NLO study of novel synthesized complexes: synthesis, spectral characterization and non-linear optical responses of thiomolybdate complexes with Cu (I) and N,S-donor amino carboditioate ligands

M.H. Sadr[a], V.M. Mohammadi[*a], B. Soltani[a], K. Jamshidi-Ghaleh[b]

[a] Department of Chemistry, Faculty of Basic Sciences, Azarbaijan Shahid Madani University, Tabriz, Iran,
[b] Department of Physics, Faculty of Basic Sciences, Azarbaijan Shahid Madani University, Tabriz, Iran

In this research, two new polynuclear complexes of thiomolybdate homologous $(Et_4N)_2[MoS_4(Cu-L_1)_2]$ (1) and $(Et_4N)_2[MoS_4(Cu-L_2)_2]$ (2) with N,S-donor amino dithioate ligands comprise L_1 = 2-aminocyclopent-1-enecarbodithioate, L_2 = 2-aminocyclohex-1- enecarbodithioate are synthesized and characterized with are synthesized and characterized with FT-IR, ^{1}HNMR, ^{13}CNMR, UV-isible and elemental analysis. Non-linear optical properties of these complexes include linear absorption coefficient (α) and third-order non-linear refractive index (n_2) are investigated by Z-scan method under irradiation of low power 35 mW continuous wave He–Ne Laser. The optical limiting behavior is investigated by transmission measurement through the samples.

Keywords: Non-linear optical property, non-linear refraction, linear absorption, thiomolybdate complexes, N,S-donor ligands.

INTRODUCTION

The compounds with non-linear optical properties have lately become the focus of most researches in view of their potential usages in various photonic technologies, including optical switching and data processing [1]. Insomuch organometallic and coordination complexes have been widely studied for the design of chromophores for third-order non-linear optics (NLO) [2-7]. In the other hand, some medicinal applications of tetrathiomolybdate have been reported [8, 9]. In addition to industrial applications [10, 11], the non-linear optical (NLO) properties of heterothiometallic clusters are a major incentive for researchers [12-17]. Molecular materials NLO responses depend on their chromophores NLO responses. As a result, detecting the new chromophores with high NLO responses become the aim of scientific research [18]. Comparing with former organic chromophores, the transition metal molecules play the important roles in NLO activities. Because they depict large and fast NLO activities by charge-transfer transitions between the metal and ligands [19-21].

The synthesis and characterization of polynuclear thiometalate complexes with $[MS_4]^{2-}$ (M= Mo, W), Cu^{1+} and bidentate N,S-donor ligands isologues have been reported in the over recent decades [22, 23]. Also the synthesis and characterization of N,S-donor amino ditioic acid ligands (Fig. 1) have been investigated because they were applied as significant building blocks of organometallic complexes and used in assembly of charge- transfer complexes as specific π- electron delocalization in conjugated systems [24, 25].
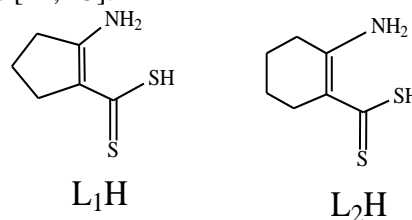

Fig. 1 Amino dithioic acid ligands.

For measurement the type and order of non-linear refractive index (n_2) we applied the Zscan technique which is particularly beneficial when the non-linear refraction is accompanied by non-linear absorption [26, 27].

In this paper, we synthesized two novel tetrathiomolybdate complexes $(Et_4N)_2[MoS_4(Cu-L_1)_2]$ (1) and $(Et_4N)_2[MoS_4(CuL_2)_2]$ (2) (L_1 = 2-aminocyclopent-1-enecarbodithioate, L_2 = 2-aminocyclohex-1-enecarbodithioate) (Fig. 2) and characterized with elemental analysis, ICP, FT IR, Uv-Visible spectroscopy, ^{1}HNMR and ^{13}CNMR. The third-order NLO properties of them in saturated acetone solutions were investigated by using the laser Z-scan technique with irradiation of low power 35 mW continuous wave He–Ne Laser. The corresponding third-order NLO parameters of aforementioned materials were determined. Some intransitive analyses and conclusion were also presented.

