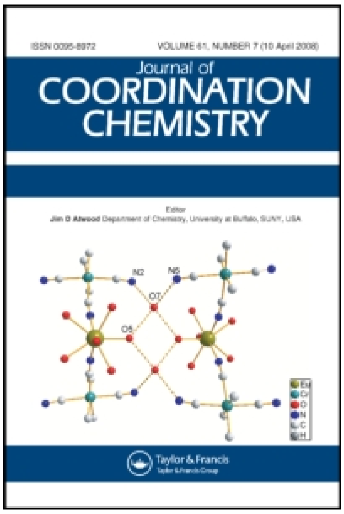

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Synthesis, characterization, crystal structure and magnetic property of asymmetrical double Schiff base heterotrinuclear complex: Cu(II)-Co(II)-Cu(II)

Rao-Jie Tao[a]; Fu-An Li[a]; Shuang-Quan Zang[a]; Yan-Xiang Cheng[b]; Qing-Lun Wang[c]; Jing-Yang Niu[a]; Dai-Zheng Liao[c]
[a] Chemistry and Chemical Engineering College of Henan University, Kaifeng 475001, China [b] Laboratory of High Molecular Chemistry, Changchun Applied Chemistry Institute, Jilin 130022, China
[c] Department of Chemistry, Nankai University, Tianjin 300071, China

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Synthesis, characterization, crystal structure and magnetic property of asymmetrical double Schiff base heterotrinuclear complex: Cu(II)–Co(II)–Cu(II)

RAO-JIE TAO*†, FU-AN LI†, SHUANG-QUAN ZANG†, YAN-XIANG CHENG‡, QING-LUN WANG§, JING-YANG NIU†, DAI-ZHENG LIAO§

†Chemistry and Chemical Engineering College of Henan University,
Kaifeng 475001, China
‡Laboratory of High Molecular Chemistry, Changchun Applied Chemistry Institute,
Changchun, Jilin 130022, China
§Department of Chemistry, Nankai University, Tianjin 300071, China

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An asymmetrical double Schiff-base Cu(II) mononuclear complex, HCuLp (H_3Lp is N-3-carboxylsalicylidene-N′-5-chlorosalicylaldehyde-1,3-diaminopropane) and a heterometal trinuclear complex with double molecular structure $(CuLp)_2Co \cdot 5H_2O$ have been synthesized and characterized by means of elemental analyses, IR and electronic spectra. The crystal structure of the heterotrinucler complex was determined by X-ray analysis. Each asymmetric unit within the unit cell of the complex contains two heterotrinuclear neutral molecules (a) [CuLpCoCuLp], (b) [$(CuLpH_2O)CoCuLp$] and four uncoordinated water molecules. In the two neutral molecules, the central Co^{2+} ions are located at the site of O_6 with a distorted octahedral geometry, one terminal Cu^{2+} ion (Cu(3)) at the square-pyramidal environment of N_2O_3, and the other three at the square planar coordination geometry with N_2O_2 donor atoms. Magnetic properties of the heterotrinucler complex have been determined in the temperature range 5–300 K, indicating that the interaction between the central Co^{2+} ion and the outer Co^{2+} ions is antiferromagnetic. The exchange integral J is equal to $-34.9(7)\,cm^{-1}$.

Keywords: Asymmetrical double Schiff base; Heterotrinuclear complex; Crystal structure; Magnetic property

1. Introduction

Magnetochemistry on heterometal polynuclear complexes has attracted much attention from materials science and model study of metal enzymes. Molecular-based magnetic materials have shown spectacular advances over the last two decades [1], in which the study of heterometal binuclear complexes has played an important and leading role.

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*Corresponding author. Email: rjtao@henu.edu.cn; yanxiang@ciac.jl.cn

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Kahn *et al.* have synthesized some heterometal binuclear complexes and investigated their magnetic properties [2]. The magnetic interaction between two nonequivalent paramagnetic centers may lead to situations which cannot be encountered in species containing only one kind of metal. A successful strategy for obtaining heterounclear species is the "complex as ligand" approach [3, 4].

