A Supramolecular structure of *bis*(1,3-diphenyl-1, 3-propanedionato-*O,O*')(1,10-phenanthroline-*N,N*')cobalt(II) based on C-H···O, C-H···π and π···π interactions

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The compound *bis*(1,3-diphenyl-1,3-propanedionato-*O,O'*) (1,10-phenanthroline-*N, N'*) cobalt(II) (Co(DBM)$_2$(1,10-phe)) was investigated as a potential host component for functional inclusion materials. The molecules of the complex in the crystal ($a = 21.015(5)$ Å, $b = 17.456(5)$ Å, $c = 9.503(3)$ Å, $\beta = 107.04(2)°$, s.g. *C* 2/*c*) are centrosymmetric and assemble by way of C–H$\cdots$O and C–H$\cdots\pi$ hydrogen bonds as well as $\pi\cdots\pi$ stacking interactions to provide a supramolecular ladder-like motif that is accompanied by a variant of the six phenyl-embrace synthon.

Introduction

Metal complexes of β-diketonate ligands have been intensively studied for years. The compounds are often used in various synthetic and industrial processes (*e.g.* extraction and catalytic processes, as well as the design of thin films). The potential of the complexes to act as host components in functional inclusion materials was pointed out several years ago.[1] Furthermore, this class of compounds has many attributes suitable for use as supramolecular ion-exchange materials, flexible and smart sorbents, as well as functional organic zeolite analogues. In that context, Soldatov and co-workers have reported a series of modified metal dibenzoylmethanates (DBM) which were used to design supramolecular host-guest materials.[2]

In the process of preparing new molecular host systems, a strategy of forming adducts of coordinatively unsaturated compounds was applied. Specifically, metal chelates with coordinatively unsaturated metal ion (Lewis base) can act as electron-acceptors and yield adducts with neutral molecular electron-donors (Lewis acids well known as molecular addends). Numerous such adducts of β-diketonate-transition metal chelates with several electron-donating heterocyclic bases have been reported.[3] In further research, beside other addends, 1,10-phenantroline was introduced as a ligand to complete the coordination of the cobalt(II) cation in the metal bis-chelate unit, *bis*(1,3-diphenyl-1, 3-propanedionato)cobalt(II) (Co(DBM)$_2$).[4]

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Experimental

All chemicals and solvents were used as purchased without purification. Cobalt(II) acetate tetrahydrate and dibenzoylmethane were commercially available from Merck, while 1,10-phenantroline and acetone were obtained from Kemika, Croatia.

Physical measurements

Elemental analyses of carbon, hydrogen and nitrogen contents were determined *via* microanalytical procedures, using the automatic CHNS Elemental Analyser from Perkin Elmer. Infrared spectra were recorded using the technique of KBr pellets on the BRUKER EQUINOX 55 spectrometer. Thermogravimetric experiments were performed on a TGA 7 Perkin Elmer thermogravimetric analyser. In a typical experiment, approximately 10 mg of the sample were heated at a constant rate of 10°C/min up to 700°C under a dynamic atmosphere (35 mL/min) of dry nitrogen or oxygen.

Calorimetric measurements were performed on a Pyris 1 Perkin Elmer differential scanning calorimeter with an attached intercooler. The temperature calibrations were done using indium and lead standard materials. Samples were analyzed in closed aluminum pans under a dynamic (35 mL/min) atmosphere of dry nitrogen and heated between 25 and 300°C at a heating rate of 10°C/min.

Synthesis of Co(DBM)$_2$(1,10-phe)

A solution of phenantroline (180 mg, 1 mmol) in acetone (10 mL) was added to a warm solution of bis(1,3-diphenyl-1,3-propanedionato)cobalt(II) dihydrate (540 mg, 1 mmol)[5] in acetone (50 mL). The resulting solution was left to stand at room temperature and allowed to evaporate slowly over a period of five days. The obtained solid was filtered, washed with acetone and dried on air to give dark red crystals of Co(DBM)$_2$(1,10-phe) (0.54 g, 79% yield). Melting point: 289°C. Anal. Calcd. for $C_{42}H_{30}CoN_2O_4$: C 73.51%; H 4.37%, N 4.08%, Found, C 73.77% H 4.2% N 4.08% IR (KBr): $\nu(C_{ar}-H)$ 3060 cm^{-1}, $\nu(C_{ar}=C_{ar})$ 1595 cm^{-1}, $\nu(C\cdots O)$ 1552 cm^{-1}, $\nu(C\cdots O)$ 1518 cm^{-1}, $\delta(C-H)$ 1478 cm^{-1}, $\nu(C-C)$ 1226 cm^{-1}, $\nu(Co-O)$ 514 cm^{-1}.