To whom all correspondence should be sent:
E-mail: mohades2004@yahoo.com
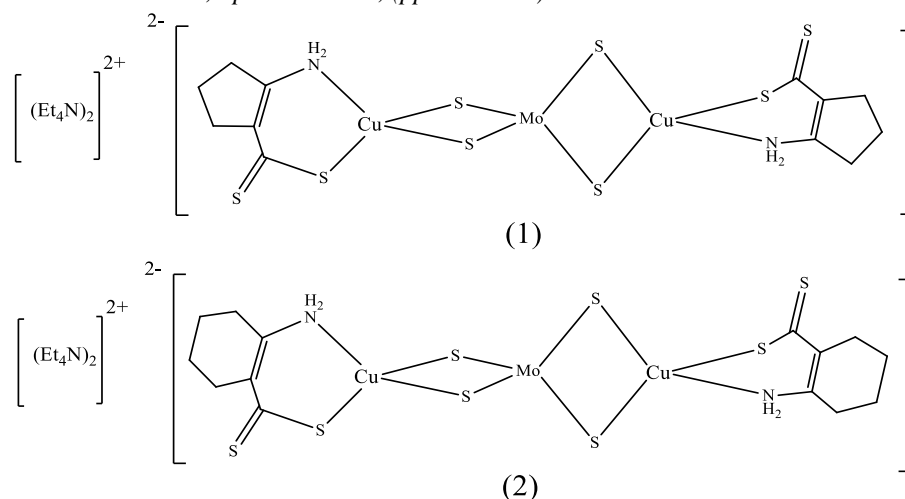
Fig. 2 Chemical structure of $(Et_4N)_2[MoS_4(Cu-L_1)_2]$ (1) and $(Et_4N)_2[MoS_4(Cu-L_2)_2]$ (2) complexes .

EXPERIMENTAL

General considerations

Thiomolybdate ligand $(Et_4N)_2[MoS_4]$ is synthesized and purified according to the reported literature procedures [28]. All chemicals such as cyclopentatone, cyclohexanone carbon disulfide and solvents were purchased form Merck Chemical Company and were used as received. All manipulations were performed under a purified nitrogen atmosphere by standard Schlenk techniques. Solvents were dried, deoxygenated, and distilled before use [29].

Physical measurements

C, H, N, S elemental analyses were performed using a Thermo Finnigan Flash 1112EA elemental analyzer. The IR spectra in 4000-400 cm^{-1} range were obtained on FT BRUKER VECTOR 22 infrared spectrophotometer using pressed KBr disks with polystyrene as reference. Melting points were determined using a BarnSteel Electrothermal BI 9300 apparatus and are uncorrected. The absorption spectra of the samples in acetone solution are recorded using a UV–visible spectrophotometer model PG Instrument T80. ^{1}HNMR and ^{13}CNMR spectra were obtained using a 400 MHz Bruker Sp AVANC spectrometer.

SYNTHESIS

Synthesis of 2-aminocyclopent-1-enecarbodithioic acid (L$_1$H)

Cyclopentanone (10 mL, 112.9 mmol) was mixed with CS$_2$ (12 mL, 206.7 mmol) and 40 mL 28% ammonia solution for 8 hours in room temperature. Sediment obtained after filtration and washing with diethyl ether, dissolved in water and 2 ml of hydrochloric acid to neutralize it. Then the obtained precipitate recrystallized with ethanol and water 1:1 solution (yield 14.8 g, 82%), mp= 173 °C.

Anal. calc. For C$_6$H$_9$NS$_2$: C, 45.24; H,5.69; N,8.79; S,40.26.

Found: C, 45.29; H,5.72;N,8.71; S,40.25.

IR (KBr, cm^{-1}): 3422 broad, 3286m, 2921m, 2850w, 2500w, 1615s, 1474s, 1455s, 1410s,1319m, 1289m, 1215m, 1052w, 976w, 917w, 876m, 775w, 611m.

Synthesis of 2-aminocyclohex-1-necarbodithioic acid (L$_2$H)

Cyclohexanone (10 mL, 96.4 mmol) was mixed with CS$_2$ (12 mL, 206.7 mmol) and 40 mL 28% ammonia solution for 8 hours in room temperature. Sediment obtained after filtration and washing with diethyl ether, dissolved in water and 2 ml of hydrochloric acid to neutralize it. Then the obtained precipitate recrystallized with ethanol and water 1:1 solution.(yield 13.5 g, 80%), mp= 201 °C.

Anal. calc. For C$_6$H$_9$NS$_2$: C, 48.51; H,6.39; N,8.08; S,37.00.

Found: C, 48.39; H,6.41; N,8.11; S,37.15.

