UDC 536.42

LASER-INDUCED MODIFICATION ON SOME PROPERTIES OF PREPARED Cu(II) COMPLEXES

Eman M. Ramadthan, Mahmoud A M Fakhri

Department of Medical Physics, College of Science,
University of Mosul, Mosul, Iraq

Received 12.08.2023
Accepted 17.10.2023

Abstract: *Two complexes - derived from dithiocarbamate ligand (L) and their adduct with nitrogen base of the general formula $[Cu(L)_2]$, $[Cu(L)_2(A)]$ obtained by the condensation of $CuCl_2.2H_2O$ with L= diisopropyl amine dithiocarbamate and A=1,10-phenanthroline weve directly been synthesized and characterized by infrared spectra, metal content and magnetic measurement. Some properties of these two complexes, including UV/VIS absorption, melting point, and molar conductivity measurement are characterized in both cases before and after applying laser diode radiation with an emission wavelength of 532 nm. It found that laser has potential effects on Cu complexes under investigation for specific conditions and doses where new complexes have been observed, and spectral data and magnetic measurement showed a tetrahedral and octahedral geometries for $[Cu(L)_2]$ and$[Cu(L)_2(A)]$, respectively.*

Keywords: *Cu(II) complex; UV/VIS absorption; laser diode; melting point; magnetic measurement; molar conductivity measurement*

DOI: 10.32737/2221-8688-2023-4-370-378

1. Introduction

It is well-known that copper (Cu) is an extremely important element for all organisms. Cu and its related compounds are used for different vital fields of science and technology. In fact, Cu is a metal ion that is involved as a cofactor in several enzymes, in ROS (Reactive Oxygen Species) production, in the tumour progression promotion. Besides, Cu element is also detected at high levels in serum and tissues for several kinds of cancers in humans [1]. Cu complexes are used as catalysts for many biological and industrial processes. Also, the importance of the Cu complex currently lies in the fact that Cu may be used to cancer treatment [2]. Dithiocarbamate ligands coordinating through sulfur atoms with transition metals, dithiocarbamate complexes can present an extreme range of applications in chemistry, agriculture, medicine, and others [3,4]. The complexes with square planar shape of Ni(II) and Cu(II) with potassium-based dithiocarbamate are directly prepared [5]. The neutral complexes are characterized by different measurement methods to ensure that the complexes are contained square planner geometry [5].

There is very limited research on the effect of lasers on Cu complexes [6]. However, laser type, operation mode, wavelength, output power, and other laser permeates should be considered in this field.

In the present work, the effects of a laser diode with an emission wavelength of 532 nm on UV/VIS absorption, melting point, magnetic measurement, and molar conductivity measurement of new Cu(II) dithiocarbamate complexes and their nitrogen bases have been considered for investigation, comparison before and after applying laser has been considered as standard criteria.

2. Experimental:

2.1. Materials and Methods

All starting materials were commercially obtained. The preparation was carried out under a nitrogen atmosphere. IR spectra were recorded on a Shimadzu FT-IR – ATR Bruker in the 400-4000 cm^{-1} range by using KBr discs. On the other hand, electronic spectra were recorded on a Shimadzu UV 160 spectrophotometer by using dimethyl formaldehyde (DMF) for 10^{-3}M solution of the complexes. Conductivity measurements were conducted on a 10^{-3} M solution of DMF at room temperature using a digital conductivity meter model – Eutech pc 700. Magnetic measurement was recorded by Bruker BM6 device under the temperature of 25 ºC by using the method of Faraday. The metallic content was spectrophotometrically estimated by analytical Jena Model Nova AA-350. Melting points were specified on the electro thermal digital melting point apparatus.

2.2. Synthesis of dithiocarbamate ligand

An aqueous solution of sodium hydroxide (0.4 g, 0.01 mole) was added with stirring to (1.7 ml, 0.01 mole) of isobutyl amine. The resulting mixture was cooled in ice, then (0.6 ml, 0.01 mole carbon sulphide was added drop wise with continuous stirring. The formed past was extracted by (100 cm^3) ether filtered off, washed with ether, and dried in a vacuum [7].