Single crystal X-ray diffraction structure determination

Single crystal X-ray diffraction experiments were performed on crystals taken from the mother liquor. A PHILIPS four circle diffractometer with a graphite monochromatic Mo-K$_\alpha$ radiation was used to collect diffraction data.[6] The structure was solved by direct methods using SHELXS97,[7] followed by differential Fourier syntheses. The non-hydrogen atoms were refined anisotropically. All H atoms were placed geometrically and included in the refinement in the riding-model approximation with thermal factors 1.2 or 1.5 times greater than those for the adjacent carbon atoms. The structure was refined using SHELXL97[7] code. The crystallographic data and results of the refinement are present in Table 1. The selected bond lengths and bond angles are given in Table 2.

Result and discussion

The title compound, *bis*(1,3-diphenyl-1,3-propanedionato-*O,O′*)(1,10-phenanthroline-*N,N′*)cobalt(II), was obtained by a reaction of *bis*(1,3-diphenyl-1,3-propanedionato)cobalt(II) and 1,10-phenanthroline in acetone at room temperature (1:1 ratio), as established by elementary analysis and FTIR spectroscopy. Whereas thermal stability is known to be a limiting factor for the storage of volatile substances (*i.e.* gases and liquids) in host materials, special attention was given to methods of thermal analysis. The inspection of the differential scanning calorimetry

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Compound	$C_{42}H_{30}CoN_2O_4$
CCDC deposit no	285567
Color/shape	Dark red/prism
M_r	685.61
Crystal system	Monoclinic
Space group	$C\,2/c$
a (Å)	21.015(5)
b (Å)	17.456(5)
c (Å)	9.503(3)
β (°)	107.04(2)
Z	4
V(Å)	3333(1)
$\rho_{calc.}$/(g cm^{-3})	1.366
Crystal dimension (mm^3)	0.60 × 0.45 × 0.35
λ (Å)	0.71073
T (K)	293
F (0 0 0)	1420
μ (MoKα, mm^{-1})	0.562
Range for data collection	$4° < 2\theta < 54°$
Absorption correction	Semi-empirical from psi scan
Range of relat. trasm. factors	0.7179/0.7902
Number of measured reflections	3891
Number of independent reflection	3666
Number of observed reflections, $I > 2\sigma(I)$	2635
Number of parameters	222
$\Delta\rho_{max}$	0.246
$\Delta\rho_{min}$	−0.331
$R\,[I > 2\sigma(I)]$	0.0357
wR	0.0958
Goodnes of Fit	1.002

Table 2. Select Bonds Lenght (Å) and Bonds Angle (°)

Co–O2 2.0555(14)	O2–Co–O1 86.18(5)
Co–O1 2.0605(13)	O2–Co–N1 90.85(6)
Co–N1 2.1430(15)	O1–Co–N1 101.59(5)
O1–C1 1.281(2)	C1–O1–Co 120.40(11)
O2–C3 1.263(2)	C3–O2–Co 124.47(12)
C1–C2 1.397(3)	C16–N1–C20 117.29(15)
C2–C3 1.398(3)	C16–N1–Co 127.37(12)
C1–C10 1.497(2)	C20–N1–Co 115.31(11)
Co–N1 2.1430(15)	O1–C1–C2 125.43(18)
N1–C16 1.328(2)	O1–C1–C10 116.29(16)
N1–C20 1.355(2)	C2–C1–C10 118.27(16)
C3–C4 1.500(2)	C1–C2–C3 125.39(17)

thermogram of Co(DBM)$_2$(1,10-phe) revealed an endothermic event at 290.4°C ($\Delta H = 54.9$ J g^{-1}). On the other hand, information obtained by way of thermogravimetric analysis indicated the compound is stable up to approximately 300°C. Notably, thermogravimetric data reveals that the