IR (KBr, cm^{-1}): 3446 broad, 3201m, 3036w, 2924m,2857w, 2557s, 1594s, 1387s,1339m, 1231m, 1157m, 1131m, 1103m,1067m, 999m, 980m, 951m, 937m, 923m, 880s798m, 657w, 606w.

Synthesis of (Et$_4$N)$_2$[MoS$_4$(Cu-L$_1$)$_2$] (1) complex

Under nitrogen atmosphere the $(NEt_4)_2[MoS_4]$ (0.049 g, 0.1 mmol) was dissolved in acetone (7 mL) and CuCl (0.021 g, 0.21 mmol) was added to the pink solution. After stirring for 3 hours, L$_1$ (0.033 gr, 0.21 mmol) was added and rising catalytic amount of triethylamine then the mixture was stirred for 18 hours at room temperature. The resulting deep violet filtrate dried by vaccum pump. The obtained

precipitate was triturated in diethyl ether (25mL) and washed with diethyl ether (2×5 mL) and dried *in vacuo*. (Yield 0.06 g, 64%).

Anal. calc. For $C_{28}H_{58}Cu_2MoN_4S_8$: C, 36.14; H,6.28; N,6.02; S,27.57.

Found: C, 36.02; H,6.42; N,6.31; S,27.93.

ICP (ppm): Cu: 2.01, Mo: 0.83.

IR (KBr, cm^{-1}): 3449 broad, 2984w, 2924w, 1618w, 1484s,1459m, 1437m, 1366s, 1172s, 1054w, 1000s, 904s, 785m, 743s, 697w, 611m, 442m.

^{1}HNMR (CDCl$_3$, 400 MHz, δ ppm): 3.44-3.49(quartet, 2H of amin group), 2.86-2.89 (triplet, 2H in C3 of cyclopentene), 2,68-2.74(triplet, 2H in C5 of cyclopentene), 2.48-2.50(broad quartet, 2H of –CH$_2$- in Et$_4$N$^+$), 1.88-1.96(broad triplet, 2H in C4 of cyclopentene), 1.37-1.43(triplet, 3H of –CH$_3$ in Et$_4$N$^+$).

^{13}CNMR (DMSO, 400 MHz, δ ppm): 7.09, 19.84, 28.12, 31.62, 51.37, 97,87, 155.90, 211.87.

Synthesis of (Et$_4$N)$_2$[MoS$_4$(Cu-L$_2$)$_2$] (2) complex

Under nitrogen atmosphere, the (NEt$_4$)$_2$[MoS$_4$] (0.049 g, 0.1 mmol) was dissolved in acetone (7 mL) and CuCl (0.021 g, 0.21 mmol) was added to the pink solution. After stirring for 3 hours, L$_2$ (0.036 g, 0.21 mmol) was added and rising catalytic amount of triethylamine then the mixture was stirred for 18 hours at room temperature. The resulting deep violet filtrate dried by vaccum pump. The obtained precipitate was triturated in THF (5mL) and washed with diethyl ether (2×5 mL) and dried *in vacuo*. (yield 0.072 g, 75%)

Anal. Calc. For $C_{30}H_{62}Cu_2MoN_4S_8$: C, 37.59; H,6.52; N,5.84; S,26.76.

Found: C, 37.52;H,6.44; N,5.71; S,26.79.

IR (KBr, cm^{-1}): 3422 broad, 2985- 2854m, 1637w, 1509s,1391s, 1314m, 1244m, 1103m, 980m, 796m, 642m, 481w, 451w.

^{1}HNMR(CDCl$_3$, 400 MHz, δ ppm): 3.44-3.49(quartet, 2H of amin group), 2.65-2.68 (triplet, 2H in C3 of cyclohexene), 2,44-2.47(triplet, 2H in C6 of cyclohexene), 2.11(broad quartet, 2H of –CH$_2$- in Et$_4$N$^+$), 1.81-1.86(broad triplet, 2H in C4 of cyclohexene), 1.56-1.58(broad triplet, 2H in C5 of cyclohexene), 1.37-1.41(triplet, 3H of –CH$_3$ in Et$_4$N$^+$).

