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ORIGINAL ARTICLE

Oligomerization of glycine and alanine on metal(II) octacynaomolybdate(IV): role of double metal cyanides in prebiotic chemistry

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Abstract Condensation reactions of amino acid (glycine and alanine) on the surface of metal(II) octacyanomolybdate(IV) (MOCMo) complexes are investigated using high-performance liquid chromatography (HPLC) and electron spray ionizations–mass spectroscopy (ESI–MS). The series of MOCMo have been synthesized and the effect of outer sphere metal ions present in the MOCMo on the oligomerization of glycine and alanine at different temperature and time found out. Formation of peptides was observed to start after 7 days at 60 °C. Maximum yield of peptides was found after 35 days at 90 °C. It has been found that zinc(II) octacyanomolybdate(IV) and cobalt(II) were the most effective metal cations present in outer sphere of the MOCMo for the production of high yield of oligomerized products. Surface area of MOCMo seems to play dominating parameter for the oligomerization of alanine and glycine. The results of the present study reveal the role of MOCMo in chemical evolution for the oligomerization of biomolecules.

Keywords Glycine · Alanine · Metal(II) octacyanomolybdate(IV) · Prebiotic chemistry · Oligomerization · HPLC · ESI–MS

Introduction

Amino acids are critical to life and have many functions in metabolism. Polymerization of amino acids is one of the most important reactions. The concentration of amino acids in the primitive oceans has been estimated variously from 4×10^{-3} to 10^{-7} M (Lahav and Chang 1976; Stribling and Miller 1987). Several experiments have been performed to trace out the steps of chemical evolution. Since the milestone experiment of Miller (1953), there have been many advances in the prebiotic synthesis of biomolecules. But still many questions remain to be answered as to how the simple biomolecules polymerize to form biopolymers. Bernal (1951) proposed that catalysis had a central role in the formation of biopolymers. Catalysis may have been important for the origin of life processes because they tend to direct the reaction along a few reaction pathways so that limited arrays of products are obtained. Bernal (1951) also support that clay minerals might not only have adsorbed and concentrated the biomonomers, but also condensation of simple molecules present in the prebiotic environment into the biopolymers.

Beside clay (Flores and Bonner 1974; Lahav et al. 1978; Lawless and Levi 1979; Ponnamperuma et al. 1982; Porter et al. 1998; Rode et al. 1999; Bujdak et al. 1995, 1996a, b, c; Bujdak and Rode 1996; 1997b; Plankensteiner et al. 2004; Lambert 2008), metal oxides also might have played crucial role for the formation of peptide bond from glycine and alanine. Glycine (Bujdak and Rode 1997a) and alanine (Bujdak and Rode 1997b) oligomerization was done below 100 °C on silica and alumina. High efficiency of catalytic activity of alumina was found for the oligomerization of alanine. It was found that neutral alumina polymerize alanine up to trimer (Bujdak and Rojas 2001).

Egami (1974, 1975) reported that there exists a good correlation between the concentration of minor transition elements in the primeval seas and their biological behavior. He proposed that the chemical evolution might have proceeded in the primeval seas. Important biotransition metals proposed by him are molybdenum, zinc, iron, copper,

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manganese, and cobalt. The concentration of these metals in primeval sea is estimated to be 7–100 nM. There are compelling thoughts that chemical evolution and origin of life occurred in primeval seas. One of the reasons that directed panspermia theory proposed by Crick and Orgel (1973) has been questioned is the richness of molybdenum in sea water rather than Earth crust (Chappell et al. 1974; Jukes 1974). Formation of cyanide in most of the simulated prebiotic experiments and its proposed localized existence on primitive Earth in cold (Keefe and Miller 1996; Orgel 1974) and also its stabilization due to formation of insoluble double metal cyanide (DMC) complexes (Arrhenius et al. 1994) encouraged us to study the role of metal(II) octacyanomolybdate(IV) (MOCMo) as prebiotic catalyst. It has been proposed that these DMC complexes might have concentrated the biomonomers on their surface through adsorption processes and subsequently catalyzed a class of reactions of prebiotic relevance (Kamaluddin et al. 1990, 1994; Viladkar et al. 1996; Alam et al. 1999, 2000a, b, 2002; Alam and Kamaluddin 1999, 2000; Ali et al. 2004; Ali and Kamaluddin 2006, 2007).

Although large number of materials have been worked out for the oligomerization of amino acid, to the best of our knowledge there is no report on catalytic activity of metal(II) octacyanomolybdate(IV) (MOCMo) complexes for the oligomerization of glycine and L-alanine. The present work described the synthesis of a series of MOCMo (M = Mn, Fe, Co, Ni, Cu, Zn, Cd) complexes to find out the effect of these complexes on the condensation of glycine and L-alanine. The experiments were performed at temperatures ranging from 60 to 120 °C for a period of up to 35 days.

Materials and methods

Chemicals

Potassium cyanide (Loba Chemie), Sodium borohydrate (E. Merck), Sodium molybdate (Rankem), Manganese(II) nitrate (E. Merck), Iron(II) nitrate (E. Merck), Cobalt(II) nitrate (E. Merck), Nickel(II) nitrate (E. Merck), Copper(II) nitrate (E. Merck), Zinc(II) nitrate (E. Merck), Cadmium(II) nitrate (E. Merck), glycine (Sigma), L-alanine, and Sigma (≥99.5 %) were used as received. All other chemicals used were of analytical grade and were used without further purification. Millipore water was used throughout the studies.

Preparation of metal octacyanomolybdate(IV)

MOCMo were synthesized from potassium octacyanomolybdate(IV), as per method of Szklarzewicz et al. (2007), while potassium octacyanomolybdate(IV) complex was synthesized as per method described in literature (Schroder and Scholtz 2000). The method for the synthesis of MOCMo involved slow addition of dilute aqueous solution of respective metal(II) nitrate(0.1 M) into 0.1 M aqueous solution of potassium octacyanomolybdate(IV). These solutions were mixed in their stoichiometric ratio with constant stirring. Slight excess of metal salt was used for complete precipitation. The reaction mixture was heated at 40 °C for 5 h and then kept as such overnight at room temperature. After 24 h, the precipitate was filtered on a Buckner funnel, washed thoroughly with millipore water, and dried at 60 °C in an oven. The dried product was powdered and sieved with 100 mesh size.