These anionic precursors are particularly suitable for designing and synthesizing heterometallic complexes. A number of symmetrical double Schiff-base complexes have been reported [5–14]. However, owing to synthetic difficulties, only a few asymmetrical double Schiff-base complexes have been both structurally and magnetically characterized [15–19]. Here, we report a new copper(II) mononuclear complex (HCuLp) of an asymmetrical double Schiff base, where H_3Lp denotes the asymmetrical double Schiff base N-3-carboxylsalicylidene-N′-5-chlorosalicylaldehyde-1,3-diaminopropane. Through "complex as ligand", we obtained a hetero-trinuclear complex with a double molecular structure (a) [(CuLp)Co(CuLp)], (b) [(CuLpH_2O)Co(CuLp)] and $4H_2O$. In this article, we report the crystal structure and magnetic property of the trinuclear complex.

2. Experimental

2.1. *Reagents and instrumentation*

3-Carboxylsalicylidene was prepared according to the literature [20], the precursor complex Cu5–ClSaPnOH [Cu5–ClSaPnOH = (N-(3-aminopropane)5-chlorosalicylaldiminato]hydroxo copper(II)) was prepared by the literature method [21]. Other chemicals were of reagent grade and obtained commercially and used without further purification.

Elemental analyses for carbon, hydrogen and nitrogen were carried out on a Perkin-Elmer 2400II analyzer. The metal contents were determined by EDTA titration. The infrared spectra were recoded on an Avatar-360 spectrometer using KBr pellets between 400–4000 cm^{-1}. UV-Vis spectra were recoded on a UV-540 spectrometer in the 400–800 nm ranges. Magnetic measurements were carried out on crystalline samples with a MPMS-7 SQUID magnetometer.

2.2. *Synthesis of the mononuclear complex, HCuLp, (1)*

A mixture of 5 mmol (1.46 g) Cu5–ClSaPnOH and 5 mmol (0.83 g) 3-carboxylsalicylidene in ethanol (50 mL) was heated for 2 h and then left to cool with stirring. The precipitate was filtered off and washed with ethanol and diethyl ether. Yield: 1.50 g, 70%. (Found: Cu, 15.00; C, 51.06; H, 3.38; N, 6.65. Calcd for $CuC_{18}H_{15}ClN_2O_4$: Cu, 15.04; C, 51.16; H, 3.58; N, 6.63).

2.3. *Synthesis of trinuclear complex*

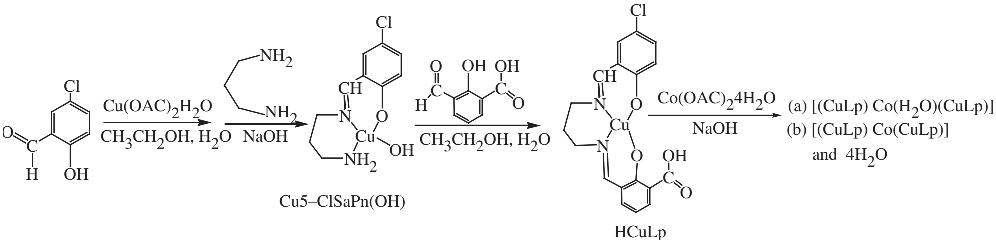
1 mmol HCuLp (422.6 mg) and 0.9 mmol NaOH (36 mg) were dissolved in 10 mL water/ethanol (v/v = 1 : 1). An aqueous solution (5 mL) containing 0.5 mmol (124.5 mg) $Co(OAC)_2 \cdot 4H_2O$ was then added. The resulting solution was heated for 2 h, then left to cool with stirring. The complex precipitated as a light violet powder and was

then recrystallized from methanol to give black rhombus crystals, which were suitable for X-ray crystal analysis. Yield: 432 mg, 87%. (Found: Cu, 13.34; Co, 6.12; C, 45.70; H, 3.42; N, 5.88. Calcd for $Cu_4Co_2C_{72}H_{66}Cl_4N_8O_{21}$: Cu, 13.43; Co, 6.20; C, 45.68; H, 3.51; N, 5.92).

