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### Syntheses, structures and properties of di-, trinuclear cobalt compounds

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## Syntheses, structures and properties of di-, trinuclear cobalt compounds

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Reactions of bis-(2-hydroxyacetophenone)trimethylenediimine (hapt) with cobalt cations lead to formation of two compounds  $[\text{Co}^{\text{II}}(\text{OAc})_2(\text{hapt})_2\text{Co}_2^{\text{III}}(\text{Py})_2](\text{ClO}_4)_2$  (**1**) and  $[\text{Co}^{\text{III}}(\text{hapt})(\text{OH})_2 \cdot 2\text{CH}_2\text{Cl}_2]$  (**2**). The structure of **1** is a linear trinuclear mixed-valence compound, while **2** is a binuclear Schiff-base compound bridged by double hydroxyl. Magnetic susceptibility data were measured in the temperature range 300 to 2 K.  $\mu_{\text{eff}}$  values of **1** are almost constant ranging from 4.37 to 5.00 B.M., suggesting that the oxidation states are  $\text{Co}^{\text{III}}(S=0)-\text{Co}^{\text{II}}(S=3/2)-\text{Co}^{\text{III}}(S=0)$ . The magnetic susceptibilities of **2** are negative, typical diamagnetic behavior.

*Keywords:* Schiff base; cobalt; polynuclear; magnetic property

### 1. Introduction

The chemistry of transition-metal compounds with Schiff base ligands has been studied extensively [1–6]. Many of these compounds are relevant to the biochemistry of vitamins, enzymes and coenzymes [7, 8]. Cobalt Schiff-base compounds have also drawn considerable attention for their important biological applications [9]. Conjugated tetradentate Schiff-base ligands are chelating reagents that coordinate to metal centers through four equatorial positions of octahedral structures, and serve as models for vitamin B<sub>12</sub> and its co-enzyme. Studies of polynuclear transition metal compounds give a better understanding of the magnetic properties for these compounds. However, only a limited number of linear trinuclear compounds have been structurally and magnetically characterized. Here we present the syntheses and the structural characterizations of two compounds  $[\text{Co}^{\text{II}}(\text{OAc})_2(\text{hapt})_2\text{Co}_2^{\text{III}}(\text{Py})_2](\text{ClO}_4)_2$  (**1**) and  $[\text{Co}^{\text{III}}(\text{hapt})(\text{OH})_2 \cdot 2\text{CH}_2\text{Cl}_2]$  (**2**). Compound **1** is a linear trinuclear mixed-valence

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cobalt compound, while compound **2** is a Schiff-base binuclear compound bridged by two hydroxides.

## 2. Experimental

### 2.1. Materials and general methods

All chemicals were reagent grade and were used as received. Elemental analyses were performed with a Vario EL III CHNOS Elemental Analyzer. The infrared spectra of KBr pellets were recorded on a FTS-40 spectrophotometer. UV-visible spectra were recorded on a Lambda 35 spectrometer. Variable temperature magnetic susceptibilities in the temperature range 2–300 K in a 10 kOe applied field were measured on a model CF-1 superconducting extracting sample magnetometer with the powdered sample kept in the capsule for weighing.

**CAUTION!** Perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled with care.

### 2.2. Synthesis

**Synthesis of the ligand.** The Schiff base ligand (hapt) was obtained by reaction of propane-1,3-diamine (1 mmol) with o-hydroxyacetophenone (2 mmol) in methanol solution at room temperature. Yellow precipitates were collected by filtration, washed with cold ethanol and dried under vacuum.

**Compound 1, [Co<sup>II</sup>(OAc)<sub>2</sub>(hapt)<sub>2</sub>Co<sup>III</sup>(Py)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>.** 1 mmol Co(OAc)<sub>2</sub>·4H<sub>2</sub>O and 3 mmol pyridine were added to a warm solution of 1 mmol hapt and an appropriate amount of triethylamine in methanol (50 mL). The reaction mixture was stirred overnight at room temperature. To the resulting green solution 2.5 mmol NaClO<sub>4</sub> was added and the final mixture was stirred for 1 h. The formed green precipitate was collected and recrystallized from dichloromethane–ethanol (1:1 v/v) mixture. The green crystals were isolated by filtration, washed with cold ethanol and dried in vacuum. (Yield 45%, based on Co). Anal. Calcd for C<sub>52</sub>H<sub>54</sub>Cl<sub>2</sub>Co<sub>3</sub>N<sub>6</sub>O<sub>16</sub> (1266.70): C, 49.26 (Calcd 49.31); H, 4.33 (4.30); N, 6.61 (6.63)%. IR (solid KBr pellet/cm<sup>-1</sup>): 3417m, 3118m, 1598s, 1562s, 1481m, 1416s, 1307s, 1245s, 1145m, 1087s, 863m, 756m, 704m, 623m, 529w, 481w.