Experimental set up for NLO

The optical geometry handled for transmittance measurement is shown in Fig. 3. A CW He–Ne laser was used for the light source. The maximum measurable output power of the laser was 35 mW. An attenuator was used to control the incident power on the sample. A small part of the input beam was split by a glass plate to monitor the input power. The major part of the laser beam was focused with 10 cm focal length quartz lens, to enhancement the beam irradiance at the sample. The laser beam size was measured by edge scan method. The beam waist diameter (FW1/e2M) at the sample was m 30. With this optical geometry, the utmost applied irradiance on the sample target was 105 Wcm^{-2}. Two large area power meters (P1 and P2) were used to measure the incident and transmitted power of the laser beam. In transmittance measurement, the output energy monitor is located close to the glass sample sans aperture. This optical geometry provides a transmittance measurement that is sensitive to non-linear absorption. In closed aperture Z-scan measurement, a 25% transmittance aperture was placed at far-field of the lens. The saturated solution of two complexes in acetone solvent prepared and filled in a glass cell with 1 mm thickness. In the case of Z-scan measurements, the sample was moved by a micrometer translating stage along the z-axis. The closed aperture permitted measurement of both sign and value of non-linear refraction in the sample.
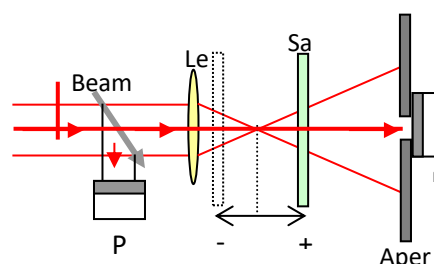

Fig. 3 The optical geometry used to investigate the non-linear optical responses in the complexes (1) and (2).

RESULTS AND DISCUSSION

FT- IR spectra

The vibrational bands for L$_1$H and L$_2$H and related complexes (1) and (2) is collected in Table 1. Vibrational bonds in complexes is slightly shifted to the lower frequencies. Also, the vibrational band of S-H has been omitted in complexes which were appeared around 2500 cm^{-1} in the ligands, but there is not any vibrational bond in these regions for related complexes, which is shown that, the acidic proton has been removed in coordination process and linked Cu metal center. Besides, the Mo-S vibration peak in the range of 400-500 cm^{-1} was observed. These reasons enough to conclude that, all three species [MoS$_4$]$^{2-}$, Cu^{1+} and aminodithioate N,S-donor ligands have been connected to each other.

Table 1. Compare selected IR bands for ligands and complexes. (ν, cm^{-1})

Compound	L_1H	L_2H	(1)	(2)
C=C	1615	1595	1618	1637
C=S	1052	1067	1054	1103
C - S	611	606	611	642
NH_2	3286	3201	3449	3422
S - H	2500	2557	-	-
Mo - S	-	-	491	451

Non-linear optical properties

The UV-visible absorption spectra of the title compounds in acetone solution (1×10^{-3} mol in 10mL solvent) are given in Fig. 4 In this research the non-linear optical properties of two thiomolybdate complexes (1) and (2), have been studied under low power continuous wave (CW) He–Ne laser irradiation. The UV–vis absorption spectrum displayed three broad bands with maxima at 497, 448, 409 nm for complex (1) and two wide maxima at 416 and 338 nm for complex (2), due to the ligand-to-metal charge transfer transitions within the $[MoS_4]^{2-}$ cores. There is also a slight absorption in the 630-635 nm. The aim of this work is to evaluate the linear absorption coefficient and non-linear refractive index of these complexes by irradiation of a focused 35 mW CW He–Ne at 632.8 nm laser irradiation. Non-linear transmission measurement [30] and z-scan method [27] have been used to measure the linear absorption and the non-linear refractive index at the applied wavelength.
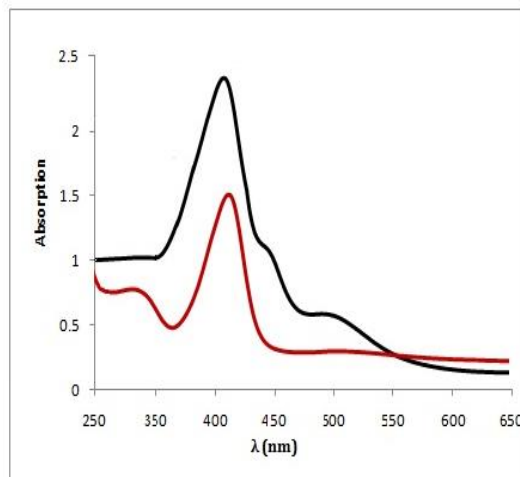