The synthesis route is shown in scheme 1.

2.4. *Crystal structure determination and refinement*

Single crystals used for data collection of the title complex were selected and mounted on a Bruker Smart APEX diffractometer with CCD detector using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Data were collected by the ω scan mode at 293(2) K to a θ_{max} of 26.46° with a total 23,588 reflections collected including 16,161 independent reflections ($R_{int} = 0.0557$). A summary of the crystallographic data is given in table 1. The structure was solved with direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the SHELXTL-97 program [22]. A full-matrix least-squares refinement on F^2 was carried out using the SHELXTL-97 program. The final agreement factor values are $R_1 = 0.0530$, $wR_2 = 0.1211$ ($I > 2\sigma(I)$). Selected bond distances and angles are given in table 2.



Scheme 1. Synthetic route.

Table 1. Crystal data and structure refinement for the title complexes.

Empirical formula	$Cu_4Co_2C_{72}H_{66}Cl_4N_8O_{21}$
Formula weight	1893.068
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	11.8535(14)
b (Å)	16.1418(19)
c (Å)	23.143(3)
α (°)	79.525(2)
β (°)	98.04(3)
γ (°)	68.46
V (Å^3)	4039.5(8)
Z	2
D_c (Mg m^{-3})	1.639
λ(Mo-Kα) (Å)	0.71073
μ(Mo-Kα) (mm^{-1})	1.647
T (K)	293(2)
$R_1[(I > 2\sigma(I))]$	0.0527
wR_2	0.0962

Table 2. Selected bond lengths(Å) and bond angles (°) for the complex.