**Compound 2, [Co<sup>III</sup>(hapt)(OH)]<sub>2</sub>·2CH<sub>2</sub>Cl<sub>2</sub>.** To a mixture of 1 mmol hapt and an appropriate amount of triethylamine in pure methanol (30 mL) was added 1 mmol CoCl<sub>2</sub>·6H<sub>2</sub>O. After the resulting green mixture was stirred at room temperature for about 2 h, green precipitate was obtained. Crystals suitable for X-ray crystallography were obtained by recrystallization from dichloromethane–ethanol (2:1 v/v) at room temperature, and were isolated by filtration and washed with cold ethanol and dried in vacuum. (Yield 40%, based on Co). Anal. Calcd for C<sub>40</sub>H<sub>46</sub>Cl<sub>4</sub>Co<sub>2</sub>N<sub>4</sub>O<sub>6</sub> (938.47): C, 51.23 (Calcd 51.19); H, 5.10 (4.94); N, 6.01 (5.97)%. IR (solid KBr pellet/cm<sup>-1</sup>): 3551m, 3395m, 1600s, 1537s, 1523s, 1461m, 1400s, 1334s, 1261s, 1232s, 1207m, 1137m, 1033w, 935w, 874m, 860m, 852s, 754s, 615m, 582w, 536m, 460m.

### 2.3. X-ray crystallography

Green crystals of **1** and **2** were carefully selected and glued to thin glass fibers with epoxy resin. Crystal structure measurements were performed on a Siemens SMART CCD diffractometer with graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at room temperature. An empirical absorption correction was applied using SADABS program [10]. The structures were solved using direct methods. The metal atoms were first located, and the carbon, nitrogen, and oxygen atoms were found in the final difference Fourier maps. All the H atoms were placed geometrically. The structures were refined on  $F^2$  by full-matrix least-squares methods using the SHELX97 program package [11]. All non-hydrogen atoms were refined anisotropically. For **1**, a total of 3514 independent reflections were collected and all non-hydrogen atoms were refined with anisotropic thermal parameters for 1513 reflections with  $I > 2\sigma(I)$  to final  $R_1 = 0.0969$ ,  $wR_2 = 0.1874$ . The maximum and minimum peaks on the final difference Fourier map were 1.429 and  $-0.876 \text{ e \AA}^{-3}$ , respectively. For **2**, a total of 3242 independent reflections was collected and all non-hydrogen atoms were refined with anisotropic thermal parameters for 2665 reflections with  $I > 2\sigma(I)$  to final  $R_1 = 0.0511$ ,  $wR_2 = 0.1313$ . The maximum and minimum peaks on the final difference Fourier map were 0.857 and  $-0.493 \text{ e \AA}^{-3}$ , respectively. Experimental details for the structural determinations of **1** and **2** are presented in table 1. Selected bond distances and angles for **1** and **2** are listed in table 2.