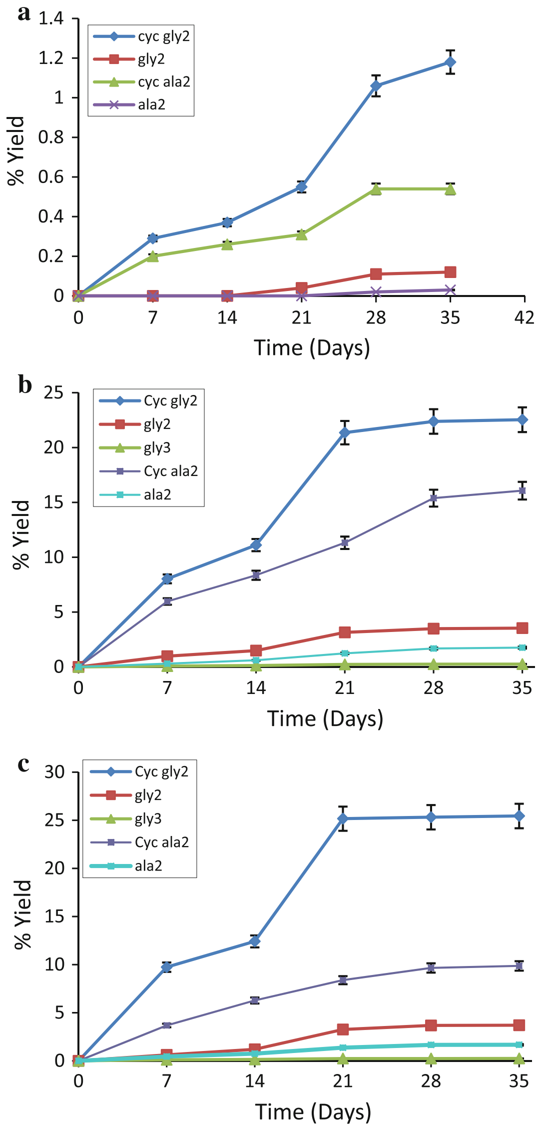

Fig. 1 MnOCMo catalyzed formation of DKP and oligomers of glycine and alanine at **a** 60 °C, **b** 90 °C and **c** 120 °C

CHN, AAS, TGA/DTA, FE-SEM

The percentage of carbon, hydrogen, and nitrogen present in MOCMo was recorded on an Elementar Vario ELHI CHNS analyzer while the percentage of transition metal was determined by atomic absorption spectroscopy (GBC Avanta M, Australia). In order to measure the water of crystallization present in MOCMo, thermogravimetric analysis (TG) was carried out with the thermal analyzer (EXSTAR TG/DTA 6300, SII Nano Technology Inc., Japan). Field emission scanning electron microscopy (FE-SEM) images were recorded using a FEI Quanta 200F microscope operating at 20 kV. The microscope was also used to record the EDXA (Energy dispersive X-ray analysis) spectra.

Infrared spectra

The infrared absorbances of the synthesized potassium octacyanomolybdate and MOCMo were in good agreement with the reported values (Mcknight and Haight 1973). MOCMo, shift infrared C–N stretches towards higher frequencies than those of $K_4[Mo(CN)_8]\cdot 2H_2O$, show coordination of the metals present in outer sphere.

Surface area measurement

The Brunauer–Emmett–Teller (BET) method has been used to determine the surface area of MOCMo complexes on a surface area analyzer (Micromeritics ASAP 2010, UK). In this technique the surface area was determined by

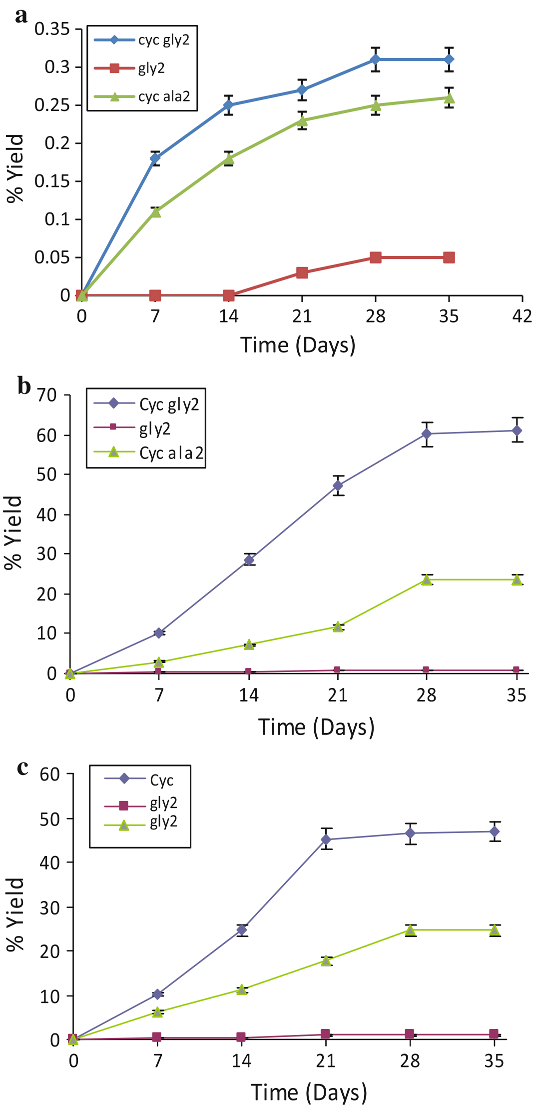

Fig. 2 FeOCMo catalyzed formation of DKP and oligomers of glycine and alanine at **a** 60 °C, **b** 90 °C and **c** 120 °C

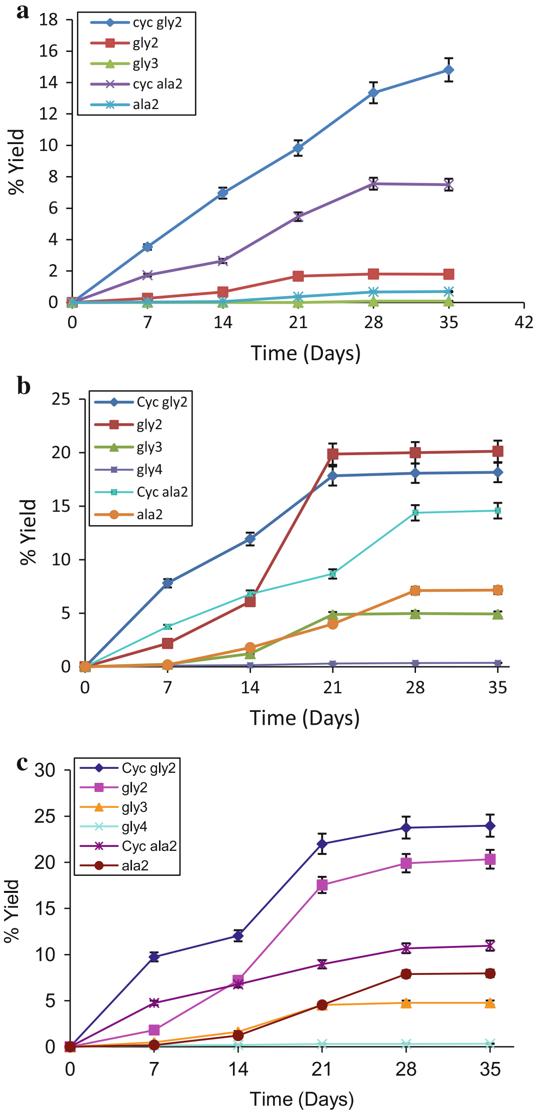

Fig. 3 CoOCMo catalyzed formation of DKP and oligomers of glycine and alanine at **a** 60 °C, **b** 90 °C and **c** 120 °C

physical adsorption of gases at their boiling temperatures. The determined values of the surface areas are 41.71, 3.91, 73.74, 36.69, 40.32, 189.89, and 26.24 $m^2\ g^{-1}$ in case of manganese, iron, cobalt, nickel, copper, zinc, and cadmium octacyanomolybdate(IV), respectively.

