

Synthesis and thermal characterization of sulfur containing methionine bridged cobalt(III) and copper(II) complex

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Abstract The sulfur containing amino acid bridging polynuclear transition metal complex has been synthesized and characterized by different measurements such as UV–Vis, FT–IR, C–H–N–S, TG–DTA, ICP–AES, differential scanning calorimeter (DSC), and XRD. DSC has showed negative specific heat of this polynuclear system and has used to evaluate some thermodynamic constants like activation energy (E_a), frequency factor (A), enthalpy, and entropy of that system. The specific heat capacity is measured at heating rate of $10\text{ }^\circ\text{C min}^{-1}$ in room atmosphere of this polynuclear complex. The characterization of this complex has showed five Co(III) and four Cu(II) atoms and this complex contained ten sulfur containing methionine amino acid units.

Keywords Methionine · DSC · Negative specific heat · TG–DTA · ICP–AES · XRD

Introduction

Sulfur containing methionine is one of the nine essential amino acids needed by human beings and is the only essential amino acid containing sulfur in its structure. Reactions between various classes of amines and *trans*-[CoCl₂(en)₂]⁺ have been widely investigated since first reported by Meisenheimer [1]. Surprisingly, the reactions

between *trans*-[CoX₂(en)₂]⁺ (X = Cl or Br) and amino acids have received relatively scant attention. Nevertheless, treatment of the dichloro-complex with some optically active amino acids (AA), in the presence of equimolar amount of base, was found to give on heating the optically active complexes [Co(en)₂(AA)]²⁺, in which the amino acids fulfill their customary bidentate roles [2]. Reactions between *trans*-[Co(en)₂X₂]⁺ and amino acid esters, AE [3, 4] and amides, AAm [5], gave the products, *cis*-[Co(en)₂X(AE)]²⁺ and *cis*-[Co(en)₂X(AAm)]²⁺, respectively, in which the ester and amide ligands are both monodentate and amino bonded to the metal ion. Some N-bonded monodentate amino acid complexes, *cis*-[Co(en)₂Cl(AA)]²⁺, have also been prepared by hydrolysis of the corresponding ester complexes in hydrochloric acid solutions [4]. Nolan et al. investigated the reactions of amino acids with *trans*-[CoX₂(en)₂]⁺ and have found that under weakly basic conditions, complexes of the type *trans*-[Co(en)₂X(AA)]²⁺, in which the amino acid is monodentate and bonded through its carboxylate group to the metal ion are formed. Methionine-based copper(II) complex showed some antiulcer activity as revealed by animal model studies [6] and has also found some interest in veterinary medicine, for copper supplementation [7, 8]. The binuclear and polynuclear complexes of transition metals have attracted extensive interest [9–11]. Motivated further by this fact, the study of specific heat beyond the weak-coupling limit has recently received considerable attention, in particular in view of the validity of the third law of thermodynamics [12–18]. Apart from fundamental thermodynamical questions, the study of specific heat in the quantum regime is also of interest because it can be related to entanglement properties [19]. Recently, two different methods toward the evaluation of a specific heat are proposed and discussed [12]. One possibility based on the thermal expectation value of the

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Hamiltonian describing the isolated system. Another approach, on which I have focused in this article, is widely used expression for the partition function of the dissipative system [12, 15, 20–27]. It is defined in terms of partition functions of the coupled system and of the uncoupled system.

$$Z = \frac{T_{\text{TS+B}} e^{-\beta H}}{T_{\text{B}} e^{-\beta H_{\text{B}}}} \quad (1)$$

where the total Hamiltonian, $H = H_{\text{S}} + H_{\text{B}} + H_{\text{SB}}$, consisted of contributions from the system, bath, and coupling between them. In the absence of coupling between system and bath, Z reduces to the partition function of the system. Partition function (1) appears naturally in the Feynman-Vernon approach to dissipative systems [12] and can be related to the equilibrium properties of the system [28]. In this system, the amino acid methionine attached to Co(III) complex in *trans*-position revealed from UV-Vis spectrophotometer and Cu(II) directly attached to the carboxylic group of methionine bound Co(III) center.