Fig. 4. The Uv-Visible spectra of complex (1) black and complex (2) red.
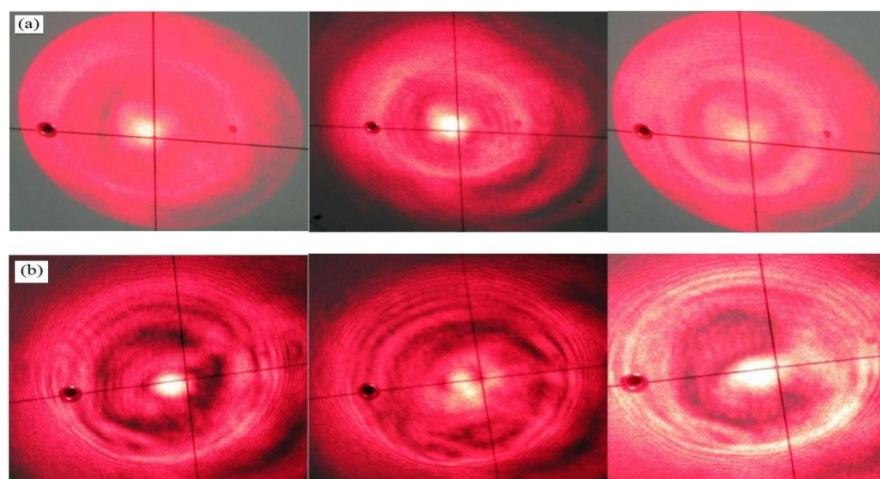

Fig. 5. Images about laser treatment with a) Complex (1) and b) Complex (2).

The spatial profiles of the incident beam and the beam modified by the non-linear medium are inscribed in order to study the intensity distribution. The profiles are shown in Fig. 5(a) for complex (1) and 5(b) for complex (2).

For optical limiting measurements, the sample is put near the focal plane of the lens and the input power is changed. Fig. 6 shows the typical results of the transmission measurements in samples at saturated concentration as a function of incident power, changing from 0 mW up to 15 mW. As it is displayed clearly for incident beam power of above 12 mW (for complex (1)) and 9 mW (for complex (2)), the transmissions becomes non-linear. For example at low incident powers, up to 12 mW for complex (1) from Beer law produces the linear absorption coefficient of 1.63 cm^{-1}. For considerable decrease was observed in transmitted power at incident powers above 13 mW. The thiomolybdate complexes transmission measurement result verifies that it may be a good applicant for optical limiting at 632.8 nm continuous wave lasers. The same course of action is followed for complex (2) and the results are summarized in Table 2.
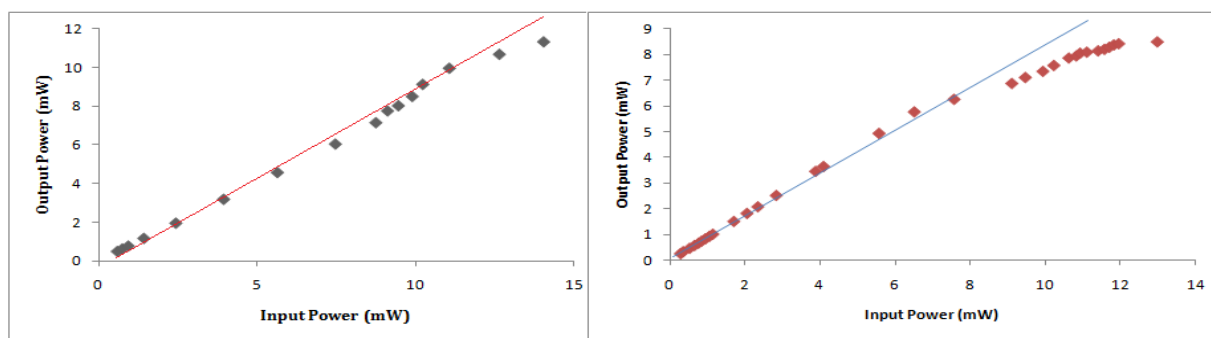
Fig. 6. The non-linear transmission behavior in complex (1), black left diagram and complex (2), red right diagram at saturated concentration exposed to 35 mW CW He–Ne laser at 632.8 nm wavelength. The line curves show the linear transmission of both complexes. At higher power intensity non-linear absorption is visible.