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

| Compound   | <b>1</b>   | <b>2</b>  |
|--|--|---|
| Formula  | C <sub>52</sub> H <sub>54</sub> Cl <sub>2</sub> Co <sub>3</sub> N <sub>6</sub> O <sub>16</sub> | C <sub>40</sub> H <sub>46</sub> Cl <sub>4</sub> Co <sub>2</sub> N <sub>4</sub> O <sub>6</sub> |
| Formula weight   | 1266.70  | 938.47  |
| Crystal size (mm <sup>3</sup> )  | 0.36 × 0.34 × 0.22   | 0.20 × 0.10 × 0.08  |
| Crystal color  | Green  | Green   |
| Crystal system   | Monoclinic   | Triclinic   |
| Space group  | <i>P</i> 2(1)/ <i>c</i>  | <i>P</i> $\bar{1}$  |
| <i>a</i> (Å)   | 13.3942(3)   | 9.8781(19)  |
| <i>b</i> (Å)   | 14.0607(4)   | 9.8966(19)  |
| <i>c</i> (Å)   | 15.1854(3)   | 11.088(2)   |
| $\alpha$ (°)   |  | 105.842(3)  |
| $\beta$ (°)  | 107.141(1)   | 92.312(3)   |
| $\gamma$ (°)   |  | 105.107(3)  |
| <i>V</i> (Å <sup>3</sup> )   | 2732.86(11)  | 999.5(3)  |
| <i>Z</i>   | 2  | 1   |
| <i>D</i> <sub>Calcd</sub> (g cm <sup>-3</sup> )                                      | 1.539  | 1.559   |
| <i>F</i> (000)   | 1302   | 484   |
| Absorption coefficient (mm <sup>-1</sup> )   | 1.073  | 1.150   |
| $\theta$ for data collection (°)   | 2.15 to 25.01  | 2.62 to 25.16   |
| Reflections collected  | 8469   | 5304  |
| Unique reflections   | 4744   | 3514  |
| ( <i>R</i> (int))  | [ <i>R</i> (int) = 0.0400]   | [ <i>R</i> (int) = 0.0487]  |
| Parameters   | 359  | 254   |
| GOF  | 1.093  | 1.014   |
| <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] | 0.0622, 0.1457   | 0.0969, 0.1874  |
| <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)                            | 0.0927, 0.1706   | 0.1952, 0.2356  |

$$R_1 = \sum(|F_o| - |F_c|) / \sum |F_o|, \quad wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{0.5}$$

Table 2. Selected bond lengths (Å) and angles (°) for compounds **1** and **2**.

| <i>Compound 1</i>         |          |                               |            |  |            |
|---------------------------|----------|-------------------------------|------------|--|------------|
| Co(1)–O(2)                | 1.896(3) | O(2)–Co(1)–O(1)               | 82.37(15)  | O(3) <sup>I</sup> –Co(2)–O(1) <sup>I</sup>   | 94.74(14)  |
| Co(1)–O(1)                | 1.903(4) | O(2)–Co(1)–N(3)               | 92.76(17)  | O(2)–Co(2)–O(1) <sup>I</sup>                 | 108.00(13) |
| Co(1)–N(3)                | 1.948(4) | O(1)–Co(1)–N(3)               | 91.35(17)  | O(2) <sup>I</sup> –Co(2)–O(1) <sup>I</sup>   | 72.00(13)  |
| Co(1)–N(1)                | 1.949(4) | O(2)–Co(1)–N(1)               | 171.18(18) | O(3)–Co(2)–O(1)                              | 94.74(15)  |
| Co(1)–N(2)                | 1.958(5) | O(1)–Co(1)–N(1)               | 90.19(18)  | O(3) <sup>I</sup> –Co(2)–O(1)                | 85.26(15)  |
| Co(1)–O(4)                | 1.938(4) | N(3)–Co(1)–N(1)               | 92.15(19)  | O(2)–Co(2)–O(1)                              | 72.00(13)  |
| Co(2)–O(3)                | 2.020(4) | O(2)–Co(1)–N(2)               | 90.68(18)  | O(2) <sup>I</sup> –Co(2)–O(1)                | 108.00(13) |
| Co(2)–O(2)                | 2.116(4) | O(1)–Co(1)–N(2)               | 172.71(18) | O(1) <sup>I</sup> –Co(2)–O(1)                | 180.0      |
| Co(2)–O(1)                | 2.141(3) | N(3)–Co(1)–N(2)               | 86.8(2)    | O(3)–Co(2)–O(3) <sup>I</sup>                 | 180.0(2)   |
|                           |          | N(1)–Co(1)–N(2)               | 96.9(2)    | O(3)–Co(2)–O(2)                              | 92.70(15)  |
|                           |          | O(2)–Co(1)–O(4)               | 89.04(16)  | O(3) <sup>I</sup> –Co(2)–O(2)                | 87.30(15)  |
|                           |          | O(1)–Co(1)–O(4)               | 90.59(16)  | N(1)–Co(1)–O(4)                              | 86.29(18)  |
|                           |          | N(3)–Co(1)–O(4)               | 177.52(17) | N(2)–Co(1)–O(4)                              | 91.48(19)  |
| <i>Compound 2</i>         |          |                               |            |  |            |
| Co(1)–O(1)                | 1.880(4) | O(1)–Co(1)–O(2)               | 87.49(15)  | O(2)–Co(1)–N(1)                              | 90.9(3)    |
| Co(1)–O(2)                | 1.906(4) | O(1)–Co(1)–O(3)               | 88.01(15)  | O(3)–Co(1)–N(1)                              | 174.2(3)   |
| Co(1)–O(3)                | 1.920(4) | O(2)–Co(1)–O(3)               | 94.46(16)  | O(3) <sup>I</sup> –Co(1)–N(1)                | 93.9(3)    |
| Co(1)–O(3) <sup>II</sup>  | 1.927(4) | O(1)–Co(1)–O(3) <sup>II</sup> | 92.01(15)  | N(2)–Co(1)–N(1)                              | 89.3(3)    |
| Co(1)–N(2)                | 1.941(8) | O(2)–Co(1)–O(3) <sup>II</sup> | 175.18(8)  | O(1)–Co(1)–Co(1) <sup>II</sup>               | 90.02(12)  |
| Co(1)–N(1)                | 1.943(8) | O(3)–Co(1)–O(3) <sup>II</sup> | 80.73(16)  | O(2)–Co(1)–Co(1) <sup>II</sup>               | 134.92(13) |
| Co(1)–Co(1) <sup>II</sup> | 2.932(3) | O(1)–Co(1)–N(2)               | 175.9(2)   | O(3)–Co(1)–Co(1) <sup>II</sup>               | 40.46(11)  |
|                           |          | O(2)–Co(1)–N(2)               | 88.5(3)    | O(3) <sup>I</sup> –Co(1)–Co(1) <sup>II</sup> | 40.27(11)  |
|                           |          | O(3)–Co(1)–N(2)               | 93.1(3)    | N(2)–Co(1)–Co(1) <sup>II</sup>               | 93.4(2)    |
|                           |          | O(3)#1–Co(1)–N(2)             | 92.1(3)    | N(1)–Co(1)–Co(1) <sup>II</sup>               | 134.1(2)   |
|                           |          | O(1)–Co(1)–N(1)               | 90.0(3)    |  |            |