Experimental

Trans-[CoCl₂(en)₂]Cl was prepared by the literature method [29]. The complex, *trans*-[Co(en)₂(methionine)₂], was prepared as follows. *Trans*-[CoCl₂(en)₂]Cl (0.01 mol) and the amino acid (0.01 mol) were ground together and made into a paste by the addition of a little water. Diethylamine (ca. 0.2 cm³) was added dropwise with continuous grinding to the paste until the color change to mauve was complete. The mixture was then treated with 0.5 mol dm⁻³ HClO₄ (20 cm³) and heated on a steam bath until most of the solid material had dissolved. This was filtered while hot and filtrate then was treated with concentrated HClO₄ (1 cm³). On cooling, the complex crystallized as mauve needles. The complex was re-crystallized from 1 mol dm⁻³ HClO₄ and was obtained in 60–80% yields. To an aqueous solution of cobalt(II) complex (2 mmol in 20 mL water), one half equivalent of CuSO₄·5H₂O solution was added and the pH of the resulting solution was maintained at 4.0 by the addition of 0.1 mol dm⁻³ NaOH solution. Addition of few crystals of NaClO₄ followed by cooling resulted in separation of dark bluish colored crystals of the polynuclear complex. Highly purified, de-ionized water was used in all solutions. Second distillation was carried out from alkaline KMnO₄ using all glass distillation apparatus.

Physical measurements

The IR spectrum was obtained using a Thermo-Nicolet Avatar 370 DTGS of solid sample. DSC measurement was

performed on a Mettler Toledo, DSC 822 on 10 °C min⁻¹ under atmospheric condition. C–H–N–S analyzer was performed on an Elementar systeme, Vario EL III. Thermogravimetric analysis (TG) and Differential thermal analysis (DTA) studied for the complex was made using Perkin Elmer, Pyris Diamond thermal analyzer between 28.74 and 1083 °C. ICP-AES measurement was performed using Thermo Electron IRIS Intrepid II XSP DUO system for Co, Cu, and S determination as follows. The sample was dissolved in 5 mL HNO₃ and made up into 100 mL using HPLC grade water. IR, DSC, TG-DTA, ICP-AES, C–H–N–S analyses were performed at ST & IC, Cochin University of Science and Technology, Cochin. pH measurements were performed using a Nucleonix type DP 301 digital pH meter equipped with combination of glass-Ag/AgCl/Cl⁻ (3 mol dm⁻³ NaCl) electrode. It was calibrated with standard buffers of pH 4.0, 7.0, and 9.0 (Merck). UV-Visible spectra were recorded with a Cecil UK model CE-7200 UV-Visible spectrophotometer using cell block housing a pair of 10 mm Quartz Suprasil cells.

Results and discussion

UV-Visible spectra

The electronic absorption spectra are particularly helpful in distinguishing whether the sulfur atom is coordinated or uncoordinated [30–33]. The visible spectrum showed three bands in their electronic solution spectra in the 250–750 nm range with λ_{max} value as 276, 352, and 443 nm. This indicated that no sulfur atom of methionine coordinated to the complex in this study [34, 35]. This consisted with a configuration in which Cl⁻ and methionine occupy *trans*-position. Low spin regular octahedral Co(III) complexes generally show two bands in this region due to the ¹A_{1g} → ¹T_{1g} (Lower energy) and ¹A_{1g} → ¹T_{2g} transitions [36]. In complexes of the type *trans*-[Co(en)₂AB]³⁺, where A and B are relatively weak-field ligands, the low energy band is resolved into two components due to splitting of the ¹T_{1g} state and these complexes, therefore, show three bands in their visible and UV spectra.

