was mounted on a glass fibre and data collection was performed on a STOE IPDSII image plate detector using Mo-K α radiation (λ = 0.71073 Å). Data collection: Stoe X-Area [39]. Cell refinement: Stoe X-Area [39]. Data reduction: Stoe X-RED [39]. The structure was solved by direct methods using SIR97 [40], and anisotropic displacement parameters were applied to non-hydrogen atoms in a full-matrix least-squares refinement based on F² using SHELXL-97 [41]. Molecular graphics: ORTEP-3 for Windows [42]; software used to prepare material for publication: WinGX [43]. H atoms attached to the O1,

O6 atoms of water and the N atoms were located in a difference Fourier map and their coordinates and U_{iso} parameters were refined freely. The remaining H atoms were placed geometrically and allowed to ride on their parent atoms, with C–H = 0.93 Å and $U_{iso}(H) = 1.2 U_{eq}(C)$. At this stage, the maximum difference density of 1.37 eÅ^{-3} (the ratio of maximum / minimum residual density is 2.87) indicated the presence of a possible atom site. A check for the solvent-accessible volume using PLATON showed a total potential solvent area volume of 74 Å^3 .

Preparation of **1** and **2**

A solution of phen (0.54 g, 3 mmol) or pia (0.25 g, 2 mmol) in ethanol (10 cm^3) was added dropwise with stirring to a solution of $\text{CoSq} \cdot 2\text{H}_2\text{O}$ [25] (0.21 g, 1 mmol) in distilled water (20 ml). The solution was heated to 60°C in a temperature-controlled bath and stirring continued for 5 h at 60°C . The reaction mixture was then slowly cooled to r.t. The orange crystals formed were filtered and washed with 10 ml of water and ethanol and dried *in air*.

1 – UV/vis (H_2O): λ_{max} (nm) = 235, 275, 475 and 890. $\text{C}_{40}\text{H}_{40}\text{N}_6\text{O}_{12}\text{Co}$ (855.72): calcd. C 56.09, H 4.67, N 9.82; found C 56.56, H 4.29, N 9.55.

2 – UV/vis (H_2O): λ_{max} (nm) = 237, 276, 506 and 885. $\text{C}_{16}\text{H}_{16}\text{N}_4\text{O}_8\text{Co}$ (451.26): calcd. C 42.55, H 3.55, N 12.41; found C 42.54, H 3.11, N 12.24.

Supplementary data

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as the supplementary publications no CCDC 297121 and 297122. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgement

The authors wish to acknowledge the Faculty of Arts and Sciences, Ondokuz Mayıs University, Turkey, for the use of the Stoe IPDS-II diffractometer (purchased under grant No. F279 of the University Research Fund).