Symmetry transformations used to generate equivalent atoms: I:  $-x, -y + 1, -z$ ; II:  $-x + 1, -y + 3, -z + 1$ .

### 3. Results and discussion

#### 3.1. Structure

Single X-ray crystal structure analysis revealed that **1** contains one  $[\text{Co}_3(\text{hapt})_2(\text{AcO})_2\text{Py}_2]^{2+}$  cation, and two  $\text{ClO}_4^-$  anions. The  $[\text{Co}_3(\text{hapt})_2(\text{AcO})_2\text{Py}_2]^{2+}$  contains three cobalt atoms, all in Jahn-Teller-distorted octahedral environments. Each terminal cobalt is coordinated by two amine nitrogen atoms and two oxygen atoms from the Schiff-base ligand (Co–N = 1.949(4) and 1.958(5) Å) (Co–O = 1.896(3) and 1.903(4) Å), occupying the four equatorial positions [O(1)–Co(1)–O(2) = 82.37(15)°, O(1)–Co(1)–N(1) = 90.19(18)°, O(2)–Co(1)–N(2) = 90.68(18)°, N(1)–Co(1)–N(2) = 96.9(2)°]. Two axial positions for each terminal cobalt are occupied by pyridine and bridging acetate [Co–N = 1.948(4) Å, Co–O = 1.938(4) Å, N(3)–Co(1)–O(4) = 177.52(17)°]. The central cobalt is coordinated by four bridging oxygen atoms from hapt and two oxygen atoms from acetates (Co–O = 2.020(4)–2.141(3) Å). The dihedral angle between the Co(1)O(1)Co(2) plane and the Co(1)O(2)Co(2) plane is 24.85(2)°. By careful comparison of the coordination environments and bonding parameters of cobalt atoms in **1**, the oxidation states of these metal centers should be different. Based on charge balance requirements and bond-valence sum calculations [12], Co(1) atom should be +3, while Co(2) is +2. The conclusions have also been confirmed by magnetic susceptibilities studies (see below). The Co(1)···Co(2) distance is 3.1025(7) Å, while the Co(1)–O–Co(2) angles of each pair of neighbors are 100.04(15)° and 101.15(16)° respectively for O(1) and O(2). Thus **1**, shown in figure 1, is a linear trinuclear mixed ligand compound. Very few trinuclear cobalt compounds with  $\text{Co}^{\text{III}}\text{–Co}^{\text{II}}\text{–Co}^{\text{III}}$  arrangement are found in the CSD database [1a].

