

The Synthesis, Characterization and Structural Analysis of a Co(III) Complex of 1,10-Phenanthroline and Perfluorosebacic Acid, [Co(HL)(phen)₂(H₂O)]L·H₂O

Ibrahim Kani^a, Orhan Büyükgüngör^b, and Filiz Şişman^a

^a Department of Chemistry, Anadolu University 26470, Eskisehir, Turkey

^b Department of Physics, Ondokuz Mayıs University, TR-55139, Samsun, Turkey

Reprint requests to I. Kani. E-mail: ibrahimkani@anadolu.edu.tr

Z. Naturforsch. **61b**, 1198 – 1204 (2006); received April 11, 2006

The hexacoordinated mononuclear Co(III) complex **1**, [Co(HL)(phen)₂(H₂O)]L·H₂O, with the mixed ligands (H₂L = HO₂C(CF₂)₈CO₂H and 1,10-phenanthroline) has been synthesized and characterized by elemental analysis, IR and UV/vis spectroscopy, magnetic susceptibility, TG analysis and X-ray diffraction techniques. The Co(III) atom is coordinated asymmetrically by two bidentate 1,10 phenanthroline ligands, one hydrogencarboxylate ligand, (O₂C(CF₂)₈CO₂H)⁻, and one water molecule. In the crystal structure, there are also dicarboxylate anions and one water molecule attached through hydrogen bonds. Intermolecular π - π interactions between the adjacent phenanthroline ligands also support the packing of the components.

Key words: Cobalt(III) Complex, Hydrogen Bonding, π - π Interactions, Perfluorosebacic Acid, 1,10-Phenanthroline

Introduction

Research on transition metal dicarboxylate complexes with hetero aromatic N-donor chelating ligands has been of great interest for the synthesis of coordination polymers in the past decade. A large number of publications have appeared in the literature highlighting antifungal activity of novel transition metal-based drug agents with potential applications for the control of fungal infections [1, 2] and interest has also occurred to explore the potential applications of metal complexes containing symmetric aromatic ligands as non-radioactive probes of nucleic acid structures and as possible DNA cleaving agents [3].

The self assembly of the supramolecular coordination network is the result of coordination *via* several types of forces including not only coordinative bonding but also weak interactions such as hydrogen bonding [4, 5], π - π stacking [6, 7] and electrostatic interactions [8, 9]. One of the efficient routes to form coordination polymers is to employ multifunctional ligands. For example, mono- or dicarboxylate anions are found at metal atoms in both low and high oxidation states and are bound in different modes such as monodentate and bidentate, or act as bridging ligands to two metal ions. In contrast to monocarboxylic

acids, the coordination chemistry of dicarboxylic acids ([O₂C(CH₂)_nCO₂]²⁻, $n = 1 - 8$) is far less developed and indeed structural information for this class of complexes is relatively scarce. In most cases, metal salts react with dicarboxylic acids to yield insoluble polymeric materials which are difficult to characterize and almost impossible to crystallize. To overcome this problem, Devereux and co-workers [10, 11] showed that introduction of a second competing ligand (such as 1,10-phenanthroline, 2,2-bipyridine) lowers the dimensionality of the structures since their chelation to the metal ion leaves fewer sites for dicarboxylic acid coordination. Synergetic coordination of dicarboxylates and heteroaromatic N-donor ligands as a source of hydrogen bonding and π - π stacking interactions, respectively, has been shown to generate a variety of supramolecular motifs [12, 13]. Most work has been restricted to the lower members of the series of saturated α , ω -dicarboxylate anions, and only few studies have been carried out with long chain dicarboxylates as ligands [14].

Hitherto, reports about usage of phen and long chain α , ω -dicarboxylate ligands to construct coordination supramolecular complexes are very scarce, and no report has been found on X-ray analyses of Co(III) complexes with phen and perfluorosebacate ligands in the

Table 1. Crystallographic data for the title complex **1**.