Reaction method

MOCMo (0.1 g) were impregnated with aqueous solution of the amino acid, glycine or L-alanine (0.1 ml, 0.01 M) separately. The suspension was dried at 90 °C for 3 h and used for the investigation of peptide bond formation. The samples were heated at three different temperatures of 60, 90, and 120 °C for 1–35 days. The reaction was monitored after every 7 days. No fluctuating drying/wetting conditions were simulated. Control experiment was performed by heating only amino acids in an empty test tube of glass 150 × 15 mm at the required temperature. After the heating experiments, peptide condensation products obtained were treated with 1 ml of 0.1 M calcium chloride solution to liberate adsorbed amino acids and related reaction products. The supernatant liquid was filtered and divided into two parts; one part of the filtrate was used for HPLC analysis while other for ESI–MS analysis.

HPLC analysis

All solutions obtained from the reaction systems were analyzed using HPLC (Waters 2489, binary system)

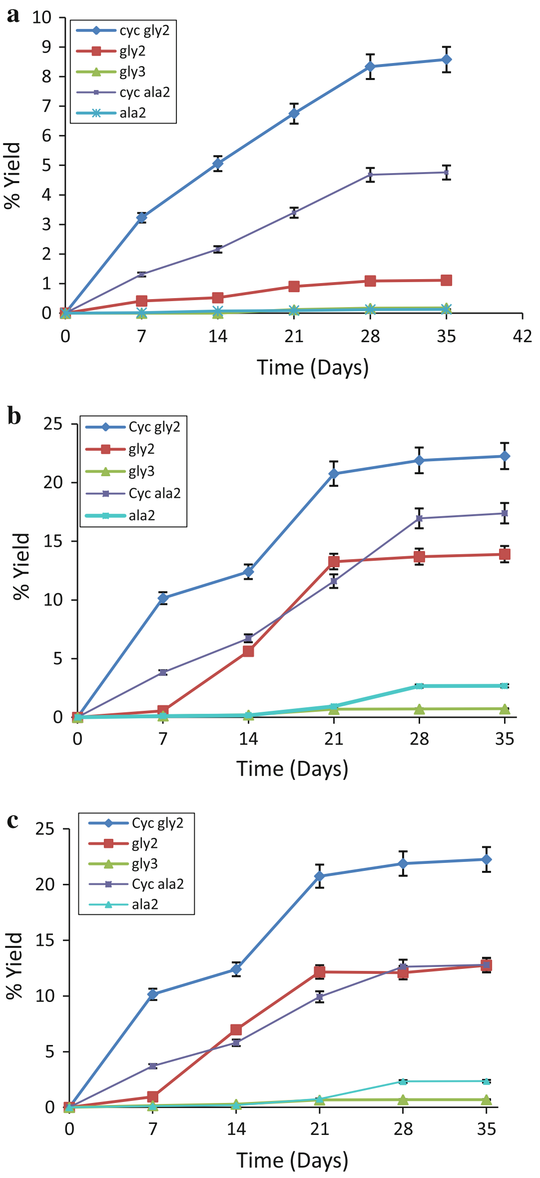

Fig. 4 NiOCMo catalyzed formation of DKP and oligomers of glycine and alanine at **a** 60 °C, **b** 90 °C and **c** 120 °C

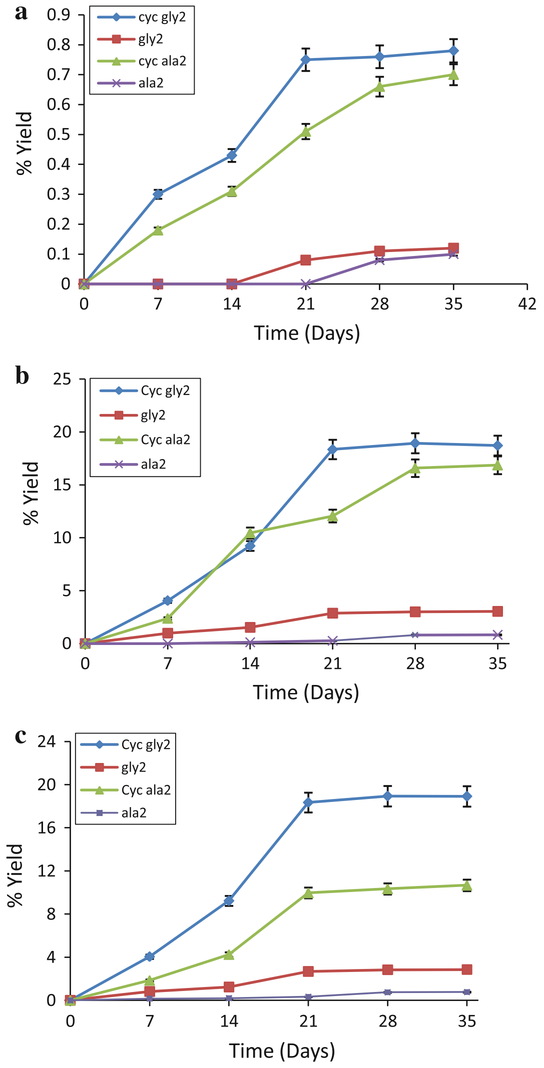

Fig. 5 CuOCMo catalyzed formation of DKP and oligomers of glycine and alanine at **a** 60 °C, **b** 90 °C and **c** 120 °C

equipped with a column of Waters (Spherisorp 5 μm ODS2 4.6 × 250 mm). UV detection was performed at 200 nm wavelength. The mobile phase compositions were 10 mM sodium hexane sulphonate acidified with phosphoric acid to pH ∼2.5 (solvent A) and acetonitrile of HPLC grade (solvent B) with a flow rate of 1 ml/min. The reaction products were identified using retention times and co-injection method. Yields of the products were determined by comparing peak area of products with the standards Figs. 1a–c, 2a–c, 3a–c, 4a–c, 5a–c, 6a–c, 7a–c. Representative chromatograms are shown in Figs. 8a–g and 9a–g.

Electrospray ionization–mass spectrometry analysis

A Bruker Esquire 4000 (Bruker Daltonic, Bremen, Germany) ion trap mass spectrometer interfaced to an electrospray ionization (ESI) source was used for mass analysis and detection. Ionization of analytes was carried out using the following setting of ESI: nebulizer gas flow 10 psi, dry gas 5 L min^{-1}, dry temperature 300 °C, capillary voltage 4,000 V. Calibration MS^n spectra were obtained after isolation of the appropriate precursor ions under similar experimental conditions. Figures 10 and 11 represents the ESI MS spectra of products obtained when glycine and alanine were heated at 90 °C for 35 days in the presence of ZnOCMo.