2.3. Preparation of $[Cu(L)_2]$ complex

To a well-stirred solution of ligand (0.002 mole) in ethanol (15 cm^3) was added (10 cm^3) solution $CuCl_2 \cdot H_2O$ (0.17 gm, 0.001 mole) in ethanol solvent too. As a result, an immediate precipitation of the interested Cu complex is obtained. In addition, refluxing of focuses was also carried out in order of ensuring complete precipitation. It was also filtered off, then washed with ethanol, next with ether. Finally, it was dried under vacuum for several hours.

2.4. Preparation of $[Cu(L)_2 (A)]$ complex

A mixture of $[Cu(L)_2]$ (0.001 mole) in dimethyl formaldehyde (10 cm^3) and 1,10 phenanthroline (0.001 mole) in ethanol (10 cm^3) was stirred for 3 hours, which afforded a thick precipitate, it was flittered then washed with ethanol and, as a final step, dried under a vacuum.

3. Procedure and laser parameters

Laser-induced modification on Cu (II) complexes in the liquid state were carried out by exposing these complexes to a semiconductor laser radiation in a different time (t) ranging from 0 to 45 minutes (m) with the interval of 15 m, it is clear that 0 m represents the reference (sample without radiated by laser).

Laser parameters used in this investigation are listed in Table1.

Laser power (P) is defined as:

$$P = E / t,$$

where E is laser energy. Laser beam diameter (d) on the samples is measured to be 1.25 cm. Since the laser beam is the circle, the spot area (A) on the interested samples is found to be: A = 1.23 cm^2

Laser dose (D) can be calculated as [8]:

$$D = E / A$$

For times of 15, 30, and 45 m, doses were: 2.44, 4.87, and 7.3 J/cm^2 respectively.

Table 1. Laser parameters used for the study.

Parameter	Symbol	Value	Unit
Wavelength	*Λ*	532	Nm
Operation mode	*CW*		
Output power	*P*	200	Mw
Irradiation area (spot size)	*A*	1.23	cm^2
Power density (Irradiance)	*I*	162.6	mW/ cm^2

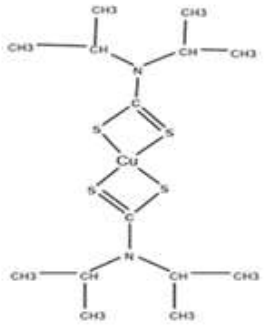
4. Results and discussion

The chemical and physical parameters and conditions for obtaining of various d-elements with nitrogen and sulphur-containing ligands were analyzed [4,9]. Laser-induced modification on absorption, melting point, molar conductivity measurement of Cu(II) complexes were examined through considering the effect of the used laser irradiation on these properties for Cu(II) complexes (the samples are in liquid phases) by measuring these quantities before and after the exposure to laser radiation with different doses.

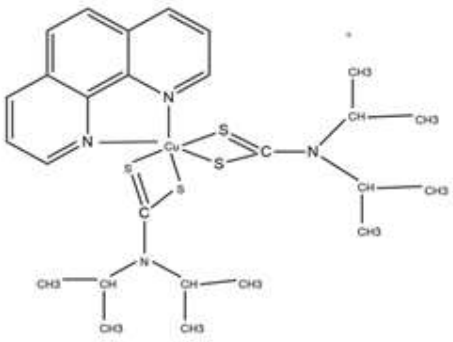
First of all, the suggested geometrical structures of the prepared complexes are shown in Fig. 1. Bi dentate coordination of ligand, the physical properties of ligand, and complexes are shown in Table 2, melting points at (315, 208)ºC for complex 1 and complex 2 without laser and (160-295)ºC for complex 1 and complex 2 with laser.