IR spectrum

The methionine possesses three different donor atoms (N, O, and S) and thus can have three geometrical isomers. The infrared spectrum showed the coordinated COO⁻ stretching vibration at 1608 cm⁻¹ shifted from 1583 cm⁻¹ [37]. The peaks 667, 958, and 1022 cm⁻¹ are assigned for Co^{III}-N stretching, CH₂ rocking, and C–C stretching vibration of ethylenediamine, respectively. The peak 1608 cm⁻¹

assigned for C=O group of methionine. The COO^- asymmetric stretching vibration shifted from 1583 to 1683 cm^{-1} . This indicated that COO^- of methionine formed bond either with Co(III) or Cu(II) center. The peak at 1404 cm^{-1} was due to C–O stretching vibration of methionine in Cu–O bond [37]. The NH_2 vibration of methionine observed at 1168 cm^{-1} [37]. This conformed for Co–N and Cu–O bond with methionine which acted as bidentate ligand. The NH_2 stretching vibration of methionine observed at 3100 cm^{-1} .

Elemental analysis

The elemental analysis of complex was carried out by C–H–N–S. The elemental analysis of the bulk product was also consistent with the theoretical values. Anal. calcd. for complex $\{\text{Co}_5^{\text{III}}\text{Cu}_4^{\text{II}}(\text{en})_{10}(\text{methionine})_{10}\cdot 8\text{H}_2\text{O}\cdot 7\text{SO}_4\cdot \text{ClO}_4\}$ is H: 5.79%; C: 23.63%; N: 11.81%; S: 15.30%; found H: 5.82%; C: 23.58%; N: 11.78%; S: 15.40%.

ICP-AES analysis

The elemental analysis of complex was carried out by ICP-AES. The Co, Cu, and S were also consistent with the theoretical values. Anal. calcd. for complex $\{\text{Co}_5^{\text{III}}\text{Cu}_4^{\text{II}}(\text{en})_{10}(\text{methionine})_{10}\cdot 8\text{H}_2\text{O}\cdot 7\text{SO}_4\cdot \text{ClO}_4\}$ is S: 15.30%; Co^{III} : 8.29%; Cu^{II} : 7.14% found S: 15.45%; Co^{III} : 8.30%; Cu^{II} : 7.12%.

TG-DTA analysis

From TG analysis (Fig. 1), the mass loss occurred in four steps as temperature increased from 28.74 to $1083\text{ }^\circ\text{C}$. The mass loss in the first step of onset temperature $68.28\text{ }^\circ\text{C}$ was 1.03% (calc. $1.02 \pm 0.015\%$). At this temperature, two non-coordinated water molecules removed from the complex. The mass loss in the second step of onset temperature $232.46\text{ }^\circ\text{C}$ was 11.42% (calc. $11.25 \pm 0.17\%$). At this temperature, eight coordinated water molecules and the fraction of ethylenediamine, $8\{\text{CH}_2\text{--CH}_2, 2\text{H}_2\}$, removed from the samples. The mass loss in the third set of onset temperature $494.47\text{ }^\circ\text{C}$ was 19.91% (calc. $19.66 \pm 0.25\%$). At this temperature, two ethylenediamine fraction, $2\{\text{CH}_2\text{--CH}_2, 2\text{H}_2\}$ and five methionine fraction, S- CH_3 , removed from the complex. The mass loss in the last step of onset temperature $877.41\text{ }^\circ\text{C}$ was 25.03% (calc. $24.95 \pm 0.05\%$). At this temperature, four methionine fraction, S- CH_3 , removed from the complex. From DTA spectrum (Fig. 2), the reaction is found exothermic in nature which was also observed to be similar with DSC spectra below $700\text{ }^\circ\text{C}$. Above this temperature, the reaction was found endothermic in nature.

Differential scanning calorimeter

From Eq. 1, one obtained by means of standard thermodynamic relations a specific heat [15]

$$C = k_B \beta^2 \frac{\partial}{\partial \beta^2} \ln(Z) \quad (2)$$

Here, k_B is the Boltzmann constant and the temperature T appears $\beta = 1/k_B T$. In the following, I assumed the removal particle to consist of harmonic oscillators and the coupling to be bilinear in complex and removal coordinates. In order to know the appearance of negative specific heat (2), it was sufficient to consider a stylized minimal model where the remove particle consisted of only a single degree of freedom described by the Hamiltonian.