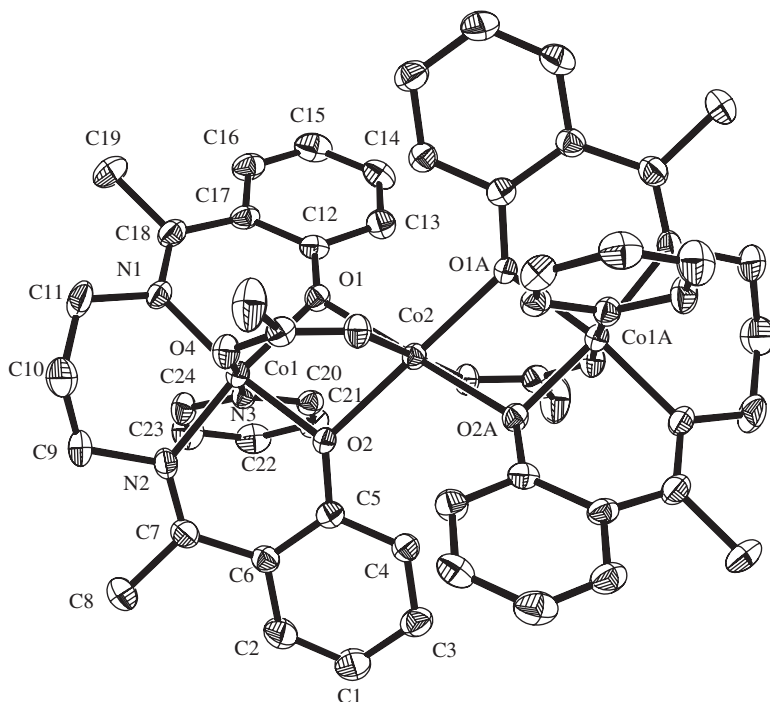


Figure 1. ORTEP representations of the trinuclear unit for **1** (30% probability ellipsoids, for clarity hydrogen atoms and two  $\text{ClO}_4^-$  were omitted).

As shown in figure 2, the structure of **2** shows that cobalt is in a distorted octahedral environment. In the dimeric unit, two cobalt atoms are held together by  $\mu$ -hydroxy while each cobalt atom is surrounded by two nitrogen atoms, two oxygen atoms from ligand (Co–N = 1.941(8) and 1.943(8) Å) (Co–O = 1.880(4) and 1.906(4) Å), and two oxygen atoms from two  $\mu$ -OH groups (Co–O = 1.920(4) and 1.927(4) Å). The four equatorial positions are occupied by two  $\mu$ -hydroxyl oxygen atoms, one nitrogen atom, and one oxygen atom from ligand [O(1)–Co(1)–O(2) = 87.49(15)°, O(1)–Co(1)–O(3) = 88.01(15)°, O(1)–Co(1)–O(3A) = 92.01(15)°, O(1)–Co(1)–N(1) = 90.0(3)°], while two apical positions are occupied by one nitrogen and one oxygen from the ligand [O(1)–Co(1)–N(1) = 176.1(3)°]. Co(1)···Co(1A) distance is 2.932(3) Å. Bond lengths and bond angles in compound **2** are in good agreement with values found in compound **1**.

### 3.2. Electronic spectra

The electronic spectra of the two compounds in dichloromethane were recorded in the range of 200–800 nm. Three absorption peaks (239, 355 and 585 nm) of **1** were observed, while **2** has two absorption peaks (257 and 376 nm). The intense absorption bands at short wavelength, 239 nm for **1** and 257 nm for **2**, may be assigned to intra-ligand  $\pi$ – $\pi^*$  transitions in the compound. The absorptions at 355 nm for **1** and