The low values of molar conductivity under investigation complexes indicate that all prepared complexes are not electrolytes in DMF, [9,10]. Table 2 shows this property before and after applying the used laser.

The measurements of the magnetic moment of the complexes in Table 2, were measured at 25 ºC. The magnetic moment for Cu (II) (1,2) is (2.26, 1.69) B.M. respectively suggests a tetrahedral and octahedral configuration [11,12].



$[Cu\ (C_7H_{14}NS_2)_2]$



$[Cu\ (C_7H_{14}NS_2)_2(C_{12}H_8N_2)]$

Fig. 1. Suggested structures of the prepared complexes.

UV/Vis spectra of the ligand with their two complexes in 10^{-3}M DMF solution were recorded; they are listed in Table 3. The electronic spectra of the complex (1) show one band at 674 nm, this band is assigned to a $^2T_2 \rightarrow {}^2E$ transition that suggests a tetrahedral geometry around copper ion [13] as indicated in Fig. 2(a). Fig. 2(a) shows the standard absorption spectrum of complex 1(i.e. without applying laser irradiation); while Fig. 2(b) shows the standard absorption spectrum of the complex 2. It is clear that both of them were subjected and applied for a wide range of spectrum spanning from the visible to near-

infrared (IF) of the electromagnetic spectrum. The normal and well-known peaks for these complexes can be clearly shown. Some regions of spectra ranges will be considered for the present work

Table 2. Physical properties of the complex before and after applying laser diode radiation.

No.	Compound	Colour	Λ 10^{-3}M DMF	Λ10^{-3} M DMF With laser		μeff. (B.M)	M.P. (C)º	M.P.(C)º With laser		M٪ Cal (found)
1	[Cu $(C_7H_{14}NS_2)_2$]	Brown	24.3	15m.	15	2.26	315	15m.	247	15.28 (14.92)
				30m.	29			30m.	160	
				45m.	36			45m.	295	
2	[Cu $(C_7H_{14}NS_2)_2(C_{12}H_8N_2)$]	Green	45	15m.	27	1.69	208	15m.	159	10.66 (9.89)
				30m.	35			30m.	189	
				45m.	14			45m.	201	

Table 3. Electronic and IR spectral data ligand and complexes before and after applying laser diode radiation.

Comp .No.	U.V. –Vis bands nm	U.V. –Vis bands nm With laser	IR bands cm^{-1}					
			ν (C-S)	ν (C=S)	ν (M- S)	ν (M-N)	ν (C-N)	ν (C-H)
$C_7H_{14}NS_2$	314,301		848	1064		-	1470	3120
1	674	433—264	754	1028	482	-	1456	3101
2	992,608, 380	261—385	850	1036	467	418	1458	3064

Cu (II) Complex (2) shows three absorption bands at 992 nm, 608nm, 380 nm, which are belonged to three transitions of $2B_1g \rightarrow 2A_1g$, $2B_1g \rightarrow 2B_2g$, and $2B_1g \rightarrow 2Eg$ in an octahedral configuration [6,14] as shown in Fig. 2(b).