thermal decomposition of Co(DBM)$_2$(1,10-phe) occurs in a single step that spans the range from 290 to 450°C. Such results suggest the title compound exhibits satisfactory thermal stability to be considered as a candidate for gas storage applications. In order to further investigate whether the arrangement of Co(DBM)$_2$(1,10-phe) molecules in the crystal of the pure substance would be supportive of host-guest chemistry, the compound was further examined by way of single crystal X-ray diffraction. The crystal structure analysis revealed the cobalt(II) cation is sitting on a crystallographic mirror plane, and is surrounded by six donor atoms arranged at the vertices of a distorted octahedron (Fig. 1). Notably, the coordination polyhedron Co(II) is constructed of four oxygen of two crystallographically identical 1,3-diphenyl-1,3-propanedionato ligands and two nitrogen atoms of 1,10-phenantroline. Consequently, the octahedron is defined by two symmetrically independent cobalt-oxygen bonds (Co–O1, 2.0605(15) Å and Co–O2, 2.0554(13) Å) and a single crystallographically unique cobalt-nitrogen bond (Co–N1, 2.1431(14) Å). The observed cobalt-heteroatom bond lengths compare well with the ones previously observed in adducts of Co(DBM).[8−10]

The discrepancy of the coordination poly-hedron of Co(II) from the ideal octahedral arrangement is well illustrated by the angles O1–Co–O2 and N1–Co–N1 of 86.18(5)° and 76.45(8)°, respectively. The O1···O2 bite distance in Co(DBM)$_2$(1,10-phe) molecules is found to be 2.81 Å, that is significantly longer than in any of the polymorphs of the free ligand.[11−13] In contrast, the N···N bite distance in Co(DBM)$_2$(1,10-phe) is smaller, as compared to the free ligand.[14] The chelate ring, defined by atoms O1, C1, C2, C3 and O2, exhibits a deformation that is best described by the 30.90(8)° angle between planes defined by atoms Co, O1, O2 and O1, C1, C2, C3, O2. The phenyl rings, defined by sets of atoms C4, C5, C6, C7, C8, C9 and C10, C11, C12, C13, C14, C16, are twisted out of the plane of the chelate ring atoms Co, O1, O2, C1, C2, C3 by 8.71(10)° and 24.16(9)°, respectively. The bond lengths
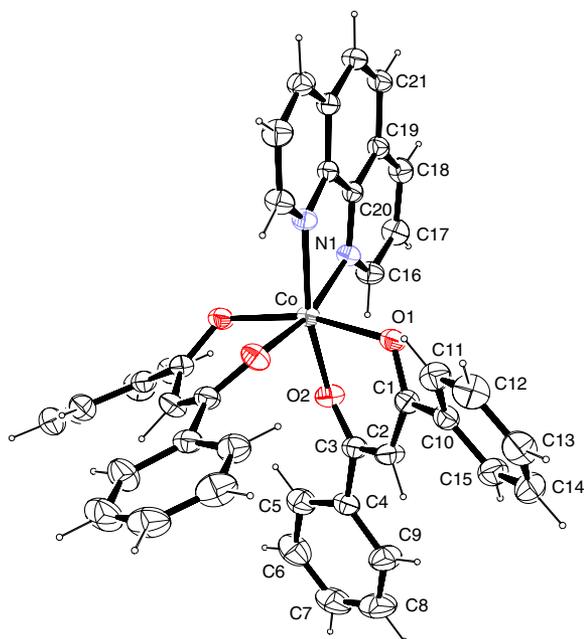
Fig. 1. The molecular structure of *bis*(1,3-diphenyl-1,3-propanedionato-*O,O′*) (1,10-pehenanthroline-*N,N′*)cobalt (II), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level for non-H atoms

Table 3. C–H···π Interaction Geometry (Å, °) for Co(DBM)$_2$1,10-phe

C–H···*Cg*	Symmetry code	H···*Cg*	C–H···*Cg*	C···*Cg*
C7–H7···Cg2	−*x*, 1 − *y*, 1 − *z*	3.2682	128.50	3.916(3)
C8–H8···Cg1	*x*, 1 − *y*, −1/2 + *z*	3.2642	143.77	4.052(3)
C15–H15···Cg1	−*x*, *y*, 1/2 − *z*	3.3727	141.64	4.142(3)