Formula	C ₃₉ H ₂₂ Co F ₂₄ N ₄ O ₈
Molecular weight	1189.54
Temperature [K]	100 (2)
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	<i>P</i> 1̄
<i>a</i> [Å]	10.0659(5)
<i>b</i> [Å]	12.6196(6)
<i>b</i> [Å]	18.0948(8)
α [°]	76.454(4)
β [°]	81.039(4)
γ [°]	72.644(4)
Volume [Å ³]	2123.70(17)
<i>Z</i>	2
Calculated density [g/cm ³]	1.859
μ [mm ⁻¹]	0.569
<i>F</i> (000)	1182
Crystal size [mm]	0.18 × 0.34 × 0.53
θ Range [°]	1.88–26.00
<i>h, k, l</i> index ranges	–12 → 12, –15 → 15, –22 → 22
Reflections collected	30912
Independent reflections [<i>R</i> _{int}]	8356 (0.0571)
Reflections observed [<i>I</i> ≥ 2σ(<i>I</i>)]	6848
Absorption correction	Integration (X-RED32; Stoe & Cie, 2002)
Max. and min. transmission	0.7964, 0.9363
Data/restraints/parameters	8356/6/701
Goodness-of-fit on <i>F</i> ²	1.018
<i>R, wR</i> [<i>I</i> ≥ 2σ(<i>I</i>)]	0.0320, 0.0757
<i>R, wR</i> (all data)	0.0433, 0.0794
Largest diff. peak and hole [e Å ⁻³]	0.387 and –0.487

Cambridge Structural Data Base. Herein, we report first the synthesis and the crystal structure of the title compound along with its thermal and spectroscopic characterization.

Results and Discussion

Synthesis and characterization

The Co(III) complex, **1**, has been synthesized from Co(CO₃)_y · *x*H₂O, 1,10-phenanthroline and [HO₂C(CF₂)₈CO₂H], respectively, in a methanol-water mixture under aerobic conditions. Similar aerial metal oxidation of Co(II) has been reported by Maiti *et al.* [15] and John *et al.* [16] in methanol solution. The experimental magnetic moment value of 0.78 BM suggests that the complex has no unpaired electron as a diamagnetic low-spin system.

The ORTEP view of the complex with the formula [Co(HL)(phen)₂(H₂O)](L)H₂O and its atom labeling are shown in Fig. 1. In Fig. 2 the unit cell is presented. The crystallographic data are summarized in Table 1. Selected bond lengths and an-

Table 2. Selected bond lengths [Å] and angles [°] for complex **1**.

Co1-O1	2.0649(15)	N1-Co1-N2	78.65(6)
Co1-O2	2.1393(13)	N1-Co1-N3	98.80(6)
Co1-N1	2.1125(16)	N1-Co1-N4	174.55(6)
Co1-N2	2.1354(15)	N2-Co1-N3	87.38(6)
Co1-N3	2.1243(16)	N2-Co1-N4	96.50(6)
Co1-N4	2.1257(16)	N3-Co1-N4	78.36(6)
F18-C36	1.350(3)	Co1-O2-C25	127.33(11)
O1-Co1-O2	91.93(5)	H1A-O1-H1B	103(3)
O1-Co1-N1	90.53(6)	Co1-O1-H1A	114(2)
Co1-N3-C24	113.33(12)	Co1-O1-H1B	102.5(19)
O1-Co1-N2	91.65(6)	Co1-N1-C12	113.23(12)
Co1-N4-C23	113.57(12)	Co1-N1-C1	128.30(13)
O1-Co1-N3	170.22(6)	Co1-N2-C10	128.40(13)
Co1-N4-C22	128.60(13)	Co1-N2-C11	112.90(12)
O1-Co1-N4	92.10(6)	O2-Co1-N4	91.70(5)
O2-Co1-N1	92.98(5)	O2-Co1-N3	90.49(6)
O2-Co1-N2	170.92(6)		

Table 3. Hydrogen bonding parameters (Å, °).

D–H...A	D–H	H...A	D...A	D–H...A
O1–H1A...O6	0.83(2)	1.82(2)	2.650(2)	177(3)
O1–H1B...O3	0.84(3)	1.93(3)	2.739(2)	161(3)
O4–H4...O8 ⁱ	0.820(3)	1.720(3)	2.527(2)	168.8
O8–H8A...O3	0.83(2)	1.96(2)	2.769(2)	165(3)
O8–H8B...O7	0.85(3)	1.87(2)	2.699(2)	165(4)

Symmetry codes: ⁱ 1 – *x*, 2 – *y*, 2 – *z*.

gles are listed in Table 2. The structure comprises a [Co(O₂C(CF₂)₈CO₂H)(phen)₂(H₂O)]²⁺ complex dication, a perfluorosebacate dianion and a water molecule. Within the complex cation, the cobalt(III) ion is six coordinate being bound to four nitrogen atoms [N1, N2, N3 and N4] of the chelating bidentate phenanthroline ligands, one oxygen atom of a unidentate perfluorosebacate ligand, [O₂C(CF₂)₈CO₂H][–], [Co1-O2 = 2.1394(12) Å] and one oxygen atom of a water molecule [Co1-O1 = 2.0649(13) Å] which is in a *cisoid* position with respect to the coordinated carboxylate ligand. The pendant carboxylate oxygen atoms of the perfluorosebacate [O4 and O5] are uncoordinated. There are one lattice water and one dianionic carboxylate ligand which are involved in hydrogen bonding (Fig. 1, Table 3).