$$H_R = \frac{P^2}{2m} + \frac{f_R}{2} q^2 \quad (3)$$

where f_R denotes the spring constant. The complex governed by the Hamiltonian

$$H_C = \frac{P^2}{2M} + \frac{f_C}{2} Q^2 \quad (4)$$

In the case of free particle, oxidation (O_2) (spring constant $f_C = 0$) and of a harmonic oscillator ($f_C > 0$), the coupling Hamiltonian is given by

$$H_{CR} = -f_R q Q + \frac{f_R}{2} Q^2 \quad (5)$$

The mass of a single remove particle oscillator was “ m .” This removal particle coupled with complex having mass “ M ” harmonically. In my analysis, a free particle (O_2) was in contact with the single degree of freedom environment described by Eqs. 3 and 5. Complex and removal particles are assumed to stay in thermal equilibrium with each other at the inverse temperature β . Hence, the density matrix of the total system is given by a Gibbs’s state.

$$\rho_{CR} = Z_{CR}^{-1} \exp[-\beta(H_C + H_R + H_{CR})] \quad (6)$$

where $Z_{CR} = T_r \exp[-\beta(H_C + H_R + H_{CR})]$ denotes the partition function of the total system.

The partition function $Z_R = T_r \exp[-\beta H_R]$ of the removal particle’s degree of freedom is given by

$$Z_R = \frac{1}{2 \sin\left(\frac{\hbar \beta \omega_0}{2}\right)} \quad (7)$$

where

$$\omega_0^2 = \left(\frac{f_R}{m}\right) \quad (8)$$

ω_0 was the frequency of remove particle oscillator. From Eq. 2, the specific heat capacity of these removal particles are given below.

Fig. 1 TG spectrum of methionine bridged Co(III) and Cu(II) complex

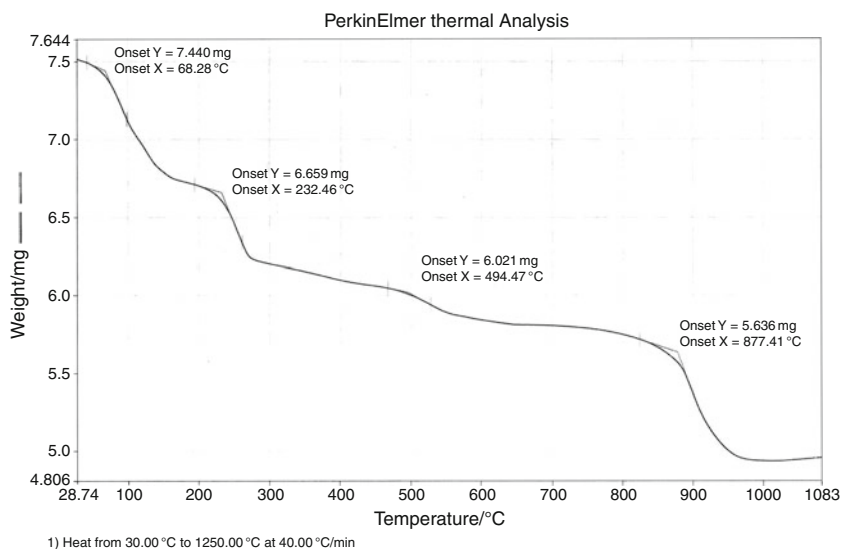
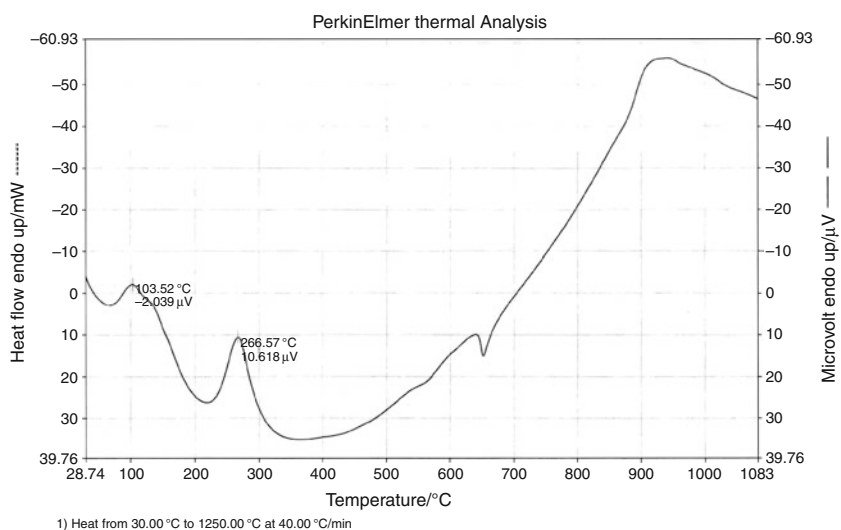