Note. Cg represent the centre of gravity of the following rings: Cg1 (phenil ring I), Cg2 (phenil ring II)

ladder structures, propagating parallel to the crystallographic c-direction. The ladders further connect by way of C–H···π forces between pairs of Co(DBM)$_2$(1,10-phe) molecules. Notably, such C–H···π forces employ four phenyl rings and two phenantroline rings of two neighboring molecules, so as to form a distorted variant of the well-known six-phenyl embrace synthon (Table 4 and Fig. 2). The analysis of solvent-accessible voids in the Co(DBM)$_2$(1,10-phe) crystal, performed by calculating the packing coefficient *via* the SOLV module of PLATON[16] program, provided a typical value suggesting the absence of any solvent-accessible voids.

and angles in all other segments of the molecule exhibit no unexpected features.[15] The molecules of the complex arrange in the crystal primarily by way of hydrogen bonds of the C–H···O and C–H···π type (Table 3). However, the most prominent feature of the arrangement of Co(DBM)$_2$(1,10-phe) molecules in the crystal is the formation of a ladder-like structure involving coordinated 1,10-phe molecules. Specifically, offset π···π stacking of phenantroline fragments that belong to neighboring Co(DBM)$_2$(1,10-phe) molecules results in the formation of inclined

Conclusion and outlooks

In this communication we have established that a potentially functional host, Co(DBM)$_2$(1,10-phe), was prepared using the well known concept of coordination-driven self-assembly of coordinatively unsaturated metal complexes, Co(DBM)$_2$, with electron-donating molecules (1,10-phe) into functional metal-organic complexes. A thermogravimetric analysis

Table 4. π···π Interaction Geometry (Å, °) for Co(DBM)$_2$1,10-phe

Cg*I*···Cg*J*	Symmetry code	Cg···Cg	Dihedral angle	Interplanar distance	Offset
Cg2···*Cg2*	1/2 − *x*, 1/2 − *y*, 1 − *z*	3.722(2)	0.02	3.433	3.336
Cg3···*Cg3*	−*x*, −*y*, 1 − *z*	3.723(2)	1.67	3.500	1.706

Note. Cg represent the centre of gravity of the following rings: *Cg1* (phenil ring I), *Cg2* (phenil ring II) *Cg3* 1,10-phenanthroline ring.
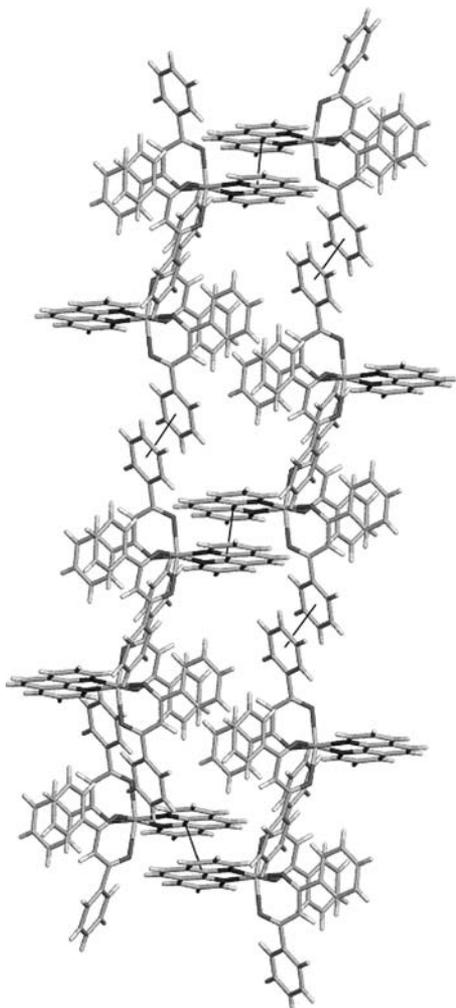
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Fig. 2. Packing diagram of *bis*(1,3-diphenyl-1,3-propane-dionato-*O,O'*) (1,10-pehenanthroline-*N,N'*)cobalt(II) in direction of crystal a axis. The solid line showing $\pi\cdots\pi$ interaction

of Co(DBM)$_2$(1,10-phe) indicate a high thermal stability (up to 300°C). This thermal stability is due to C–H$\cdots$O, C–H$\cdots\pi$ and $\pi\cdots\pi$ intermolecular interactions which stabilize the crystal lattice.

As mentioned, the crystal structure provides no potential solvent accessible voids.

Acknowledgments

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