The sixfold coordination around the cobalt atom differs from a regular octahedral geometry due to the small bite angles of the phenanthroline ligands [N1-Co1-N2 = 78.65(6)°, N3-Co1-N4 = 78.36(6)°]. The three diagonal angles of the Co polyhedron are O1-Co1-N3 = 170.22(6)°, N1-Co1-N4 = 174.55(6)° and N2-Co1-O2 = 170.93(5)°. All Co-N bonds are slightly larger as compared to those in similar Co(III) compounds with an average of 2.1244 Å [17]. The Co-N

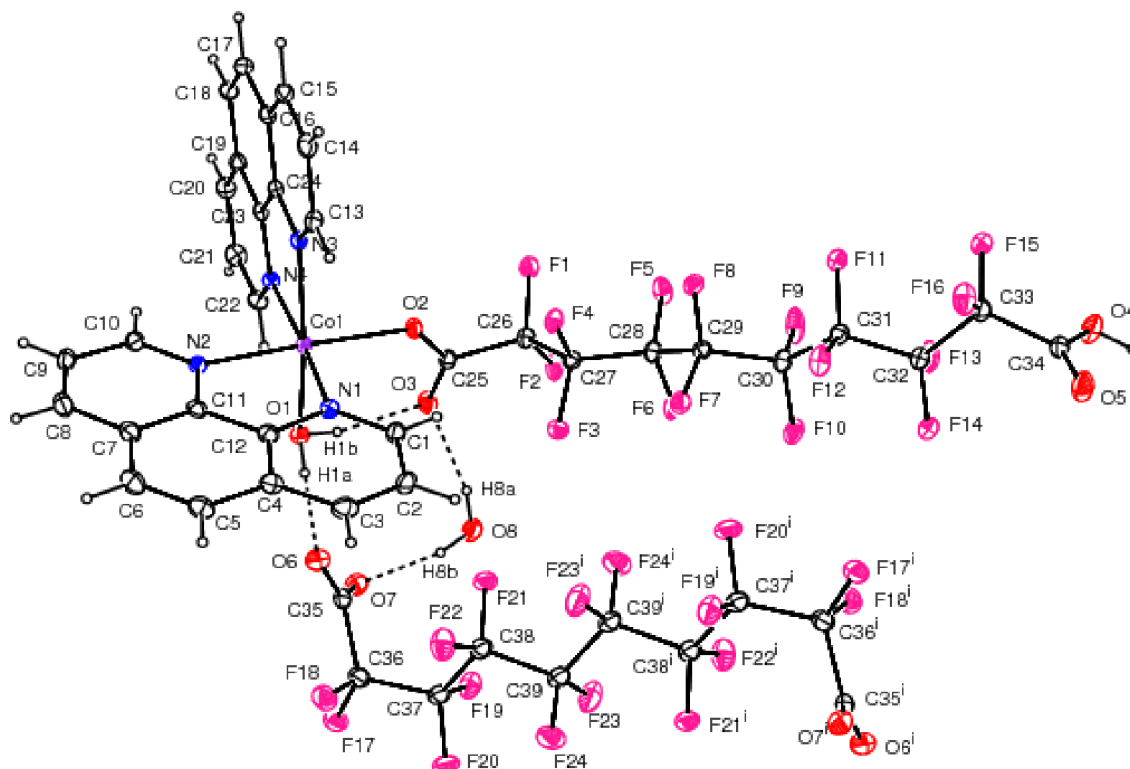


Fig. 1. View of complex **1** with displacement ellipsoids (50% probability) and atom labeling.