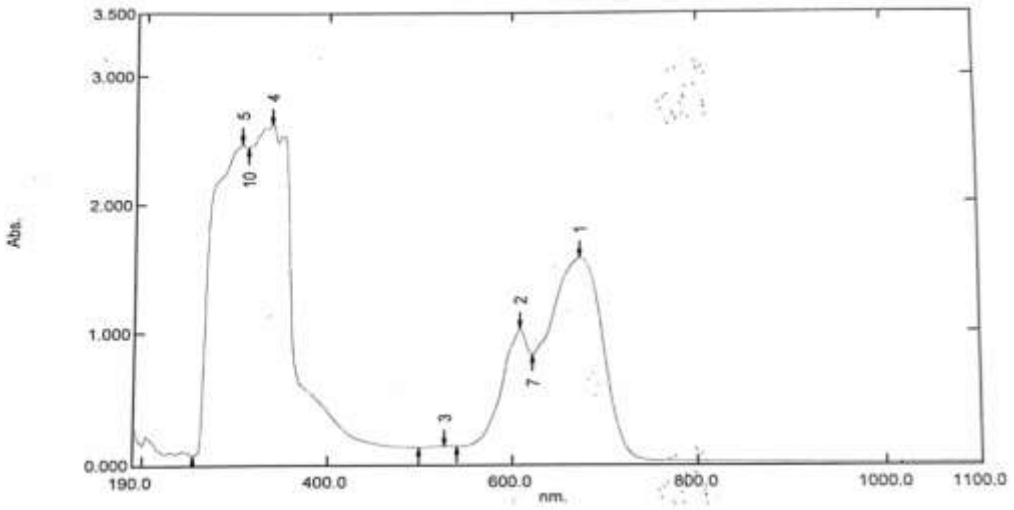


Fig. 2(a). Spectrum electronic of [Cu $(C_7H_{14}NS_2)_2$] without applying laser.

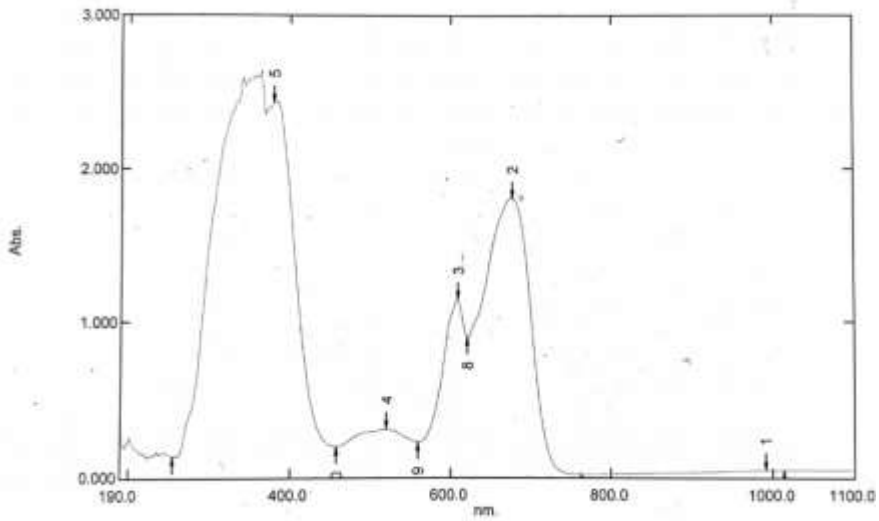


Fig. 2(b). Spectrum electronic of [Cu $(C_7H_{14}NS_2)_2(C_{12}H_8N_2)$] without applying laser.

Used laser was applied on complex 1 for times of 0, 15, 30, and 45 minute. New bands at the wavelength ranging from 433 nm to 264 nm appeared. These interesting results can be attributed to the transitions of n→ π and π → π*. The disappearance of the wideband from 642 nm suggests that the shape was tetrahedral as indicated in Fig. 3(a). This result may suggest that the complex was decomposed under laser irradiation exposure. For complex 2 the same above parameters were used but new bands at the wavelength ranging from 261 nm to 385nm were observed instead. The interesting results can also be attributed to the transitions of n→ π*and π → π*. The disappearance of the wideband from (992 nm and 608nm) suggests that the shape was octahedral geometry as indicated in Fig. 3(b). This result may suggest that the complex was also decomposed by the applied laser.

One can observe that the effects of laser irradiation with a wavelength of 532 nm on the Cu complexes were non-linear. This result may be interpreted for appearing new complexes as it can be seen on the UV/VIS spectra in Fig. 3 (a, b).