Results and discussion

From the experimental data of % composition of the synthesized complexes were evaluated by CHN analysis, atomic

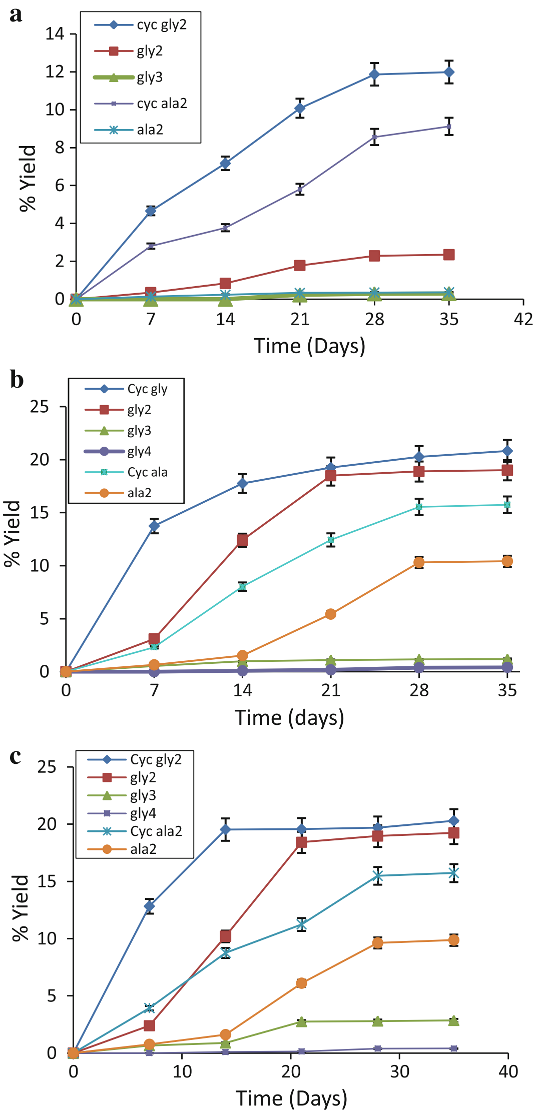

Fig. 6 ZnOCMo catalyzed formation of DKP and oligomers of glycine and alanine at **a** 60 °C, **b** 90 °C and **c** 120 °C

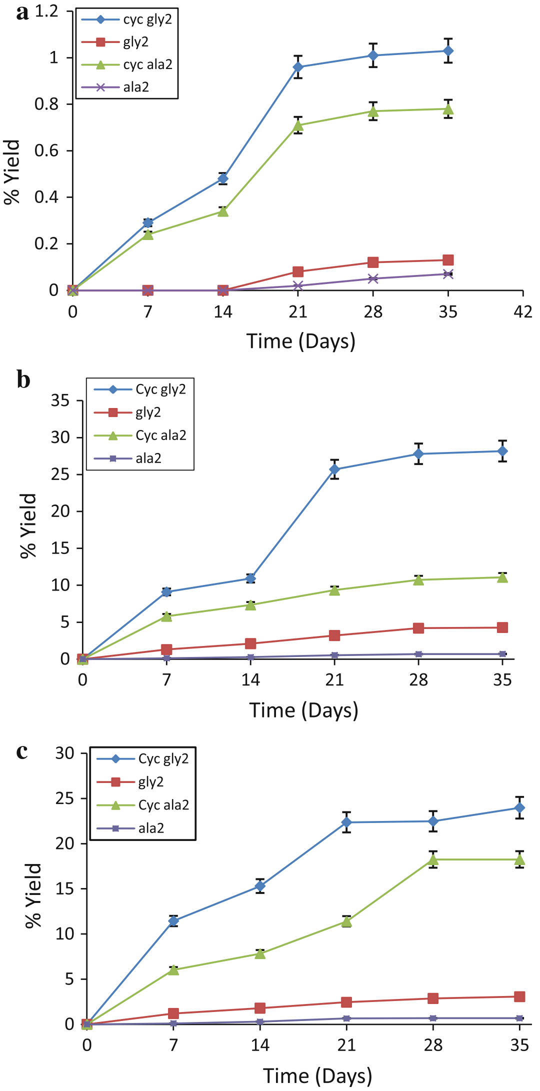

Fig. 7 CdOCMo catalyzed formation of DKP and oligomers of glycine and alanine at **a** 60 °C, **b** 90 °C and **c** 120 °C

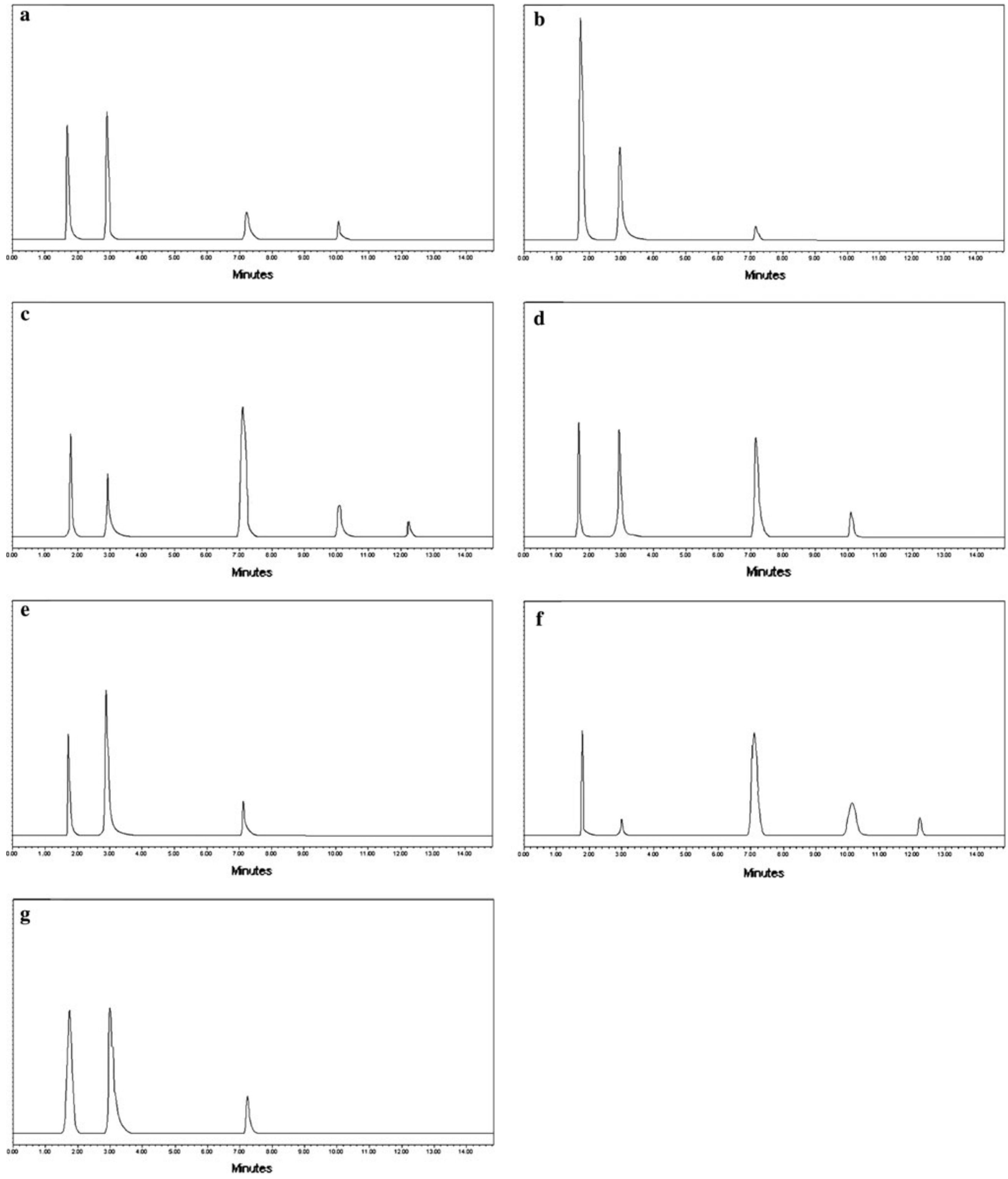

Fig. 8 HPLC chromatogram showing the products formed when glycine was heated at 90 °C for 35 days in the presence of **a** MnOCMo, **b** FeOCMo, **c** CoOCMo, **d** NiOCMo, **e** CuOCMo, **f** ZnOCMo, **g** CdOCMo. Retention times of analyzed products (min): Cyc $(gly)_2$ (1.94), gly (3.03), $(gly)_2$ (7.11), $(gly)_3$ (10.17), $(gly)_4$ (12.36)