- [1] A. Bulut, İ. Uçar, O. Z. Yeşilel, H. İcbudak, H. Ölmez, O. Büyükgüngör, *Acta Crystallogr.* **C60**, m526 (2004).
- [2] I. Catro, M. L. Calatayud, J. Sletten, F. Lloret, M. Julve, *Inorg. Chim. Acta* **287**, 173 (1999).
- [3] R. Soules, F. Dahan, J. P. Laurent, P. Castan, *J. Chem. Soc., Dalton Trans.* 587 (1988).
- [4] I. Castro, M. L. Calatayud, J. Sletten, F. Lloret, M. Julve, *J. Chem. Soc., Dalton Trans.* 811 (1997).
- [5] A. Crispini, D. Pucci, I. Aiello, M. Ghedini, *Inorg. Chim. Acta* **304**, 219 (2000).
- [6] L. H. Huo, X. L. Cheng, H. Zhao, W. Ng, *Acta Crystallogr.* **E61**, m460 (2005).
- [7] I. Castro, J. Faus, M. Julve, Y. Journaux, J. Sletten, *J. Chem. Soc., Dalton Trans.* 2533 (1991).
- [8] G. Bernardinelli, D. Deguenon, R. Soules, P. Castan, *Canadian J. Chem.* **67**, 1158 (1988).
- [9] I. Castro, M. L. Calatayud, J. Sletten, M. Julve, F. Lloret, *C. R. Acad. Sci. Paris, Chimie / Chemistry* **4**, 235 (2001).
- [10] B. D. Alleyne, L. A. Hall, H. A. Hosein, H. Jagger-nauth, A. J. P. White, D. J. Williams, *J. Chem. Soc., Dalton Trans.* 3845 (1998).
- [11] C. Robl, A. Weiss, *Z. Naturforsch.* **41b**, 1341 (1986).
- [12] A. Weiss, E. Riegler, I. Alt H. Böhme, C. Robl, *Z. Naturforsch.* **41b**, 18 (1986).
- [13] A. Weiss, E. Riegler, C. Robl, *Z. Naturforsch.* **41b**, 1329 (1986).
- [14] A. Weiss, E. Riegler, C. Robl, *Z. Naturforsch.* **41b**, 1333 (1986).
- [15] L. S. Liebeskind, M. S. Yu, R. H. Yu, J. Wang, C. Glidewell, *J. Am. Chem. Soc.* **115**, 9048, (1993).
- [16] G. Seitz, P. Imming, *Chem. Rev.* **92**, 1227 (1992).
- [17] C. V. Sastri, D. Eswaramoorthy, L. Giribabu, B. G. Maiya, *J. Inorg. Biochem.* **94**, 138 (2003).
- [18] M. Beaden, F. Berny, C. Madle, R. Schurhammer, G. Wipff, *Solvent Extraction Ion Exch.* **21**, 199 (2003).
- [19] H. Pasaoglu, F. Tezcan, O. Z. Yesilel, H. Ölmez, H. İcbudak, O. Büyükgüngör, *Acta Crystallogr.* **C60**, m335 (2004).
- [20] I. Ucar, A. Bulut, O. Z. Yeşilel, H. Ölmez, O. Büyükgüngör, *Acta Crystallogr.* **E60**, m1945 (2004).
- [21] I. Ucar, O. Z. Yesilel, A. Bulut, H. Ölmez, O. Büyükgüngör, *Acta Crystallogr.* **E61**, m947 (2005).
- [22] A. Bulut, H. İcbudak, O. Z. Yesilel, H. Ölmez, O. Büyükgüngör, *Acta Crystallogr.* **E59**, m736 (2003).
- [23] O. Z. Yesilel, H. Ölmez, *J. Therm. Anal. Cal.* (2006), in press.
- [24] O. Z. Yesilel, I. Ucar, A. Bulut, H. Ölmez, O. Büyükgüngör, *Z. Naturforsch.* **61b**, 147 (2006).
- [25] R. West, H. Y. Niu, *J. Chem. Soc.* **85**, 2589 (1963).
- [26] F. G. Baglin, C. B. Rose, *Spectrochim. Acta Part A* **26a**, 2293 (1970).
- [27] M. L. Hu, J. X. Yuan, H. P. Xiao, F. Chen, *Acta Crystallogr.* **C60**, m235 (2004).
- [28] M. H. Huang, L. H. Bi, S. J. Dong, *Acta Crystallogr.* **C60**, m30 (2004).
- [29] M. L. Hu, J. X. Yuan, H. P. Xiao, J. X. Yuan, *Acta Crystallogr.* **C60**, m112 (2004).
- [30] S. Gao, I. H. Huo, C. S. Gu, J. W. Liu, J. G. Zhao, *Acta Crystallogr.* **E61**, m496 (2005).

- [31] Q. Miao, M. L. Hu, F. Chen, *Acta Crystallogr.* **E60**, m1314 (2004).
- [32] Y. Liu, D. J. Xu, C. H. Hung, *Acta Crystallogr.* **E60**, m297 (2003).
- [33] J. W. Liu, S. Gao, L. H. Huo, S. W. Ng, *Acta Crystallogr.* **E60**, m501 (2004).
- [34] İ. Uçar, A. Bulut, *Acta Crystallogr.* **E61**, m1320 (2005).
- [35] S. R. Fang, L. G. Zhu, *Acta Crystallogr.* **E61**, m1598 (2005).
- [36] M. D. Ye, H. P. Xiao, Y. Q. Cheng, M. L. Hu, *Acta Crystallogr.* **E60**, m219 (2004).
- [37] J. Y. Wu, L. M. Xie, H. Y. He, X. Zhou, L. G. Zhu, *Acta Crystallogr.* **E61**, m568 (2005).
- [38] L. M. Xie, H. Y. He, Y. L. Zhou, L. G. Zhu, *Acta Crystallogr.* **E60**, m105 (2004).
- [39] Stoe&cie (2002). X-area (version 1.18) and X-red32 (version 1.04). Stoe&cie, Darmstadt, Germany.
- [40] A. Altomare, M. C. Burla, M. Camalli, G. I. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **32**, 115 (1999).
- [41] G. M. Sheldrick, Shelxl-97, University of Göttingen, Germany (1997).
- [42] N. Burnett, C. K. Johnson, OrtepIII. Report Ornl-6895. Oak Ridge National Laboratory, Tennessee, U.S.A. (1996).
- [43] L. J. Farrugia, WinGX Suite for Single Crystal Small Molecule Crystallography, *J. Appl. Crystallogr.* **32**, 837 (1999).