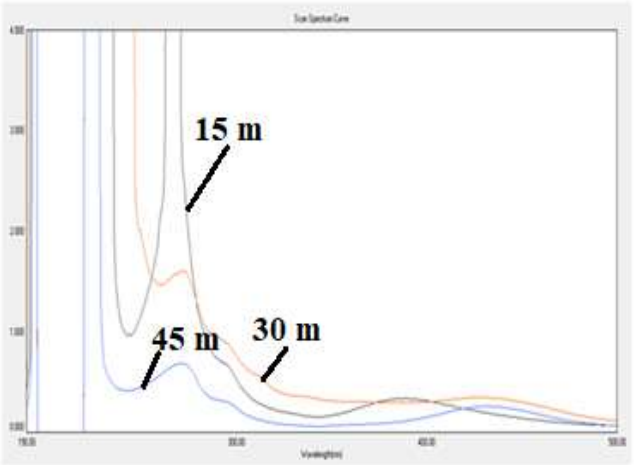


Fig. 3(a). Spectrum electronic of [Cu $(C_7H_{14}NS_2)_2$] with applying laser**.**

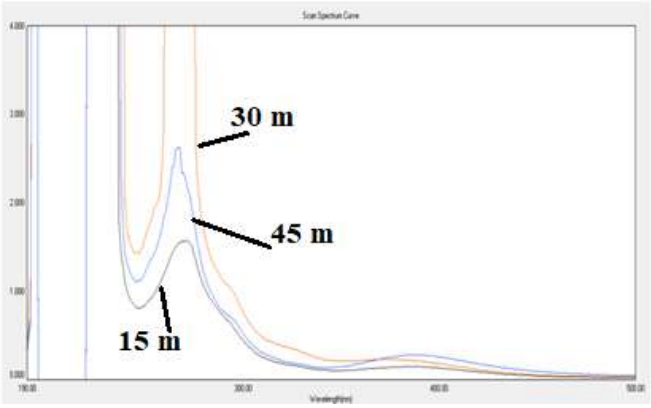


Fig. 3(b). Spectrum electronic of [Cu $(C_7H_{14}NS_2)_2(C_{12}H_8N_2)$] with applying laser.

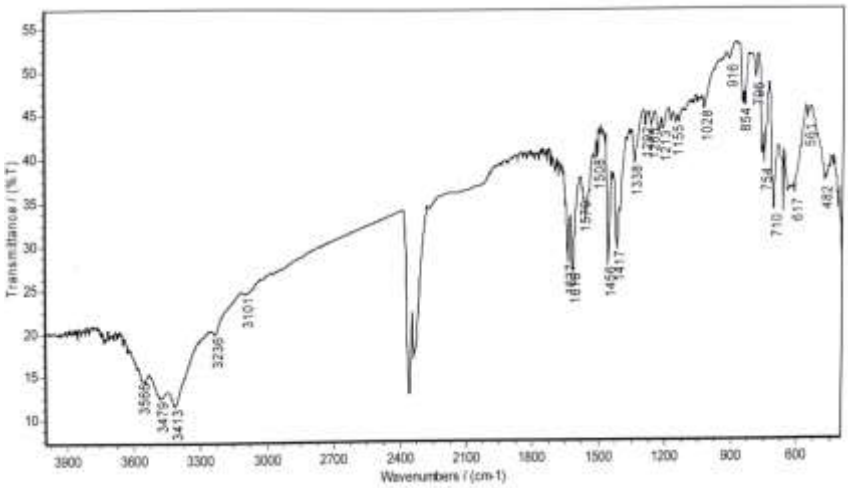


Fig. 4(a). The IR Spectrum of complex [Cu $(C_7H_{14}NS_2)_2$]