Cu(1)–N(2)	1.921(4)	Cu(1)–O(2)	1.942(3)	Cu(1)–O(1)	1.918(4)
Cu(1)–N(1)	1.968(4)	Co(1)–O(5)	2.150(3)	Co(1)–O(7)	1.979(3)
Co(1)–O(1)	2.177(3)	Co(1)–O(3)	1.980(3)	Co(1)–O(6)	2.060(3)
Co(1)–O(2)	2.0593(3)	Cu(2)–N(4)	1.921(4)	Cu(2)–O(5)	1.917(3)
Cu(2)–O(6)	1.932(3)	Cu(2)–N(3)	1.965(4)	Cu(3)–O(W)	2.258(4)
Cu(3)–N(5)	1.969(4)	Cu(3)–O(10)	1.978(3)	Cu(3)–O(9)	1.945(3)
Cu(3)–N(6)	1.979(4)	Co(2)–O(15)	1.999(4)	Co(2)–O(9)	2.141(3)
Co(2)–O(13)	2.181(3)	Co(2)–O(11)	1.983(3)	Co(2)–O(10)	2.073(3)
Co(2)–O(14)	2.094(3)	Cu(4)–O(13)	1.930(3)	Cu(4)–N(7)	1.955(4)
Cu(4)–O(14)	1.944(3)	Cu(4)–N(8)	1.936(4)		
O(1)–Cu(1)–N(2)	162.59(16)	O(2)–Cu(1)–N(2)	92.33(15)	N(1)–Cu(1)–N(2)	97.65(18)
O(1)–Cu(1)–O(2)	81.83(13)	O(1)–Cu(1)–N(1)	93.34(17)	O(2)–Cu(1)–N(1)	159.10(15)
O(7)–Co(1)–O(3)	98.67(15)	O(2)–Co(1)–O(6)	175.16(12)	O(1)–Co(1)–O(7)	93.05(14)
O(7)–Co(1)–O(2)	97.47(13)	O(7)–Co(1)–O(5)	156.51(13)	O(3)–Co(1)–O(1)	158.22(14)
O(2)–Co(1)–O(3)	87.03(13)	O(3)–Co(1)–O(5)	93.60(14)	O(2)–Co(1)–O(1)	73.23(12)
O(7)–Co(1)–O(6)	86.01(13)	O(2)–Co(1)–O(5)	103.13(12)	O(1)–Co(1)–O(6)	103.31(12)
O(3)–Co(1)–O(6)	95.80(13)	O(6)–Co(1)–O(5)	72.83(12)	O(5)–Co(1)–O(1)	82.33(12)
N(4)–Cu(2)–O(5)	162.62(15)	O(6)–Cu(2)–N(4)	92.70(14)	N(3)–Cu(2)–O(5)	93.25(15)
O(5)–Cu(2)–O(6)	81.03(13)	O(6)–Cu(2)–N(3)	158.59(15)	N(3)–Cu(2)–N(3)	98.14(16)
O(10)–Cu(3)–N(6)	156.42(16)	O(9)–Cu(3)–O(W)	93.03(14)	N(5)–Cu(3)–O(W)	86.59(17)
O(10)–Cu(3)–O(W)	97.83(13)	O(9)–Cu(3)–N(5)	171.34(16)	O(9)–Cu(3)–O(10)	80.21(12)
N(5)–Cu(3)–O(10)	91.15(15)	O(9)–Cu(3)–N(6)	91.28(15)	N(5)–Cu(3)–N(6)	96.92(18)
O(11)–Co(2)–O(14)	94.07(13)	O(6)–Cu(3)–O(W)	104.72(16)	O(13)–Co(2)–O(9)	82.73(12)
O(15)–Co(2)–O(14)	86.88(13)	O(14)–Co(2)–O(9)	103.53(12)	O(11)–Co(2)–O(13)	94.65(14)
O(11)–Co(2)–O(15)	98.18(15)	O(10)–Co(2)–O(14)	175.60(12)	O(15)–Co(2)–O(13)	156.15(13)
O(11)–Co(2)–O(10)	88.17(13)	O(11)–Co(2)–O(9)	160.35(13)	O(10)–Co(2)–O(13)	103.89(12)
O(15)–Co(2)–O(10)	96.56(14)	O(15)–Co(2)–O(9)	91.50(14)	O(14)–Co(2)–O(13)	72.17(12)
N(8)–Cu(4)–O(13)	164.10(15)	O(10)–Co(2)–O(9)	73.71(12)	N(7)–Cu(4)–O(14)	162.02(16)
O(13)–Cu(4)–O(14)	81.10(13)	N(7)–Cu(4)–N(8)	96.74(18)	N(7)–Cu(4)–O(13)	93.64(16)
Cu(1)–O(1)–Co(1)	99.31(14)	N(8)–Cu(4)–O(14)	92.36(16)	Cu(1)–O(2)–Co(1)	102.68(14)
Cu(3)–O(10)–Co(2)	102.79(13)	Cu(2)–O(5)–Co(1)	100.24(15)	Cu(2)–O(6)–Co(1)	102.99(14)
Cu(4)–O(14)–Co(2)	103.09(14)	Cu(3)–O(9)–Co(2)	101.48(13)	Cu(4)–O(13)–Co(2)	100.47(14)

3. Results and discussion

3.1. *Synthesis*

The intermediate complex Cu5–ClSaPnOH of the 1 : 1 : 1 reaction product of copper acetate monohydrate, 5-chlorosalicylaldehyde and 1,3-diaminopropane (scheme 1) plays a very important role during the synthesis of the asymmetrical double Schiff-base heterotriunclear complex. In order to obtain the intermediate product Cu5–ClSaPnOH, the template reaction method is adopted in synthesis of Cu5–ClSaPnOH. The product from template reaction is recrystallized 2–3 times in ethanol–water (v/v = 1 : 1) mixed solution, obtaining pure Cu5–ClSaPnOH. Through the pure intermediate Cu5–ClSaPnOH, we have synthesized an asymmetrical double Schiff base copper mononuclear complex HCuLp, and further obtained hetero-trinuclear complex Cu–Co–Cu with double molecular structure (a) [CuLpCoCuLp], (b) [CuLp(H_2O)CoCuLp] and $4H_2O$.