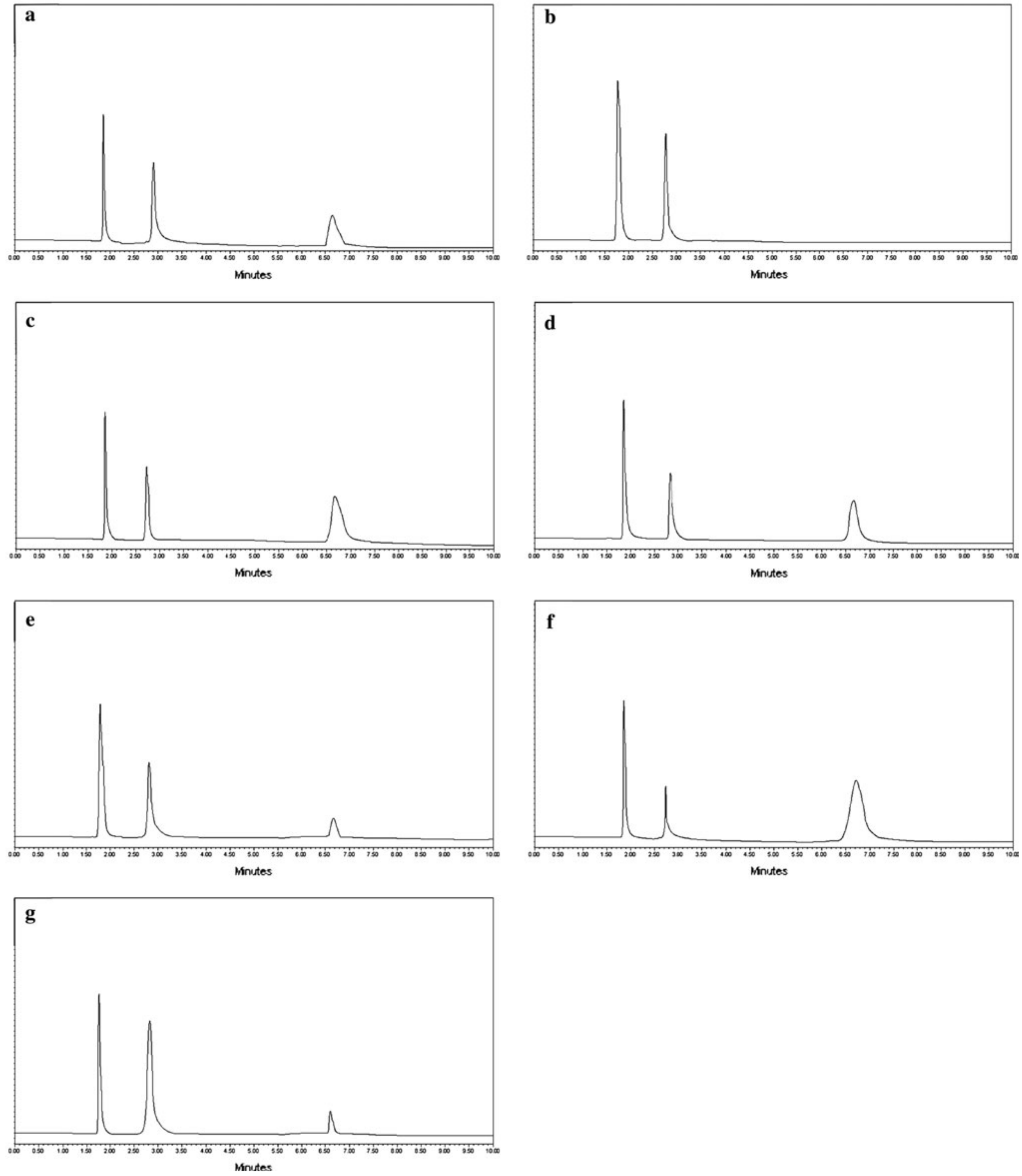

Fig. 9 HPLC chromatogram showing the products formed when alanine was heated at 90 °C for 35 days in the presence of **a** MnOCMo, **b** FeOCMo, **c** CoOCMo, **d** NiOCMo, **e** CuOCMo, **f** ZnOCMo, **g** CdOCMo. Retention times of analyzed products (min): Cyc (ala)$_2$ (1.94), ala (2.89), (ala)$_2$ (6.73)

absorption spectrometric studies, and thermogravimetric and differential thermal analysis; the molecular formula of the synthesized MOCMo complexes are proposed as follows:

1. $Mn_2[Mo(CN)_8]\cdot 3\cdot 3H_2O$ (Brown)
2. $Fe_2[Mo(CN)_8]\cdot 4H_2O$ (Blue)
3. $Co_2[Mo(CN)_8]\cdot 5H_2O$ (Orange)

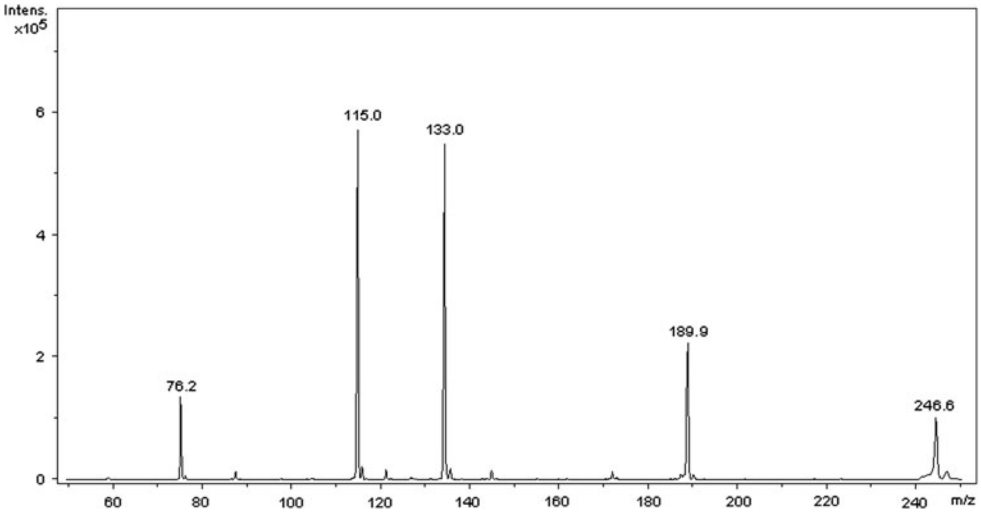

Fig. 10 ESI MS spectra showing the products formed when glycine was heated in the presence of ZnOCMo for 35 days at 90 °C. *m/z* of analyzed products: gly (76.2), Cyc $(gly)_2$ (115.0), $(gly)_2$ (133.0), $(gly)_3$ (189.9), $(gly)_4$ (246.6)