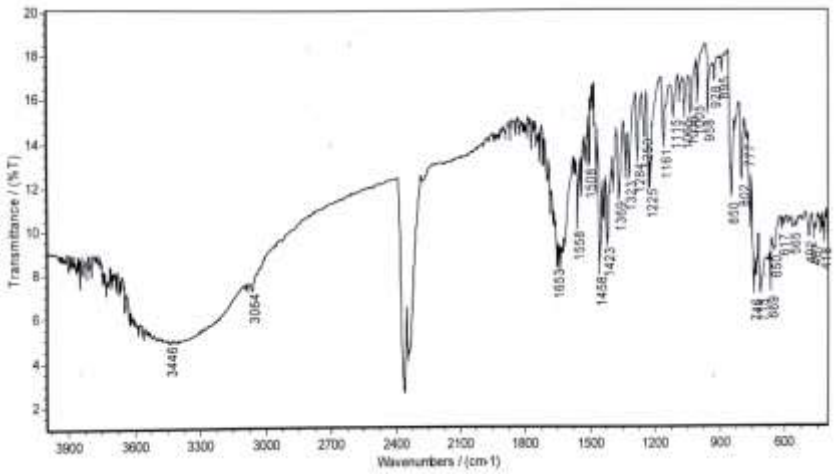


Fig. 4(b). The IR spectrum of complex[Cu $(C_7H_{14}NS_2)_2(C_{12}H_8N_2)$].

Table 3 shows the most influenced bands which are recorded by IR spectra for complexes examined. In IR spectrum of the ligand the sharp bands observed at 1064 cm^{-1}, and 848 cm^{-1} which belong to the ν (C=S) [6,15], and ν (C-S) [16,17]. The infrared spectra of the complex (1) showed a sharp band at the 482, 1028,754 cm^{-1} which assigned to ν (M-S), ν (C=S), ν (C-

S) [18,19] respectively, see Fig. 4(a) ,while for complex (2) the following bands are observed at 467, 418, 1036, 850 cm^{-1} which assigned to ν (M-S), ν (M- N), ν (C=S), ν (C-S) [20,21] respectively. See Fig. 4(b).

5. Conclusion

The green laser emission with a wavelength of 532 nm has potential effects on the properties of Cu (II) with diisopropylamine dithiocarbamate and Cu(II) and 1,10-phenanthroline. In this way, new Cu complexes can be synthesized and characterized before and after applying laser. Besides, other laser types and wavelengths with different doses may be considered for preparing new complexes.