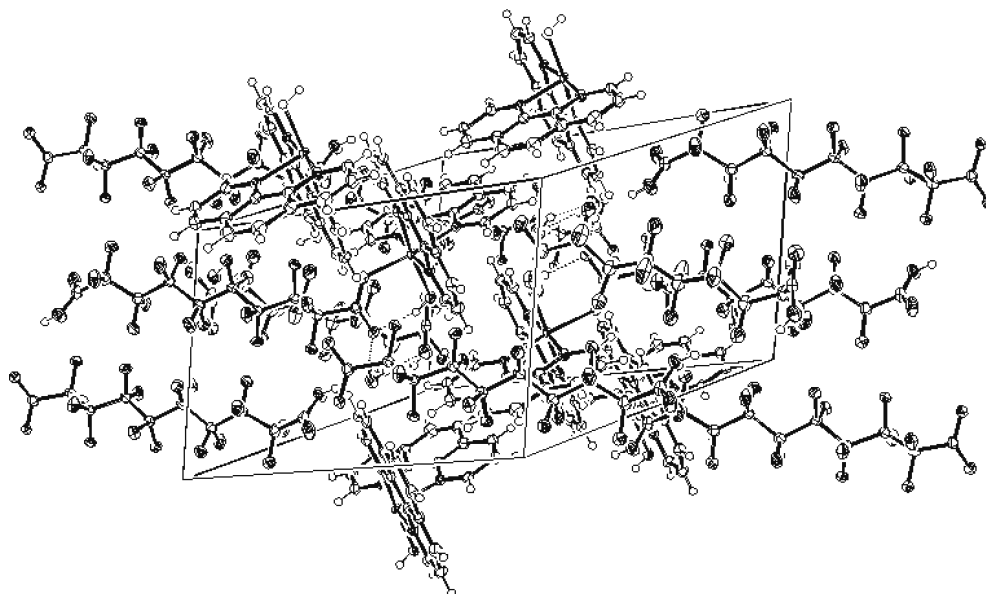


Fig. 2. The packing diagram of complex **1**.

bond lengths of the apical positions are slightly shorter, Co1-N3 = 2.124(2) Å, Co1-O1 = 2.064(2) Å, than the

Co-N bond lengths in the equatorial plane, Co1-O2 = 2.139(1) Å, Co1-N2 = 2.135(2) Å. Around the central