3.2. *IR spectra*

There are strong $\nu_{C=N}$ vibration bands at 1621 cm^{-1}, and 1625 cm^{-1} for the mononuclear and the triunclear complexes respectively, which indicate the general character of Schiff-base complexes. The mononuclear complex exhibits one $\nu_{as(COOH)}$ vibration band at 1710 cm^{-1}. This band is missing in the IR spectra of the triunclear complex because of the loss of the proton of the COOH group, indicating the formation of the trinuclear complex.

3.3. *Electronic spectra*

The diffuse reflectance spectrum of the mononuclear compound exhibits a very broad peak around 19.24×10^3 cm^{-1}, which is consistent with a nearly square-planar geometry. The electronic spectra of the trinuclear complex show a broad absorption band in the visible region with maximum at 18.60×10^3 cm^{-1}. The frequencies are lower than for the mononuclear complex. Such a red shift of the d–d band may be attributed to decreased planarity of the [CuN_2O_2] chromophore and/or a square-pyramidal [CuN_2O_3] chromophore for the complex. The d–d transitions of octahedral [CoO_6] should also be observed but must be obscured by the d–d band of Cu(II).

3.4. *Structural description of the trinuclear complex*

The crystal structure was determined by single-crystal *x*-ray diffraction analyses; the crystallographic data are summarized in table 1. Selected bond distances with their estimated standard deviations in parentheses are given in table 2. Figure 1 shows a unit cell structure of the trinuclear complex, which consists of two neutral heterotrinuclear molecules, [$(CuLp)_2Co$], [$(CuLpH_2O)Co(CuLp)$] and four uncoordinated water molecules in the crystal lattice. The difference between the two heterotrinuclear molecules is that one has a coordinated water molecule, and the other does not.

Figure 1(a) shows that the neutral heterotrinuclear molecule, including Cu1, Co1, and Cu2 ions, consists of two mononegative, mononuclear copper complexes and a Co^{2+} central ion. Copper ions (Cu1 or Cu2) of the two mononuclear moieties have square-planar coordination geometry with the N_2O_2 donor atoms of the nonequivalent tetradentate ligand Lp^{3-}. The Cu–N distances of the 5-chlorosalicylaldehyde moiety (Cu1–N1 = 1.968(4) Å, Cu2–N3 = 1.965(4) Å) are considerably longer than the corresponding values of the 3-carboxylsalicylidene moiety (Cu1–N2 = 1.921(4) Å, Cu2–N4 = 1.921(4) Å), but the Cu–O distances of the 5-chlorosalicylaldehyde (Cu1–O1 = 1.918(3) Å, Cu2–O5 = 1.917(3)) are considerably shorter than the corresponding values of the 3-carboxylsalicylidene moiety (Cu1–O2 = 1.942(3), Cu2–O6 = 1.932(3) Å). For each mononuclear moiety, the two phenoxo and the carboxylic oxygen atoms (O1, O2, O3 or O5, O6, O7) on one side of the planar Cu^{2+} mononuclear complex coordinate to the central ion Co1 as a tridentate ligand with distances of Co1–O1 = 2.177(3) Å, Co1–O2 = 2.059(3) Å, Co1–O3 = 1.980(3) Å, Co1–O5 = 2.150(3) Å, Co1–O6 = 2.060(3) Å, Co1–O7 = 1.979(3) Å. Such the central Co^{2+} ion is located at a distorted octahedral environment consisting of four phenoxo atoms and two carboxylic oxygen atoms from two terminal Cu^{2+} mononuclear moieties $CuLp^{-1}$. The octahedral geometry has four almost coplanar bonds [for Co1–O2, Co1–O5, Co1–O6, Co1–O7] and two axial bonds [for Co1–O1, Co1–O3]. The two axial coordination atoms [O1 and O3] come from the same $CuLp^{-1}$ moiety, with one axial bond from phenolato oxygen atom O1 the longest Co–O bond.