Fig. 2 DTA spectrum of methionine bridged Co(III) and Cu(II) complex



$$C_R = k_B g \left(\frac{\hbar\beta\omega_0}{2} \right) \tag{9}$$

where

$$g(x) = (x/\sin x)^2$$

In order to obtain a well-defined partition function for the free particle, I restricted its motion to a region of inside the system. The system is supposed to be sufficiently large such that the energy level spacing can be neglected in compared with the thermal energy $k_B T$ [15]. Under this condition, the space of this system will turn out to be irrelevant in the sequel.

The frequency of underdamped complex ($\zeta < 1$)

$$\omega = \omega_0 \left\{ \zeta \pm (\zeta^2 - 1)^{\frac{1}{2}} \right\}$$

ζ is called as damping ratio. In this case, the complex loses energy along with removal particles and return to the thermally stable state.

The specific heat capacity of complex is given below:

$$C_C = k_B g \left(\frac{\hbar\beta}{2} \right)$$

The total heat capacity of the system is given below:

$$C = C_C + C_R = -k_B g \left(\frac{\hbar\beta}{2} \right) + k_B g \left(\frac{\hbar\beta\omega_0}{2} \right)$$

Since, damping ratio < 1 , the specific heat capacity of the complex was negative. Hence, the specific heat capacity of the total system was negative.

The experimental molar heat capacities, enthalpy, entropy, and specific heat factor are listed in Table 1.

These are fitted in polynomial equation with temperature. The entropy is calculated from $C_p \ln T$. The activation energy and frequency factor are calculated from Arrhenius equation by plotting $\ln k$ versus $1/T$

$$\ln k = \ln A - \frac{E_a}{RT}$$

where k is the specific heat capacity at each temperature and A is the frequency factor. The polynomial equation for

specific heat capacity, enthalpy, and entropy derived from DSC (Fig. 3) is given below:

$$Y\{(C_p), (H_T - H_{303}), (S_T - S_{303})\} \\ = a_n T^n + a_{n-1} T^{n-1} + \dots + a_2 T^2 + a_1 T + C$$

The values of $a_1, a_2, a_3, \dots, a_n$, and C are tabulated in Table 1.

At the heating rate of $10 \text{ }^\circ\text{C min}^{-1}$, all experimentally calculated specific heat capacity are found negative due to

Table 1 The value of activation energy, frequency factor and the coefficient of enthalpy, entropy, specific heat capacity at heating rate $10 \text{ }^\circ\text{C min}^{-1}$

	89.5–106/ $^\circ\text{C}$			240–266/ $^\circ\text{C}$		
Activation energy (E_a)/ kJ mol^{-1}	38.57			96.70		
Frequency factor (A)/ $^\circ\text{C}$	692			739.37×10^4		
Heat evolve/ Jg^{-1}	−54.73			−182.87		
Coefficients	a_1	a_2	C	a_1	a_2	C
Enthalpy/ Jg^{-1}	-1.91×10^{-1}	3.0×10^{-4}	30.00	-6.02×10^{-1}	6.0×10^{-4}	147.85
Entropy/ $\text{Jg}^{-1} \text{ }^\circ\text{C}^{-1}$	-2.0×10^{-3}	3.0×10^{-6}	0.29	-6.2×10^{-3}	-6.0×10^{-6}	1.52
Specific heat/ $\text{Jg}^{-1} \text{ }^\circ\text{C}^{-1}$	9.0×10^{-5}	–	−0.03	-1.0×10^{-3}	1.0×10^{-6}	0.24