References

1. Sebastiano M., Vaˇnhara P., Cabiddu M.G., Moráˇn L., Havel J., Cadoni E., and Pivetta T. Copper(II) phenanthroline-based complexes as potential anticancer drugs: a walkthrough on the mechanisms of action. *Molecules*. 2022, vol. 27(1), 49.
2. Alberto R., Braband H. SPECT/PET Imaging with Technetium, Gallium, Copper, and Other Metallic Radionuclides, In: Alberto R; Braband H. Comprehensive inorganic chemistry II: from elements to applications. Amsterdam: Elsevier, 2013, pp. 785-817.
3. Tatyana A.R., Alexander V.I., Andrey V.G., Maxim A.I., S.Z. Anna, S.P. Tatyana, and Oleg N.A. A pyridine adduct of bis (di-iso-butyldithiocarbamato-S,S) cadmium(II): multinuclear (13C, 15N,113Cd) CP/MAS NMR spectroscopy, crystal and molecular structure, and thermal behaviour. *Inorg. Chem. Acta.* 2022, vol. 368, pp. 263–270.
4. Mammadova Sh.A., Abasqulieva U.B., Zalov A. Z., Novruzova N.A. Spectrophotometric research into complexation of tungsten (VI) with o-hydroxythiophenol derivatives in the presence of hydrophobic amines. *Chemical problems*. 2022, no. 2 (20), pp. 164-174.
5. M. A. K., K. N. Kaul, Lark, B. S. Roa, and A. L. J., "Simple and Sensitive Method for Determination of Tetramethylthiuram Disulphide" (Thiram). Pestic. Sci., 53, 104È106, 1998.
6. Trifunovic S.R. , Markovix Z., Sladic D., Andjekovic K., Sabo T., and Minic D. The synthesis and characterization of nickel(II) and copper(II) complexes with the polydentate dialkyl dithiocarbamic acid ligand 3-dithiocarboxy-3-aza-5-aminopentanoate. *J. Serb.Chem. Soc*. 2002, vol. 67, no. 2, pp. 115- 122.
7. Furniss B.S., Hannaford A. J., Smith P. W. G., Tatchell A.R., and Vogle A.I. Text Book of practical organic chemistry, 5th Edition. Longman Scientific & Technical. Uk., 2008.
8. Flieger R., Grange T., Grzech-Le´sniak K., Dominiak M., and Matys J. Low-Level Laser Therapy with a 635 nm Diode Laser Affects Orthodontic Mini-Implants Stability: A Randomized Clinical Split Mouth Trial". *J. Clin. Med*. 2020, vol. 9(1), p. 112, DOI: 10.3390/jcm9010112
9. Zalov A.Z., İsgenderova K.O., Askerova Z.G. Spectrophotometric research into interaction nickel II) with 1- (2- pyridylazo) -2- hydroxy -4-mercaptofenol and aminophenols. *Chemical Problems*. 2021, no. 3 (19), pp. 150-159.
10. Al-Mukhtar S.E., Alkatib H.F. and Alnuaimy L.A. Preparation and Characterization of some Transition Metal Complexes with Crotyl xanthate Ligand and their Adducts with Nitrogen Bases. *Raf. J.Sci.*, 2017, vol. 26 (1), pp. 49-55. DOI: 10.33899/rjs.2017.138961
11. Cookson J., Emma A.L.E., John P.M., Christopher J.S., Rowena L.P., Andrew R.C., Micha G.B.D. and Paul D. Metal directed assembly of large dinuclear copper (II) dithiocarbamate Macrocyclic complexes. *Inorg Chim Acta*. 2010, vol. 363, pp. 1195-1203,
12. Lever A.B.P. Inorganic Electronic spectroscopy. 2nd ed., Elseviver, Amsterdam, 1984.
13. Al-Mukhtar S.E., and Mohammed H.A. Synthesis and Characterization of Mn(II), Fe(II) and Co(II) Complexes with 4-

Hydroxypiperidinedithiocarbamate and their Adducts with Neutral Bases. *Raf. J. Sci.*, 2014, vol. 25, pp. 53-61.
14. Zalov A.Z., Kuliev K.A., Akberov N.A. Composition and extraction of tungsten(VI) complexes with 2-hydroxy-5-bromtiphenol and aminophenols. *Chemical Problems*. 2019, no. 1 (17), pp. 50-58.
15. Zalov A.Z., Mammadova Sh.A., Hasanova N.S., Ibrahimova Sh.A. Spectrophotometric study of ternary complexes of Cr (VI) and Co (II). C*hemical Problems*. 2020, no. 2 (18), pp. 164-172.
16. Serrano J.L., Garcia L., Perez J., Perez E., Sanchez G., Garcia J., Lopez G., Garcia G., and Molins E. New dithiocarbamate and xanthate complexes of nickel(II) with iminophosphine. *Inog. Chem. Acta.* 2003, vol. 355, pp. 33-40.
17. Alsafee B.A.H. Preparation and characterization of some transition metal complexes of 4-amino-N-(5-sulfanyl-1,3,4-thiadiazol-2-yl) benzenesulfonamide. *International journal of Scientific and Engineering Research*. 2015, vol 1, no.1, pp. 37-45.
18. Sarwar M., Ahmad S., Ahmad S., Ali S., and Ahmed S.A. Copper (II) complexes of pyrrolidin Dithiocarbamate. *Trans. Met. Chem.*, 2007, vol. 32, pp. 199-203.
19. Zalov A. Z., Iskenderova K.O., Askerova Z.G., Hajiyeva A.B. Spectrophotometric study of nickel (II) complexes with 2-hydroxythiolphenol and its derivatives in the presence of hydrophobic amines. *Chemical Problems*. 2021, no. 4 (19), pp. 224-231.
20. Mohamed G.G., Ibrahim N.A.E. and Attia H.A. Synthesis and anti-fungicidal activity of some transition metal complexes with benzimidazole dithiocarbamate ligand". *Spectrochim Acta*, A., 2009, vol. 72, pp. 610–615.
21. Bond A.M. and Martin R.L. Electrochemistry and redox behaviour of transition metal dithiocarbamates. *Coord. Chem. Rev.*, 1984, vol. 54, pp. 23-98.