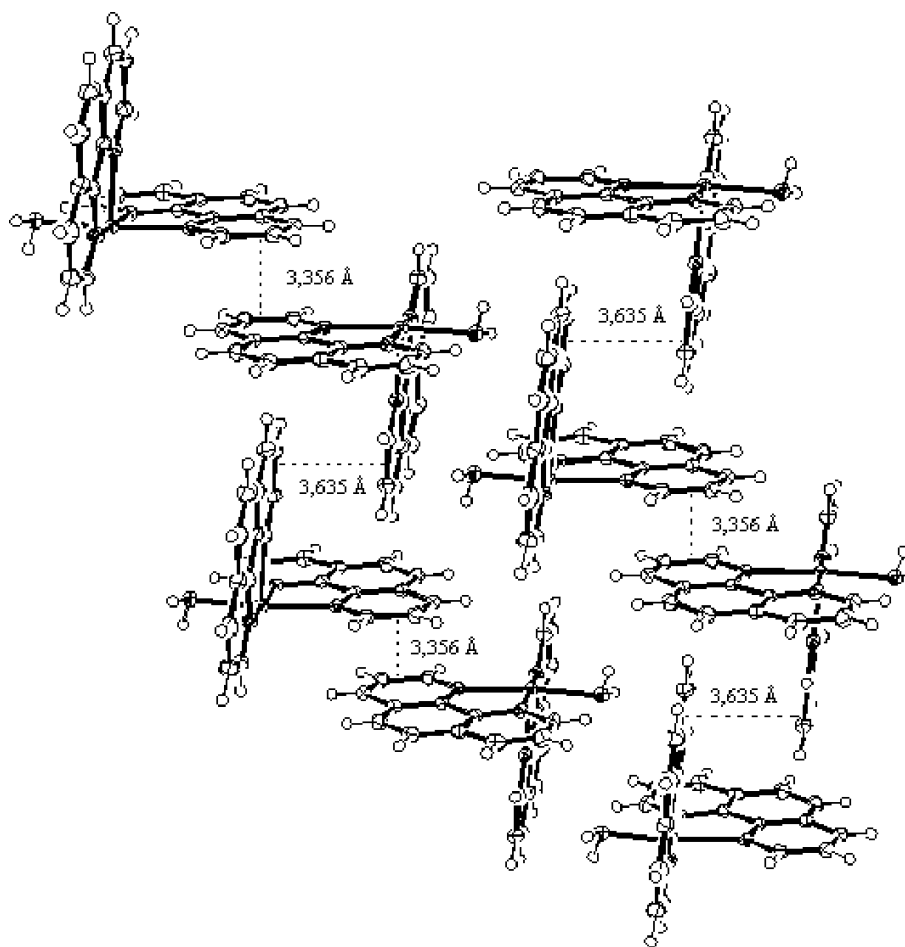


Fig. 3. Supramolecular assembly of the $[\text{Co}(\text{O}_2\text{C}(\text{CF}_2)_8\text{CO}_2\text{H})(\text{phen})_2(\text{H}_2\text{O})]^{2+}$ cations into 2D layers based on intermolecular π - π stacking interactions in **1**.

Co atom, both chelating phen planes are nearly perpendicular to each other.

The uncoordinated linear perfluorosebacate dianion is crystallographically centrosymmetric. Its aliphatic chain has a planar, extended all *anti* geometry and its carboxyl oxygen atoms form pairs of strong hydrogen bonds [$\text{O}3^{\cdots}\text{H}1\text{B} = 1.93(3)$ Å, $\text{O}3^{\cdots}\text{H}8\text{A} = 1.96(2)$ Å]. The $\text{O}3^{\cdots}\text{H}1\text{B}$ interaction is the only intramolecular hydrogen bonding between the uncoordinated carboxylate oxygen atom and the coordinated water molecule. In addition, there is extensive hydrogen bonding in the crystal, involving both coordinated and uncoordinated water molecules as well as the coordinated anionic ligand and the free dianion [$\text{O}7^{\cdots}\text{H}8\text{B} = 1.87(3)$ Å, $\text{O}6^{\cdots}\text{H}1\text{A} = 1.82(2)$ Å]. The analogous mononuclear complex $[\text{Mn}(\text{O}_2\text{C}(\text{CH}_2)_5\text{CO}_2)(\text{phen})_2(\text{H}_2\text{O})]$ has a similar coordination behavior [10]. The strongest in-

termolecular hydrogen bonding interaction has been observed between the hydrogen atom of the coordinated carboxylate ligand and the oxygen atom of the solvated water molecule [$\text{O}8^i\cdots\text{H}4 = 1.72$ Å]. The packing diagram shows clearly π - π stacking interactions (Fig. 3) between pairs of phen with characteristics interplanar distances between the rings of 3.356 and 3.635 Å, similar to known analogous Mn, Cu, Zn and Co complexes [18–19]. Obviously, both π - π stacking and hydrogen bonding interactions are responsible for the supramolecular network assembly of complex **1**.

Electronic and IR spectra

In the UV region, the intense multiple absorption bands (207, 226, 269 nm) observed for complex **1** are presumably due to intraligand $\pi \rightarrow \pi^*$ and/or $n \rightarrow \pi^*$ transitions of the coordinated groups [20]. The free lig-

ands also exhibit transitions (phen: 229 and 263; perfluorosebacic acid: 210 nm). For the low spin t_{2g}^6 configuration of Co(III) complexes two spin allowed transitions, $^1A_{1g} \rightarrow ^1T_{1g}$, $^1A_{1g} \rightarrow ^1T_{2g}$ are expected usually around 500 nm and two spin-forbidden transitions, $^1A_{1g} \rightarrow ^3T_{1g}$, $^1A_{1g} \rightarrow ^3T_{2g}$, at higher energies which are usually difficult to assign owing to overlap of interligand and charge transfer transitions [21, 22]. The expected weak $d-d$ transitions in the visible region for complex **1** have not been detected even for concentrated solutions. It may be lost in the low-energy tail of the intense charge-transfer transitions. The band at 263 nm is red shifted by about ~ 9 nm from the corresponding absorption of the free ligand.