Fig. 3 DSC spectrum of methionine bridged Co(III) and Cu(II) complex

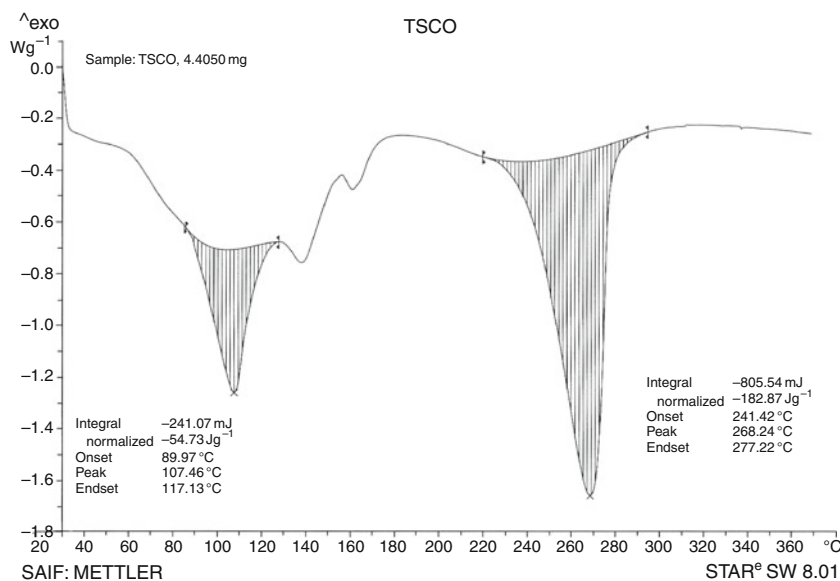


Fig. 4 The structure of methionine bridged cobalt(III) and copper(II) complex

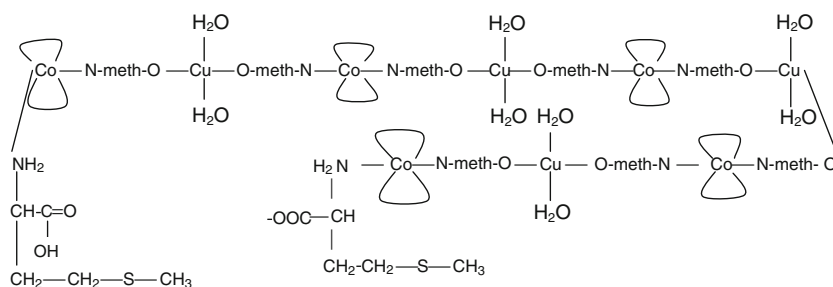


Table 2 Crystal data and experimental details of the title compound

Empirical formula	$\text{Co}_5^{\text{III}} \text{Cu}_4^{\text{II}}(\text{en})_{10}(\text{methionine})_{10} \cdot 8\text{H}_2\text{O} \cdot 7\text{SO}_4 \cdot \text{ClO}_4$
Molecular mass/g	2956.41
Wavelength/Å	1.542475
Crystal color	Dark blue
Crystal structure	Amorphous
Theta range for data collection/°	5.005–99.995
Number of points	9500
Scan axis	Gonio
Scan step size	0.01
Time per step	0.5
Scan type	Continuous
$K\alpha_2/K\alpha_1$	0.5
h k l	0 0 0

damping ratio < 1. The activation energy, E_a , and frequency factor, A , from temperature of onset to peak temperature are listed in Table 1.

From the above thermodynamical characterization, the structure of complex was found as in Fig. 4.