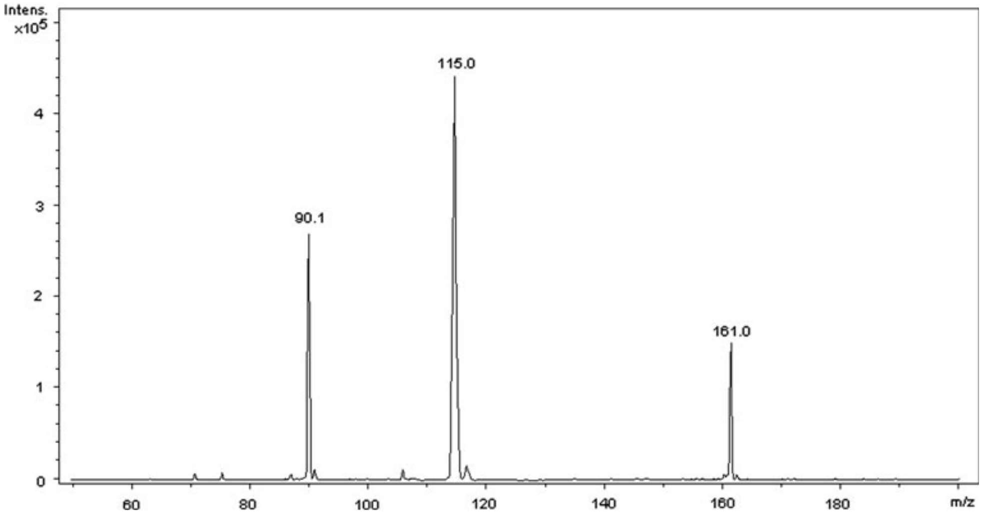

Fig. 11 ESI–MS spectra showing the products formed when alanine was heated in the presence of ZnOCMo for 35 days at 90 °C. *m/z* of analyzed products: ala (90.1), Cyc $(ala)_2$ (115), $(ala)_2$ (161.0)

Table 1 Elemental analysis of MOCMo(IV)

	H(%)	C (%)	N (%)	Mo (%)	M (%)
$Mn_2[Mo(CN)_8]\cdot3\cdot3H_2O$	1.34	20.31	23.67	20.29	23.20
	(1.39)*	(20.29)	(23.67)	(20.27)	(23.22)
$Fe_2[Mo(CN)_8]\cdot4H_2O$	1.64	19.67	23.02	19.59	22.96
	(1.64)	(19.69)	(22.97)	(19.67)	(22.91)
$Co_2[Mo(CN)_8]\cdot5H_2O$	1.93	18.70	21.89	18.63	22.09
	(1.95)	(18.76)	(21.88)	(18.75)	(22.03)
$Ni_2[Mo(CN)_8]\cdot6H_2O$	2.22	18.19	21.11	18.21	22.26
	(2.27)	(18.14)	(21.16)	(18.13)	(22.18)
$Cu_2[Mo(CN)_8]\cdot12H_2O$	3.75	14.90	17.30	14.79	19.62
	(3.71)	(14.84)	(17.31)	(14.83)	(19.64)
$Zn_2[Mo(CN)_8]\cdot2H_2O$	0.82	20.32	23.24	20.41	27.86
	(0.85)	(20.39)	(23.79)	(20.38)	(27.79)
$Cd_2[Mo(CN)_8]\cdot6H_2O$	1.95	15.18	17.69	15.16	35.37
	(1.88)	(15.08)	(17.59)	(15.07)	(35.31)

Bracket values are theoretical ones

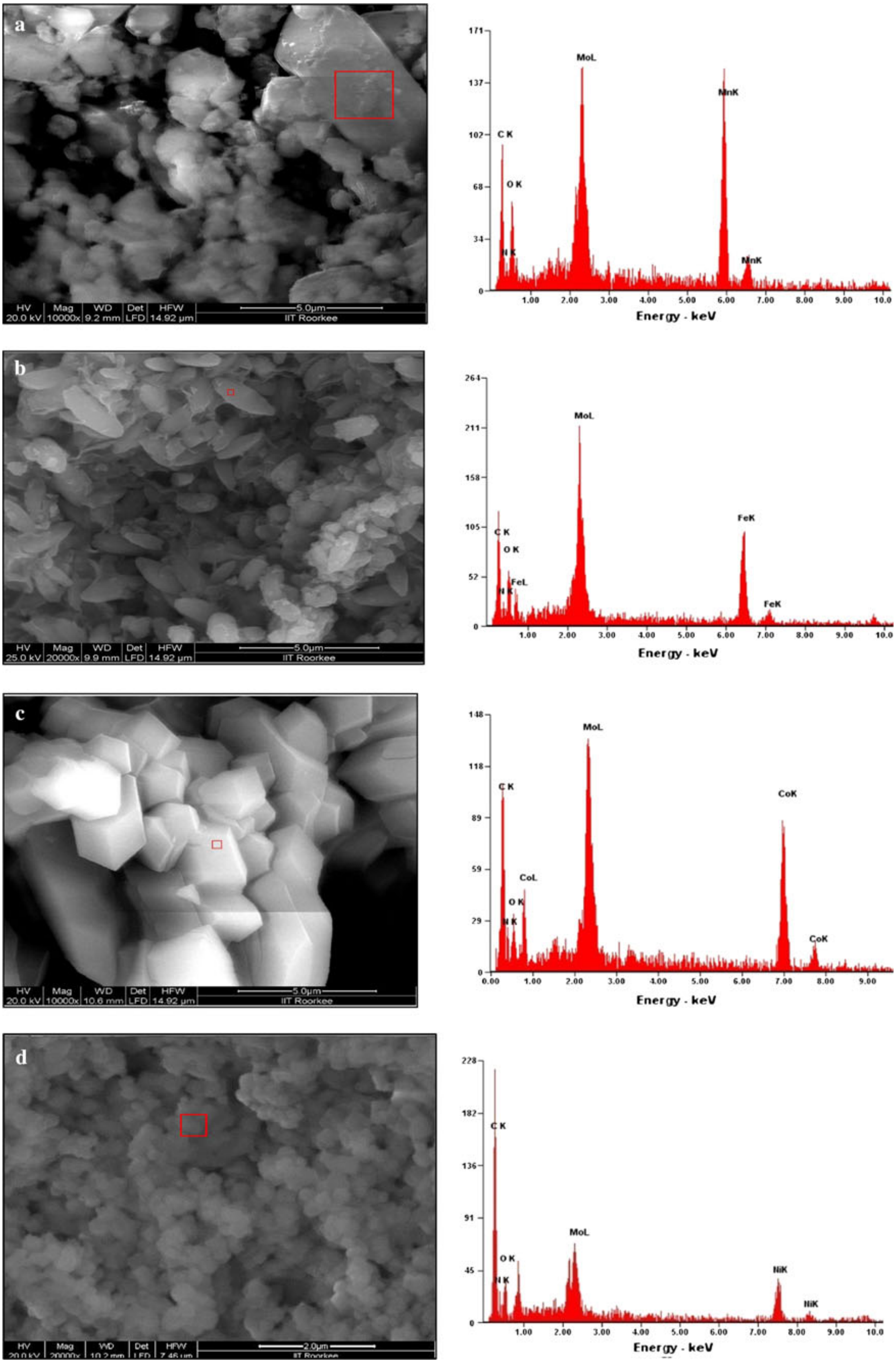

Fig. 12 FE-SEM images and EDX spectra of **a** MnOCMo, **b** FeOCMo, **c** CoOCMo, **d** NiOCMo, **e** CuOCMo, **f** ZnOCMo, **g** CdOCMo