In the IR spectrum of complex **1**, the strong broad peak centered at 3422 cm^{-1} includes the ν_{OH} , $\nu_{\text{N-H}}$, and $\nu_{\text{Ar-H}}$ vibrations of the ligands. The peaks around at 3400 cm^{-1} ($\nu_{\text{O-H}}$) and 1426 (ν_{bending}) cm^{-1} are the characteristics of lattice water molecules. The characteristic bands of the C-F stretching appear in the $1228-1143\text{ cm}^{-1}$ region. The bands at 848 and 727 cm^{-1} are assigned to the C-H out of plane bending of the phen ligands. Bands due to vibrations of the carboxylate ligand are broad strong peaks at 1668 cm^{-1} for antisymmetric and at 1393 cm^{-1} for symmetry stretching. The separation (Δ) between $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$ is 270 cm^{-1} , indicating a mono-dentate coordination mode for the coordinated carboxylate group [23, 24]. The absorption at 1760 cm^{-1} assigned to asymmetrical stretching of free carboxyl groups is showing a shift towards low frequency when compared to $\nu_{\text{as}}(\text{COO}^-)$ (1668 cm^{-1}) of carboxylic acid in which intra- and intermolecular hydrogen-bonding weakens the C=O bond in the carboxyl group. These IR results agree with the result of the X-ray diffraction analysis.

Thermal analysis

The thermal decomposition of the complex was studied by thermogravimetry (TG) under argon atmosphere from 50 to $980\text{ }^\circ\text{C}$ (Fig. 4). Complex **1** decomposes *via* endothermic solid state reactions. The TG data show that decomposition occurs in several steps. Loss of water between 121 and $138\text{ }^\circ\text{C}$ corresponds to weight loss of 2.4% (calcd. 2.5%). The release of lattice water molecule at such a high temperature is probably due to strong coordinative and hydrogen bonds. Phenanthroline ligands and uncoordinated perfluorosebacate units are lost between 200 and $326\text{ }^\circ\text{C}$ (weight loss 59.2%, calcd. 58.6%). The final decomposition

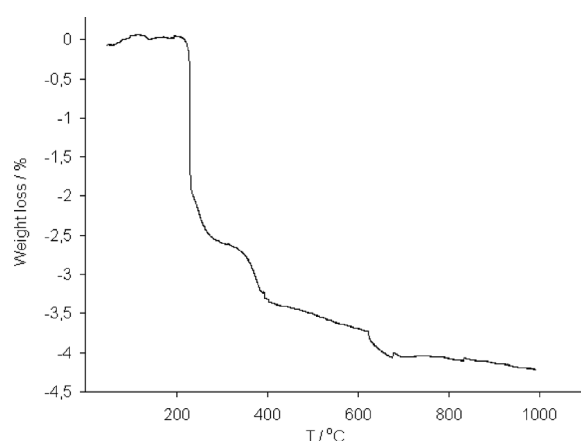


Fig. 4. The TG curve for complex **1** in the range of $50-980\text{ }^\circ\text{C}$ (weight taken = 4.607 mg).

corresponds to the release of the coordinated perfluorosebacate ligand (weight loss 33.9%, calcd. 34.1%).

In conclusion, a mixed-ligand Co(III) complex has been synthesized and its composition and crystal structure have been determined as $[\text{Co}(\text{HL})(\text{phen})(\text{H}_2\text{O})](\text{L})\text{H}_2\text{O}$ by X-ray diffraction, elemental and thermal analysis. It features a supramolecular network *via* hydrogen bonding and $\pi-\pi$ stacking interactions.

Experimental Section

Materials and instrumentation

All chemicals were commercially available in *p. a.* grade and used without further purification. Elemental analysis was performed on a VARIO ELIII CHNOS Elemental Analyzer. FT-IR spectra were recorded on a JASSCO FT/IR-300E spectrophotometer using KBr pellet technique in the range of $4000-400\text{ cm}^{-1}$. The electronic spectra were carried out on a SHIMADZU UV-2450 spectrophotometer. Thermogravimetric analyses were carried out with a SETARAM Labsys-DTA 1600:amb 1.600 $^\circ\text{C}$ unit at a heating rate of $5\text{ }^\circ\text{C}/\text{min}$ under argon atmosphere. Magnetic susceptibility measurement at r. t. was performed using a Sherwood Scientific MXI model Gouy magnetic balance.