The measurements of non-linear refractive index (n_2) was conducted using closed aperture z-scan techniques [31]. A closed aperture scheme allowed us to determine the values of the non-linear refractive index of the samples. The technique was based on the variation of transmitted radiation intensity by alteration of the geometrical parameters of the interaction territory. The experimental data were recorded by gradually moving a sample along the (z) axis of a focused Gaussian beam through its focal plane and measuring the transmission of the sample for each z-position. As the sample experiences different intensities at different locations, the recording of the transmission as a function of the z-coordinate gives accurate information about the non-linear effects present.
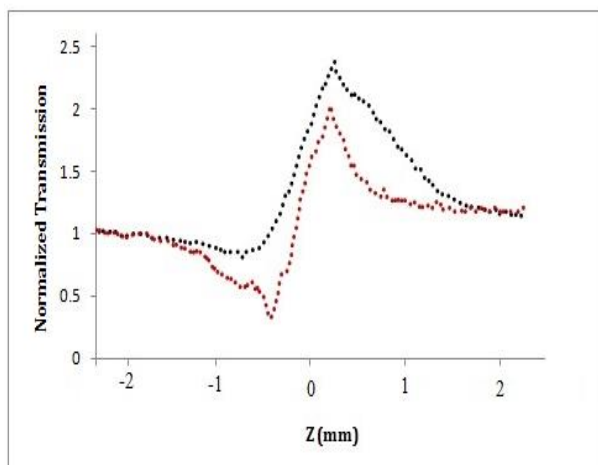
Fig. 7 The comparison of cllose aperture z-scan results at 632.8 nm for complex (1) black and complex (2) red, CW He–Ne laser with applied intensity level of 10^5 Wcm^{-2}; aperture linear transmittance was S = 0.25.

Fig.7 shows the result of the closed aperture z-scan experimental measurement. The results have been obtained at an input laser power density of about 10^5 Wcm^2 for closed aperture parameter of S = 0.25. The peak–valley, $\Delta P_{p\text{-}v}$, is related to non-linear refractive index n_2 by $\Delta T_{p\text{-}v} = (1\text{-}S)^{0.25} kn_2 I_0 L_{eff}$

where $k = 2\pi/\lambda$, I_0 is the input power density and L_{eff} is given by $L_{eff} = [1 - exp(-\alpha L)]/ \alpha$. We have measured the peak-to valley difference for each complexes and calculated the values of n_2 as summarized in Table 2. For comparison, the experimental results obtained for complexes by CW He–Ne laser are also included.

Table 2. Calculated values of linear absorption coefficient and non-linear refractive index for complexes at saturated concentration.

Compounds	α (cm^{-1})	n_2 (cm^{2}W^{-1})
(Et$_4$N)$_2$[MoS$_4$(Cu-L$_1$)$_2$] Complex (1)	1.63	1.78×10^{-9}
(Et$_4$N)$_2$[MoS$_4$(Cu-L$_2$)$_2$] Complex (2)	3.56	2.20×10^{-9}

CONCLUSIONS

Two new thiomolybdate complexes: (Et$_4$N)$_2$[MoS$_4$(Cu-L$_1$)$_2$] and (Et$_4$N)$_2$[MoS$_4$(CuL$_2$)$_2$] were synthesized and characterized by spectral methods. In IR spectra of complexes remove S-H vibrational band of dithioic acid ligands and simultaneous presence of N,S-donor ligands functional groups with vibrational band of Mo-S are reasons for successfully synthesis of them. In reviewing ^{1}H NMR, presence and chemical shift of ligands non-acidic protons in complexes with template splitting of –CH$_3$ and –CH$_2$- in Et$_4$N$^+$ group in complexes are evidence of their efficient synthesis. Also in ^{13}C NMR, carbon atoms with different chemical environment have separate peaks in different chemical shifts. Checking ICP data for 10 ppm concentration of complex (1) indicate that the ratio of Cu to Mo approximately 2 to 1. This confirms the proposed structure of complex (1).

The third-order NLO properties of complexes in saturated solutions of acetone were determined by Z-scan technique at the wavelength of 632.8 nm with continuous wave He-Ne laser duration. Also we have demonstrated the measurement results of the optical limiting performance, linear absorption and

non-linear refraction for these complexes. Input–output measurement is applied to optical limiting behavior examination. Power limiting was measured as 12 mW and 9 mW respectively for complex (1) and (2). Formal z-scan closed aperture curves are used to investigate and measure non-linear refraction coefficient in the complexes. The values of linear absorption coefficient (α) and non-linear refractive index (n_2) are measured.

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