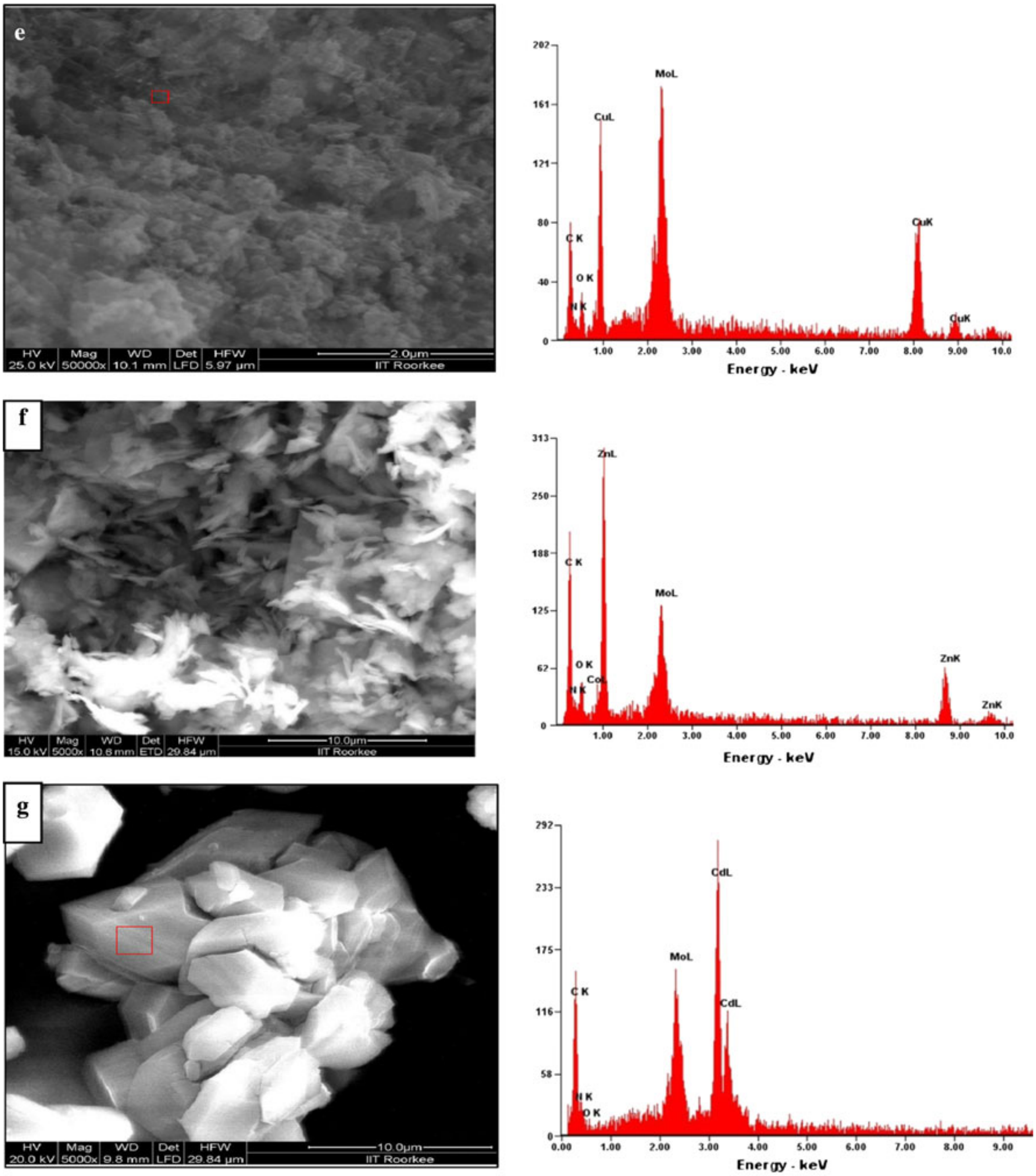

Fig. 12 continued

4. $Ni_2[Mo(CN)_8]\cdot 6H_2O$ (Green)
5. $Cu_2[Mo(CN)_8]\cdot 12H_2O$ (Violet)
6. $Zn_2[Mo(CN_{)8}]\cdot 2H_2O$ (Light Yellow)
7. $Cd_2[Mo(CN)_8]\cdot 6H_2O$ (Yellow)

The percentages of element compositions are shown in Table 1. The experimental values are found to have good agreement with the theoretical values. Elements present in the MOCMo were verified by the EDXA spectrum shown in Fig. 12a–g. SEM images show the shape and surface morphology of the MOCMo.

The primary objective of this work was to check the suitability of MOCMo as a catalyst for the oligomerization of glycine and alanine at different temperature and time. The yield of products formed on MOCMo at temperatures 60, 90, and 120 °C for 35 days are shown in Tables 2 and 3. Representative HPLC chromatograms of analyzed compound are shown in Figs. 8a–g and 9a–g. The catalytic efficiencies of tested MOCMo differ considerably with time and temperature. This study demonstrates the formation of peptides up to tetramer was observed with glycine

Table 2 The reaction yield (%) of products formed from glycine

Catalyst[a]	% Yield[b] of the products[c] formed when glycine was heated at 60°, 90° an 120 °C for 35 days											
	Cyc(Gly)$_2$			(Gly)$_2$			(Gly)$_3$			(Gly)$_4$		
	60°	90°	120°	60°	90°	120°	60°	90°	120°	60°	90°	120°
No catalyst	0.03	0.06	0.11	Trace	0.02	0.02	–	–	–	–	–	–
MnOCMo	1.18	22.24	24.45	0.12	3.54	3.70	–	0.26	0.25	–	–	–
FeOCMo	0.31	61.10	46.92	0.05	0.88	0.94	–	–	–	–	–	–
CoOCMo	14.81	18.15	23.97	1.80	20.12	20.33	0.09	4.96	4.77	–	0.36	0.33
NiOCMo	10.15	22.26	22.26	1.11	13.90	12.76	0.18	0.73	0.70	–	–	–
CuOCMo	0.78	18.72	18.92	0.12	3.04	2.85	–	–	–	–	–	–
ZnOCMo	11.99	20.83	20.30	2.35	19.01	19.23	0.3	7.2	2.85	–	0.42	0.40
CdOCMo	1.03	28.18	23.97	0.13	4.28	3.06	–	–	–	–	–	–