Preparation of $[\text{Co}(\text{HL})(\text{phen})_2(\text{H}_2\text{O})](\text{L})\cdot\text{H}_2\text{O}$ (**1**)

Addition of 0.5 ml (1M) Na_2CO_3 to a stirred solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (118.7 mg, 0.408 mmol) in 10 ml of H_2O yielded a precipitate, which was separated by filtration, washed with distilled water several times and finally added to a stirred solution of phenanthroline monohydrate (80.78 mg, 0.408 mmol) and perfluorosebacic acid (200 mg, 0.408 mmol) dissolved in 20 ml of EtOH/ H_2O (1 : 1 v/v). The mixture was stirred for *ca.* 2 h. The orange solution

was allowed to stand at r.t. Slow evaporation for 2 weeks afforded orange crystals. M. p. 143 °C, yield 310 mg (64%). Analysis for $C_{44}H_{21}N_4O_{10}F_{32}Co$ (1432.5): calcd. C 36.89, H 1.48, N 3.91; found C 38.61, H 1.76, N 4.81. – FT-IR (KBr): $\nu = 3422, 1938, 1761, 1668, 1581, 1518, 1426, 1440, 1393, 1355, 1274, 121, 1147, 1070, 968, 868, 848, 757, 727, 644, 556, 524\text{ cm}^{-1}$.

X-ray data collection and structure determination [25]

A suitable single crystal was mounted on a glass fiber and data collection was performed on a STOE IPDS II image plate detector using MoK_{α} radiation ($\lambda = 0.71019\text{ \AA}$). Intensity data were collected in the θ range $1.88\text{--}26.00^\circ$ at $100(2)\text{ K}$. The crystallographic data along with some details of data collection and structure refinement are given in Table 1. Data collection: Stoe X-Area [26]. Cell refinement: Stoe X-Area. Data reduction: Stoe X-RED. The struc-

ture was solved by Direct Methods using SHELXS-97 [27]. Anisotropic displacement parameters were applied to non-hydrogen atoms in a full-matrix least-squares refinement based on F^2 using SHELXL-97. All hydrogen atoms except the ones refined freely and bonded to water oxygen atoms were positioned geometrically and refined by a riding model with U_{iso} 1.2 times (for carbon) and 1.5 times (for oxygen) that of attached atoms. Molecular drawings were obtained using ORTEP-III [28].

Acknowledgements

The authors wish to acknowledge Anadolu University, Commission of Scientific Research Projects for financial support (Project No: 031036) and the Faculty of Arts and Sciences, Ondokuz Mayıs University, Turkey, for the use of the STOE IPDS II diffractometer (purchased under grant F.279 of the University Research Fund).