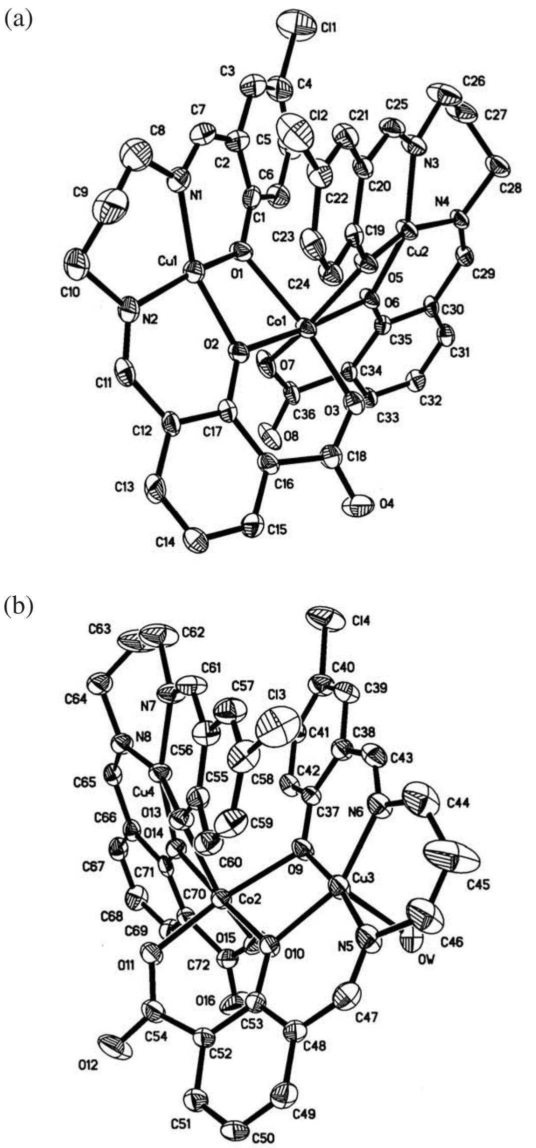


Figure 1. The molecular structure of each of the two independent trimetallic complexes in the asymmetric unit (a) [(CuLp)Co(CuLp)] and (b) [(CuLpH_2O)Co(CuLp)]. The lattice water molecules and all hydrogen atoms were omitted for clarity.

The Co–O distances with carboxylic oxygen atoms coming from the same mononuclear moiety are considerably shorter than the values of phenoxo oxygen, probably from phenoxo as bridging atoms with weaker coordination.

The structure of the trinuclear complex, including Cu3, Cu4, and Co2 ions, is similar to that of the former except the coordination environment of the terminal Cu3 ion, in which Cu3 ion lies on a classical square-pyramidal environment with a oxygen atom from a coordinated water molecular occupying the axial position

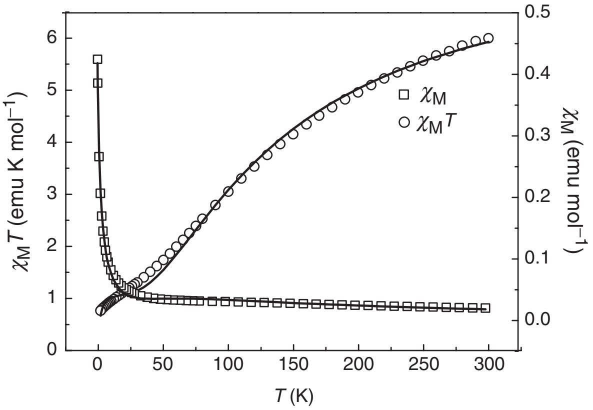


Figure 2. The plots of $\chi_M T$ and χ_M *vs.* T for the complex.

of a square pyramid. The bond lengths and angles of two neutral trinuclear molecules are slightly different, denoting that the dissymmetrical environment of the latter is stronger than the former.