[a] Reactions were performed in the presence of 100 mg of MOCMo

[b] Quantitative evaluation was performed by HPLC (Waters 2489, binary system) equipped with a column of Waters (Spherisorp 5 µm ODS2 4.6 × 250 mm). UV detection was performed at 200 nm wavelength

The mobile phase compositions were 10 mM sodium hexane sulphonate acidified with phosphoric acid to pH ~2.5 (solvent A) and acetonitrile of HPLC grade (solvent B), with a flow rate of 1 ml/min. The yields of products were calculated by comparing peak area with the standards

[c] Products were identified by co-injection analysis with authentic samples

Table 3 The reaction yield (%) of products formed from alanine

Catalyst[a]	% Yield[b] of the products[c] formed when alanine was heated at 60°, 90° an 120 °C for 35 days					
	Cyc(Ala)$_2$			(Ala)$_2$		
	60°	90°	120°	60°	90°	120°
No catalyst	0.03	0.04	0.06	–	–	–
MnOCMo	0.54	16.07	9.87	0.03	1.76	1.67
FeOCMo	0.26	23.74	24.65	–	–	–
CoOCMo	7.50	14.58	10.96	0.69	7.15	7.95
NiOCMo	4.76	17.39	12.79	0.13	2.68	2.35
CuOCMo	0.70	16.86	10.67	0.10	0.82	0.77
ZnOCMo	9.12	15.75	15.73	0.36	10.43	9.87
CdOCMo	0.78	11.09	18.25	0.07	0.69	0.67

[a] Reactions were performed in the presence of 100 mg of MOCMo

[b] Quantitative evaluation was performed by HPLC (Waters 2489, binary system) equipped with a column of Waters (Spherisorp 5 µm ODS2 4.6 × 250 mm). UV detection was performed at 200 nm wavelength

The mobile phase compositions were 10 mM sodium hexane sulphonate acidified with phosphoric acid to pH ~2.5 (solvent A) and acetonitrile of HPLC grade (solvent B), with a flow rate of 1 ml/min. The yields of products were calculated by comparing peak area with the standards

[c] Products were identified by co-injection analysis with authentic samples

while dimer, in case of alanine. In the control experiments with glycine, only formation of cyclic (gly)$_2$ and (gly)$_2$ was observed after 35 days; however, formation of peptide in the blank experiment of alanine was not at all observed. Similar results were also reported by Bujdak and Rode (1999a, b). This indicates that the MOCMo does behave as a promoter of peptide bond formation at temperature below 100 °C at relatively short time. The reaction products were identified by retention times and co-injection method.

From the Figs. 1a, 2a, 3a, 4a, 5a, 6a, 7a it was observed that peptide formation also occurs at low temperature (60 °C) and does not require the presence of localized heat source such as in case of volcanoes and hydrothermal vents, etc. Thus, in the presence of MOCMo, abiotic peptide synthesis might be highly feasible process at a very short astronomical time scale. Figures 1b, 2b, 3b, 4b, 5b, 6b, 7b showed that ZnOCMo and CoOCMo oligomerize glycine up to tetramer, and NiOCMo and MnOCMo afforded glycine up to the trimer, while the other MOCMo oligomerize up to the dimer. After 35 days at 90 °C, glycine in the presence of ZnOCMo afforded formation of (Gly)$_4$ (0.42 %) along with (Gly)$_3$ (7.20 %), (Gly)$_2$

(19.01 %) and Cyclic $(Gly)_2$ (20.83 %), while alanine afforded $(Ala)_2$ (10.43 %) and Cyclic $(Ala)_2$(15.75 %). It was also observed that at higher temperature, i.e. 120 °C, yield was almost constant (Figs. 1c, 2c, 3c, 4c, 5c, 6c, 7c).

It has also been found that the % yield of oligoglycine on MOCMo was higher compared with that of oligoalanine. The difference in the % yield may be attributed due to high activation energy for the formation of alanine peptide bond (Lawless and Levi 1979). It has been mentioned earlier that the stability constants of the transition metal complexes with peptides are lower as compared with the amino acids (Greenstein and Winitz 1961). This mechanism reveals the facts that increasing chain length of amino acid leads to the decreased concentration of the oligomers (Tables 2 and 3). The trend in catalytic activity of MOCMo for the oligomerization of glycine and alanine with the % yield was as follows:

$$\mathrm{ZnOCMo} > \mathrm{CoOCMo} > \mathrm{NiOCMo} > \mathrm{MnOCMo} > \mathrm{CuOCMo} > \mathrm{CdOCMo} > \mathrm{FeOCMo}$$

The Tables 2 and 3 shows the % yield of oligomerization for glycine and alanine as a function of metal cations present in the outer sphere of the MOCMo. It is observed that outer sphere metal in the MOCMo changes the catalytic activity and thus effects on the yield of oligomerization products of glycine and alanine are different. The present results show that octacyanomolybdate with zinc and cobalt as outer sphere metal were most effective metals for the production of long-chain oligomers of glycine and alanine in high yield while the iron was the least effective.

Among MOCMo, ZnOCMo (surface area, SA 189 $m^2 g^{-1}$) showed maximum catalytic activity while FeOCMo (SA 3.91 $m^2 g^{-1}$) showed minimum catalytic activity. This observation implies that the surface areas of the MOCMo play a dominating parameter for the peptide formation in the glycine and alanine.

In order to analyze the product formed on MOCMo with an alternate technique, the ESI–MS data obtained were also scrutinized. Figures 10 and 11 show an ESI–MS spectrum of products obtained when each glycine and alanine were heated at 90 °C for 35 days in the presence of ZnOCMo. In the ESI–MS spectra of glycine, mass 76.1 corresponds to $[Gly + H]^+$, 115 for $[Cyc\ Gly_2 + H]^+$, 132.9 for $[Gly_2 + H]^+$, 189.9 for $[Gly_3 + H]^+$, and 246.6 for $[Gly_4 + H]^+$. The MS spectra of alanine mass 90.1 corresponds to $[Ala + H]^+$, 115 for $[Cyc\ Ala_2 + H]^+$, and 160.9 for $[Ala_2 + H]^+$. The ESI–MS data provided similar results as in the case of obtained by HPLC.

Conclusion

The present study shows the potential importance of MOCMo as prebiotic catalyst in chemical evolution and in the origin of life. MOCMo are able to catalyze the formation of peptides from glycine or alanine without applying drying/wetting cycling. Even at 60 °C after 7 days formation of peptide bond was observed when MOCMo were used as a catalyst. Outer sphere metal in the MOCMo showed different catalytic activity. ZnOCMo and CoOCMo afforded Cyclic $(Gly)_2$, $(Gly)_2$, $(Gly)_3$ and $(Gly)_4$ from glycine, while Cyclic $(Ala)_2$ and $(Ala)_2$ from alanine. ZnOCMo and CoOCMo having higher surface area showed high catalytic activity and afforded high yield. The results reported here, therefore, encourage investigation for further possibilities of MOCMo as a catalyst in the prebiotic chemistry.

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