- [1] M. Petric, F. Pohleven, I. Turel, P. Segedin, A. White, D. Williams, *Polyhedron* **17**, 255 (1998).
- [2] M. Devereux, M. McCann, V. Leon, M. Geraghty, V. McKee, J. Wikaria, *Polyhedron* **19**, 1205 (2000); M. Devereux, M. McCann, V. Leon, R. Kelly, D. O'Shea, V. McKee, *Polyhedron* **22**, 3187 (2003).
- [3] K. E. Erkkilä, D. T. Odom, J. Barton, *Chem. Rev.* **99**, 2777 (1999); L.-N. Ji, X.-H. Zou, J.-G. Liu, *Coord. Chem. Rev.* **216**, 513 (2001); W.-L. Wang, H. Chao, H. Li, X.-L. Hong, Y.-J. Liu, L.-F. Tan, L.-N. Ji, *J. Inorg. Biochem.* **98**, 1143 (2004); J. Zheng, Z. Li, A. Wu, H. Zhou, H. Bai, Y. Song, *Biochem. and Biophys. Commun.* **299**, 910 (2002); Q.-L. Zhang, J.-H. Kiu, X.-Z. Ren, H. Xu, Y. Huang, J.-Z. Liu, L.-N. Ji, *J. Inorg. Biochem.* **95**, 194 (2003); S. Srinivasab, J. Annaraj, P. R. Athappan, *J. Inorg. Biochem.* **99**, 876 (2005); X.-F. He, L. Wang, H. Chen, L. Xu, L.-N. Ji, *Polyhedron* **17**, 3161 (1998).
- [4] C. M. R. Juan, B. Lee, *Coord. Chem. Rev.* **183**, 43 (1999); S. McCann, M. McCann, M. T. Casey, M. Devereux, V. McKee, P. McMichael, J. G. McCrea, *Polyhedron* **16**, 4247 (1997).
- [5] T. N. Guru Row, *Coord. Chem. Rev.* **183**, 81 (1999); S. S. Kuduva, D. C. Craig, A. Nangia, G. R. Desiraju, *J. Am. Chem. Soc.* **121**, 1936 (1999); O. Felix, M. W. Hosseini, A. deCian, J. Fischer, *Angew. Chem., Int. Ed. Engl.* **36**, 102 (1997); P. Brunet, M. Smard, J. D. Wuest, *J. Am. Chem. Soc.* **119**, 2737 (1997).
- [6] M. Munakata, L. P. Wu, M. Yamamoto, T. Kuroda-Sowa, M. Maekawa, *J. Am. Chem. Soc.* **118**, 3117 (1996); P. J. Hargman, D. Hargman, J. Zupietta, *Angew. Chem. Int. Ed.* **38**, 2638 (1999).
- [7] B. Moulton, M. J. Zaworotko, *Chem. Rev.* **101**, 1629 (2001); Y. Q. Zheng, J. L. Lin, B. Y. Chen, *J. Mol. Struct.* **646**, 151 (2003).
- [8] J. Tercero, C. Diaz, M. E. Fallah, J. Ribas, X. Solans, M. A. Maestro, J. Mahia, *Inorg. Chem.* **10**, 3007 (2001).
- [9] Y. S. Xie, H. Jiang, M. G. Yu, C. X. Du, Q. L. Liu, X. L. Xu, Y. Zhu, *J. Mol. Struct.* **608**, 169 (2002).
- [10] M. McCann, M. T. Casey, M. Devereux, M. Curran, G. Ferguson, *Polyhedron* **16**, 2547 (1997).
- [11] M. Devereux, M. McCann, J. F. Cronin, V. Ferguson, V. McKee, *Polyhedron* **18**, 214 (1999).
- [12] M. McCann, M. T. Casey, M. Devereux, M. Curran, V. McKee, *Polyhedron* **16**, 2741 (1997); D. Y. Wei, Z. P. Kong, Y. Q. Zheng, *Polyhedron* **21**, 1621 (2002).
- [13] M. Devereux, M. McCann, J. F. Cronin, V. Ferguson, V. McKee, *Polyhedron* **18**, 2141 (1999).
- [14] Y. Q. Zheng, Z. P. Kong, *J. Solid Stat. Chem.* **166**, 279 (2002).
- [15] D. Maiti, H. Paul, N. Chanda, S. Chakraborty, B. Mondal, V. G. Puranik, G. K. Lahiri, *Polyhedron* **23**, 831 (2004).
- [16] R. P. John, A. Sreekanth, R. Maliyackal, P. Kurup, S. M. Mobin, *Polyhedron* **21**, 2515 (2002).
- [17] K. Larsson, L. Öhrström, *Inorganica Chimica Acta* **357**, 657 (2004); J. Abdelhak, S. M. Cherni, T. Jouni, *Analytical Sciences* **x65** (2004).
- [18] Y. Q. Zheng, J. L. Lin, Z. P. Kong, *Polyhedron* **22**, 2699 (2003); Y. Q. Zheng, Z. P. Kong, *J. Solid Stat. Chem.* **177**, 1352 (2004); Y. Q. Zheng, E. B. Ying, *Polyhedron* **24**, 397 (2005).
- [19] M. Geraghty, M. McCann, M. Devereux, V. McKee, *Inorg. Chim. Acta* **293**, 160 (1999).
- [20] S. Chakraborty, M. G. Walawalkar, G. K. Lahiri, *J. Chem. Soc. Dalton. Trans.* 2875 (2000); D. Maiti, H. Paul, N. Chanda, S. Chakraborty, B. Mondal, V. G. Puranik, G. K. Lahiri, *Polyhedron* **23**, 831 (2004).

- [21] M. B. Ferrari, G. G. Fawa, C. Pelizzi, P. Tarasconi, *J. Chem. Soc., Dalton Trans.* 2153 (1992).
- [22] M. B. Ferrari, G. G. Fawa, C. Pelosi, M. C. Rodriguez-Aguïelles, P. Tarasconi, *J. Chem. Soc., Dalton Trans.* 3035 (1995).
- [23] G. B. Deacon, R. J. Phillips, *Coord. Chem. Rev.* **33**, 227 (1980).
- [24] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley, New York (1986).
- [25] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as the supplementary publication no. CCDC 271461. Copies of the data can be obtained free of charge from The Cambridge Crystallographic Data Center *via* www.ccdc.cam.ac.uk/data_request/cif.
- [26] Stoe & Cie X-AREA (Version 1.18) and X-RED32 (Version 1.04). Stoe & Cie, Darmstadt, Germany (2002).
- [27] G. M. Sheldrick, SHELXS97 and SHELXL-97, University of Göttingen, Germany (1997).
- [28] M. N. Burnett, and C. K. Johnson, ORTEPIII. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, U.S.A. (1996).