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Synthesis, crystal structures and spectroscopic properties of cobalt(II) complexes with chelating sulfonylamidophosphate ligands

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Two new cobalt(II) complexes with general formula Co($\mathbf{L^1}$)$_2$Phen (**1**) and Co($\mathbf{L^2}$)$_2$Phen (**2**), in which H$\mathbf{L^1}$ = dimethyl phenylsulfonylphosphoramidate and H$\mathbf{L^2}$ = dimethyl tosylphosphoramidate, were prepared in one-step synthesis and characterized by IR, UV-VIS spectroscopy, TGA-DTA and elemental analysis. Moreover, the single crystal structures of **1** and **2** were determined by single crystal X-ray diffractometry. Complexes consist of mononuclear units comprising two $\mathbf{L^1}^-$(or $\mathbf{L^2}^-$) and phenanthroline ligands bidentatly linked to metal ion. The UV-VIS spectra of complexes in the solid state show broad asymmetric band at 530 nm attributed to the *d*–*d* transition of the metal ion. Comparing of these spectra with the absorption spectra in acetone, octahedral environment of the cobalt(II) ion in solution were considered. The structural similarity of **1** and **2** leads to a similar thermal decomposition profile.

1. Introduction

The investigations of cobalt(II) β-diketonate complexes include different branches of the chemical science, among others the coordination, organic, bio- and theoretical chemistry due to their structural diversity and unique properties. The neutral moiety [Co(β-diketonate)$_2$] demonstrates coordination unsaturation and can expand its coordination sphere by oligomer formation (with bridging β-diketonates ligands) or by adduct formation with Lewis bases, such as water, 1,10-phenanthroline, 2,2-bipyridine, etc. Some cobalt(II) β-diketonate adducts are used as precursors for the preparation of cobalt oxide thin films by the chemical vapor deposition (CVD) or atomic layer deposition (ALD) methods [1,2]. For this purpose complexes should exhibit such properties as high chemical stability, high volatility and long shelf life. Cobalt(II) β-diketonate adducts are also good catalysts for a number of reactions, such as polymerisation, enantioselective Michael addition, etc. [3,4].

Herein we report the synthesis and investigations of some new heteroleptic cobalt(II) complexes based on structural analogues of β-diketones – sulfonylamidophosphates with the structural fragment S(O)$_2$NHP(O) (Scheme 1). This type of compounds was first synthesized by Kirsanov [5] and used as bactericidal agents in medicine and toxicology [6], while some of them are used as pesticides. However, the data on these compounds and their coordination properties as well as their potential use are scarce today.

Having continuous interest in study of binuclear Ln^{III}–Ln^{III} [7] and Ln^{III}–M^{II} complexes [8] (Ln = lanthanide ion, M^{II} = 3*d*-metal ion) we undertook a study of potential building block for polynuclear species, *viz.* stable coordinationally unsaturated neutral moiety {Co^{II}[(sulfonylamidophosphate)$_2$}^{0} able to bind additionally two bridging monodentate or one chelate ligand and complete coordination sphere of Co-ion up to six donor atoms. Here we report our preliminary studies of two neutral mononuclear complexes with phenanthroline and two types of sulfonylamidophosphate differing by substituents of constituting phenyl group.

2. Experimental

2.1. Materials and methods

All precursor reagents were purchased from commercial sources and used without further purification. Solvents were dried and purified by standard methods [9].

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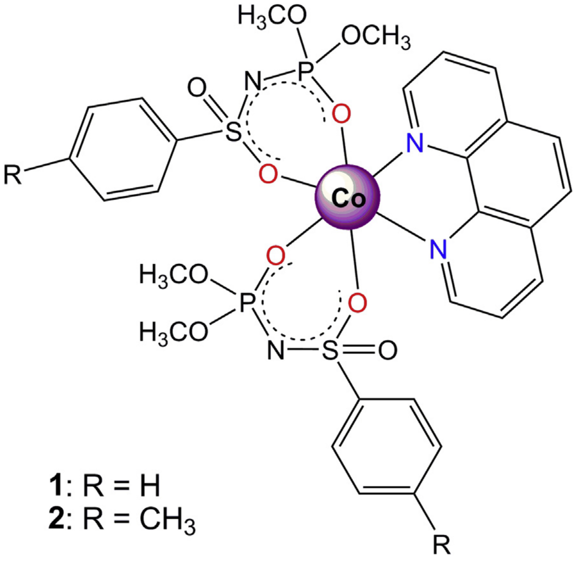

Scheme 1. Schematic representation of synthesized complexes **1** and **2**.

IR measurements were performed on Perkin–Elmer Spectrum BX spectrometer on samples in the form of KBr pellets. ^{1}H NMR spectra were recorded on Varian Mercury 400 NMR spectrometer at 25 °C. Chemical shifts are reported with reference to $SiMe_4$ (^{1}H). Elemental analysis (C, H, N) was performed on EL III Universal CHNOS Elemental Analyzer. Thermogravimetric analysis was performed using synchronous TG/DTA analyzer Shimadzu DTG-60H. The samples were heated to 1150 °C in alundum crucible under argon (300 ml/min) with heating rate of 10 °C/min. Crystalline powder of Al_2O_3 as a standart compound was used. Electronic spectra were recorded with MDR-23 "LOMO" and Specord M-40 Carl Zeiss UV-VIS spectrometers.

2.2. Synthesis of H**L**^{1}, H**L**^{2}, Na**L**^{1} and Na**L**^{2}

Ligands H**L**^{1} and H**L**^{2} were synthesized according to the reported procedures [10,11].