3.5. *Magnetic properties*

The variable temperature magnetic susceptibility data for a crystalline sample was measured on a SQUID spectrometer over the temperature range 5–300 K with an applied field of 10000 G. The plots of $\chi_M T$ and χ_M versus T are shown in figure 2; at 300 K $\chi_M T$ is equal to 6.004 BM, a value slightly higher than expected for non-interacting S = 3/2 Co(II) centers and two S = 1/2 Cu(II) centers (5.930 BM). With decreasing temperature, the $\chi_M T$ value decreases gradually approaching a minimum around 5 K with $\chi_M T = 0.8468$ BM. This magnetic behavior indicates the presence of antiferromagnetic interactions.

From a magnetic viewpoint, because the complex consists of isolated triunclear molecules and these molecules are discrete, there are no magnetic interactions between molecules. The magnetic analysis for the complex was carried out for a linear triunclear structural model:

$$\underset{S_2}{\mathrm{A}} \overset{J}{\text{————————}} \underset{S_1}{\mathrm{B}} \overset{J}{\text{————————}} \underset{S_3}{\mathrm{A}}$$

$$\chi_M = \frac{Ng^2\beta^2}{4kT} \times \frac{1 + 10e^{5J-2J'/kT} + 10e^{3J/kT} + 35e^{8J/kT}}{1 + 2e^{5J-2J'/kT} + 2e^{3J/kT} + 3e^{8J/kT}}$$

where J corresponds to the exchange integral between Co and Cu. The best-fit parameters are $J = -34.9(7)\,\mathrm{cm}^{-1}$, $g = 2.46(1)$, $zj = -0.9(1)\,\mathrm{cm}^{-1}$. Agreement factor R is equal to 9.3×10^{-3}, which corresponds to a reasonable agreement as can be seen in figure 2. The negative J value suggests that the interaction between Co$^{\mathrm{II}}$ and Cu$^{\mathrm{II}}$ is antiferromagnetic.

The magnetic susceptibility data were well reproduced over the 60–300 K range, and the theoretical curves are shown as the solid line in figure 2. The interpretation of the magnetism is complicated due to the unquenched orbital momentum of Co^{II}. The isotropic Heisenberg exchange model is not strictly applicable to octahedral Co^{II} complexes because of the strong spin–orbit splitting of the $^4T_{1g}$ ground term but can be applied to distorted octahedral geometries where the orbital degeneracy of the $^4T_{1g}$ state is removed. However, at low temperatures, the states arising from the $^4T_{1g}$ term are split into two Kramer doublets by spin–orbit coupling and the Heisenberg model may fail. The magnetic data for the complex could not be satisfactorily fit over the entire temperature range; however, a reasonable fit could be obtained in the 60–300 K regions neglecting the zero-field interaction.

4. Conclusion

We have ever reported several symmetrical double Schiff-base complexes [12–14] and asymmetrical double Schiff base heterotrinuclear complexes [19, 23]. The former are obtained from a symmetrical double Schiff-base ligand, the latter are synthesized from the intermediate product of 1 : 1 reaction of salicylaldehyde and diamino (1,2-diaminoethane or 1,3-diaminopropane). Syntheses of the intermediate are the main steps in the syntheses of asymmetrical double Schiff-base heterotrinuclear complexes, requiring appropriate reaction environment as well as appropriate mole ratio. We used the template reaction method in ethanol–water (v/v = 1 : 1) mixed solution to obtain the pure intermediate, and further obtained heterotrinuclear complexes [19, 23]. When substituting 5-chlorosalicylaldehyde for salicylaldehyde in synthesis of the intermediate, we obtained a mixture of symmetrical double Schiff-base complex and the intermediate product Cu5–ClSaPnOH. The pure intermediate product was obtained by recrystallization. For trinuclear complexes, it is difficult to obtain single crystals suitable for X-ray analysis and to study their properties. Therefore, we have only investigated structure and properties of the title compound Cu(II)–Co(II)–Cu(II) so far; other triunclear complexes are under investigation.

Supplementary material

Crystallographic data for the structure reported in this article have been deposited at the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication CCDC No. 278620 for the trinuclear complex. Copies of this information can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk; or http://www.ccdc.cam.ac.uk/deposit).

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