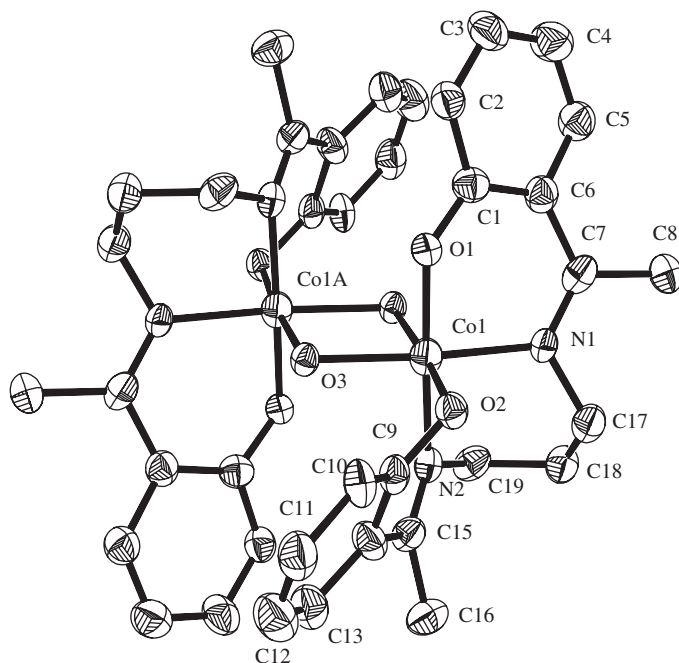


Figure 2. ORTEP representations of the binuclear unit for **2** (30% probability ellipsoids, for clarity hydrogen atoms and solvent were omitted).

376 nm for **2** may be assigned to Schiff base to metal ion charge transfer bands. A weak band in the visible range at 585 nm for **1** is assigned to a d–d transition [13].

### 3.3. IR spectra

The IR spectrum of **1** displays the characteristic bands of  $\nu(\text{C}=\text{N})$  at  $1598\text{ cm}^{-1}$ . The value of  $\Delta(\nu_{\text{as}}(\text{COO})-\nu_{\text{s}}(\text{COO}))$  is  $146\text{ cm}^{-1}$  in complex **1**, which is closed to the corresponding value in sodium acetate ( $144\text{ cm}^{-1}$ ). Such values indicate that the  $\text{COO}^-$  groups are coordinated to Co in bridging modes in accord with the X-ray diffraction analysis. The absorption at  $1087\text{ cm}^{-1}$  is characteristic for  $\text{ClO}_4^-$ . The IR spectrum of **2** displays the characteristic bands of  $\nu(\text{C}=\text{N})$  at  $1600\text{ cm}^{-1}$ , and the  $\nu(\text{O}-\text{H})$  at  $3395\text{ cm}^{-1}$  indicated the oxygen of OH is coordinated to the cobalt ions.

### 3.4. Magnetic property

The temperature dependence of the magnetic susceptibilities of **1** have been studied from 300 to 2 K in a 10 kOe applied magnetic field and all data were corrected for diamagnetism of the ligands estimated from Pascal's constants [14]. The magnetic properties of **1** are shown in figure 3. At room temperature, the measured  $\mu_{\text{eff}}$  (effective magnetic moment) is about 4.75 B.M., greater than one high-spin  $\text{Co}^{\text{II}} (S=3/2)$  (3.87 B.M.), but much smaller than three spin-only  $\text{Co}^{\text{II}} (S=3/2)$  (11.61 B.M.). The results confirm that compound **1** is in the mixed valence state  $\text{Co}^{\text{III}}(S=0)-\text{Co}^{\text{II}}(S=3/2)-\text{Co}^{\text{III}}(S=0)$ . The high  $\mu_{\text{eff}}$  value is due to the orbital contribution

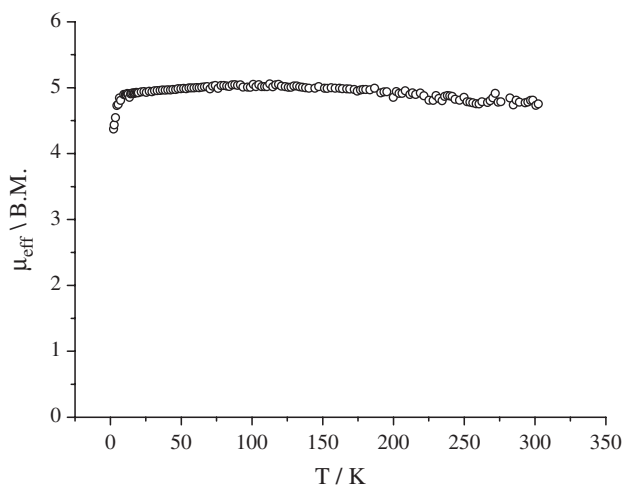


Figure 3. Plots of the experimental temperature dependences of  $\mu_{\text{eff}}$  for **1**.

as found in many  $\text{Co}^{\text{II}}$  compounds [15–18]. The magnetic susceptibilities of **2** are negative, typical diamagnetic behavior, indicating that the cobalt in **2** is low spin  $\text{Co}^{\text{III}}(S=0)$ .

### Supplementary material

CCDC-244759–244760 contains the supplementary crystallographic data for this article. These data can be obtained free of charge at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)].

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