The sodium salt Na**L**^{1} was prepared by reaction between equimolar amounts of sodium methylate and H**L**^{1} in methanol medium with stirring during 15 min. The resulting solutions was evaporated under vacuum and recrystallized from the 2-propanol-methanol (1:1) mixture. The crystals of Na**L**^{1} were filtrated, washed with hexane and air dried. Yield: 95%. Elemental analysis (%) calc. $C_8H_{11}NNaO_5PS$: C 33.46, H 3.86, N 4.88; found: C 33.47, H 3.87, N 4.91. ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): $\delta = 3.41$ (d, 6H, OCH_3, $^3J_{P-H} = 11.2$ Hz), 7.38 (m, $2H_\beta + 1H_\gamma$, C_6H_5), 7.81 (m, $2H_\alpha$, C_6H_5).

The sodium salt Na**L**^{2} was obtained by reaction between one equivalent of sodium carbonate and two equivalents of H**L**^{2} in water-2-propanol (1:3) medium with heating and stirring until complete dissolution of the sodium carbonate. The resulting solution was evaporated under vacuum and recrystallized from the 2-propanol. The crystals of Na**L**^{2} were filtrated, washed with hexane and air dried. Yield: 90%. Calc. $C_9H_{13}NNaO_5PS$: C 35.88, H 4.35, N 4.65; found: C 38.91, H 4.36, N 4.68. ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): $\delta = 2.32$ (s, 3H, CH_3), 3.37 (d, 6H, OCH_3, $^3J_{P-H} = 11.3$ Hz), 7.19 (m, $2H_\beta$, C_6H_5), 7.67 (m, $2H_\alpha$, C_6H_5).

2.3. Synthesis of complex **1**

To a stirred solution of $Co(NO_3)_2 \cdot 6H_2O$ (0.3 mmol) in 2-propanol (5 ml), a solution of Na**L**^{1} (0.6 mmol) in acetone (10 ml) was added. The mixture was refluxed for 10 min, cooled down and the sodium nitrate was filtrated off. Ultimately, a solution of 1,10-phenanthroline monohydrate (0.3 mmol) in 2-propanol (5 ml) was added to the filtrate and stirred for an additional 10 min at room temperature. The resulting solution was left in air at room temperature and the fine-crystalline needle-like precipitate of complex was obtained after 1 day. To the stirred reaction mixture methanol (8 ml) was added and refluxed until complete dissolution of the precipitate and then 2-propanol (5 ml) was added. The needle-like crystals of **1** formed after 1 day, were filtrated, washed with cold acetone and diethyl ether, and dried in air. Yield: 70%. Elemental analysis (%) calc. for $C_{30}H_{32}CoN_2Na_2O_{10}P_2S_2$: C 44.40, H 3.97, N 3.45; found: C 44.43, H 3.95, N 3.48.

2.4. Synthesis of complex **2**

Complex **2** was prepared following the identical procedure as for **1** using Na**L**^{2} as the starting compound. In this case fine needle-like crystals was obtained after 10 min, which was recrystallized by the slow cooling evaporation in a vacuum flask in the 2-propanol-acetone medium. Yield: 75%. Elemental analysis (%) calc. for $C_{32}H_{36}CoN_2N_2O_{10}P_2S_2$: C 45.78, H 4.32, N 3.34; found: C 45.77, H 4.30, N 3.32.

2.5. X-ray structure determination

Crystal data were collected using a SuperNova Dual diffractometer (Agilent Technologies) with Atlas detector using mirror monochromator (MoK$_\alpha$ radiation, $\lambda = 0.71073$ Å). The crystals were mounted on a quartz glass capillary and cooled by a cold, dry nitrogen gas stream (Oxford Cryosystems equipment). The structures

Table 1
Crystallographic data for compounds **1** and **2**.

Compounds	1	2
Empirical formula	$C_{28}H_{30}CoN_4O_{10}P_2S_2$	$C_{30}H_{34}CoN_4O_{10}P_2S_2$
Formula weight	767.55	795.60
Temperature (K)	100(1)	100(1)
Wavelength (Å)	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	P 2_1/c	P 2_1/c
Unit cell dimensions		
a (Å)	11.8591(2)	12.2514(2)
b (Å)	8.3971(1)	8.4982(1)
c (Å)	32.3529(4)	32.7135(4)
α (°)	90.00	90.00
β (°)	94.016(1)	92.138(1)
γ (°)	90.00	90.00
Volume (Å^3)	3213.86(8)	3403.59(8)
Z	4	4
D_{calc} (g/cm^3)	1.586	1.553
Absorption coefficient (mm^{-1})	0.826	0.783
F(000)	1580	1644
Crystal size (mm)	0.32 × 0.07 × 0.04	0.27 × 0.09 × 0.06
θ Range for data collection (°)	2.52–39.65	2.04–25.06
Index ranges	$-14 \le h <= 14$, $-8 \le k <= 10$, $-38 \le l <= 38$	$-14 \le h <= 14$, $-7 \le k <= 10$, $-38 \le l <= 38$
Reflections collected	42,900	29,916
Independent reflections	5689	5984
Reflections with I > 2 σ (I)	5417	5782
R(int)	0.0265	0.0208
Restraints/parameters	0/428	0/448
Goodness-of-fit on F^2	1.126	1.113
Final R indices [I > 2 σ (I)]	$R_1 = 0.0281$, $wR_2 = 0.0861$	$R_1 = 0.0309$, $wR_2 = 0.0735$
R indices (all data)	$R_1 = 0.0296$, $wR_2 = 0.0875$	$R_1 = 0.0319$, $wR_2 = 0.0740$
Largest diff. peak and hole (eÅ$^{-3)}$	0.353 and −0.409	0.467 and −0.412