XRD analysis

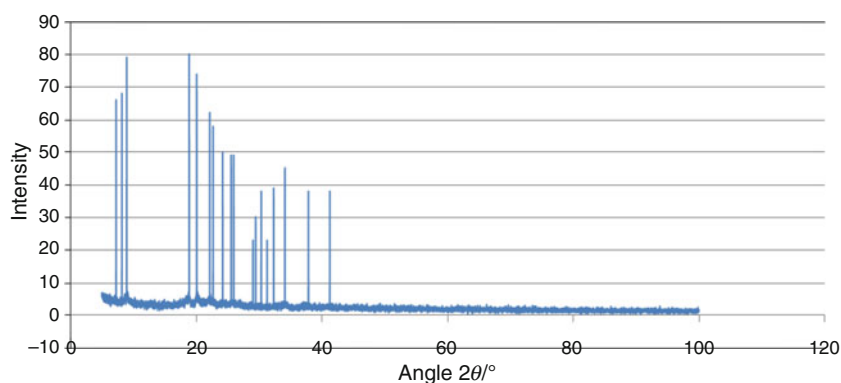
To determine the crystal structure of methionine containing multinuclear complex X-ray diffraction (XRD), data are collected at room temperature with graphite-monochromated MoK_α radiation on an XPERT PRO diffractometer operating in $\omega/2\theta$ scan mode. Crystal data and experimental details of the title complex are collected in Table 2. The XRD spectrum of complex is shown in Fig. 5.

In methionine containing complex, The carbonyl group bond length was 1.2564 Å [38] and made an angle of 37.86°. The C–O bond length of methionine was 1.3781 Å extended from C–O bond length of 1.258 Å [38] due to coordination with copper(II) and made an angle of 34.03°. The C–N bond length of methionine was 1.4448 Å instead of 1.4556 Å [38] and made an angle of 32.26°. The bond

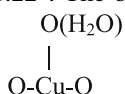
Table 3 X-ray powder diffraction numerical values and pattern of methionine containing polynuclear complex

Peak no.	$2\theta/^\circ$	d value/Å	I/I_0
1	7.245	6.11607	82.5
2	8.145	5.44659	85
3	8.905	4.98537	98.7
4	18.865	2.38551	100
5	20.045	2.25047	92.5
6	22.105	2.04952	77.5
7	22.615	2.00581	72.5
8	24.125	1.88705	62.5
9	25.585	1.78609	61.2
10	25.995	1.76001	61.2
11	29.015	1.59018	28.7
12	29.445	1.56915	37.5
13	30.315	1.52811	47.5
14	31.235	1.4874	28.7
15	32.265	1.4448	48.7
16	34.035	1.3781	56.2
17	37.865	1.2564	47.5
18	41.225	1.1702	47.5

length of C–N of ethylenediamine coordinated to Co(III) was 1.4874 Å [39] and deviated from 1.42 Å. This plane made an angle of 31.23°. The two C–C bond lengths of methionine were 1.5281 and 1.5691 Å [38] and made angles of 30.31° and 29.44°, respectively. The C–C bond length of ethylenediamine was 1.5901 Å instead of 1.567 Å [39] and made an angle of 29.01°. The two C–S bond lengths of methionine were 1.7600 and 1.7860 Å instead of 1.80 Å [38]. These planes made an angle of 25.99° and 25.58°, respectively. The copper bonded to the carboxylic group of methionine and Cu–O bond length was 1.8870 Å instead of 1.87 Å [40, 41]. This plane made an angle of 24.12°. The Co(III)-N(ethylenediamine) bond length was 2.005 Å instead of 2.022 Å [39]. This plane made an angle of 22.61°. The cobalt(III) bonded to amine group of methionine and Co(III)-N bond length was

Fig. 5 XRD spectrum of methionine bridged Co(III) and Cu(II) complex

2.0495 Å [42]. This plane made an angle of 22.10°. The Cu–O(H₂O) bond length was 2.3855 Å [43]. This plane made an angle of 18.86°. The total H–O–H bond length of water was 1.1702 Å and this plane made an angle of 41.22°. The bond length of



was 6.159 Å instead of 6.1160 Å and made an angle of 7.24°. The bond length of H–C–S–C–C was 5.3652 Å instead of 5.4465 Å and made an angle of 8.14°. The bond length of Co–N–C–C (methionine) was 5.022 Å instead of 4.9853 Å and this plane made an angle of 8.90°. The bond length of Co–N–H (ethylenediamine) was 2.255 Å and made an angle of 20.04°. The numerical values of this pattern are listed in Table 3.

Conclusions

A new sulfur containing methionine bridged polynuclear, Co(III) and Cu(II) complex synthesized and characterized by different measurements is mainly of thermodynamical and crystal structure characterization. The specific heat capacity of complex was found negative due to damping ratio < 1.

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