.

ЛАЗЕРНО-ИНДУЦИРОВАННАЯ МОДИФИКАЦИЯ НЕКОТОРЫХ СВОЙСТВ ПОЛУЧЕННЫХ КОМПЛЕКСОВ Cu(II)

Эман М. Рамадтан, Махмуд А.М. Фахри

Кафедра медицинской физики,
Университет Мосула, Ирак

Аннотация: Два комплекса - производные дитиокарбаматного лиганда (L) и их аддукта с азотистым основанием общей формулы $[Cu(L)_2]$, $[Cu(L)_2(A)]$, полученные конденсацией $CuCl_2 \cdot 2H_2O$ с L = дитиокарбаматом диизопропиламина и A=1,10-фенантролином были непосредственно синтезированы и охарактеризованы с помощью инфракрасных спектров, содержания металлов и магнитных измерений. Некоторые свойства этих двух комплексов, включая поглощение УФ/ВИД, температуру плавления и измерение молярной проводимости, охарактеризованы в обоих случаях до и после применения излучения лазерного диода с длиной волны излучения 532 нм. Было обнаружено, что лазер оказывает потенциальное воздействие на исследуемые комплексы Cu при определенных условиях и дозах, при которых наблюдались новые комплексы, а спектральные данные и магнитные измерения показали тетраэдрическую и октаэдрическую геометрию для $[Cu(L)_2]$ и $[Cu(L)_2(A)]$ соответственно.

Ключевые слова: комплекс Cu(II); поглощение УФ/ВИД; лазерный диод; температура плавления; магнитные измерения; измерение молярной проводимости

SİNTEZ EDİLMİŞ Cu(II) KOMPLEKSİNİN BƏZİ XASSƏLƏRİNİN LAZER- İNDUKSİYA MODİFİKASİYASI

Eman M. Ramadtan, Mahmud A.M. Fəxri

Tibbi fizika kafedrası,
Mosul Universiteti, İraq

Xülasə: $[Cu(L)_2]$, $[Cu(L)_2(A)]$ ümumi düsturuna malik iki kompleks - ditiokarbamat liqandının (L) törəmələri və onların $CuCl_2 \cdot 2H_2O$ ilə kondensasiyası ilə əldə edilən azot əsaslı əlavəsidir. Burada L = diizopropilamin ditiokarbamat və A =1,10-fenantrolin birbaşa olaraq sintez edilmiş və, metal tərkibi, maqnit ölçmələri və infraqırmızı spektrlərdən istifadə etməklə tədqiq edilmişdir. Bu iki kompleksin bir sıra xüsusiyyətləri, o cümlədən UV/Vis udma, ərimə nöqtəsi və molyar keçiricilik ölçmələri, hər iki halda 532 nm lazer diod şüalanmasının tətbiqindən əvvəl və sonra xarakterizə edilmişdir. Lazerin müəyyən şərtlərdə və dozalarda tədqiq edilmiş Cu komplekslərinə potensial təsir göstərdiyi müəyyənləçdirilmiş, bu zaman yeni komplekslər müşahidə edilmiş və spektral məlumatlar və maqnit ölçmələri müvafiq olaraq $[Cu(L)_2]$ və $[Cu(L)_2(A)]$ üçün tetraedrik və romboedrik quruluş nümayiş etdirmişlər.

Açar sözlər: Cu(II) kompleksi; UV/VIS udma; lazer diodu; ərimə temperaturu; maqnit ölçmələri; molyar keçiriciliyin ölçülməsi