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SYNTHESIS AND CHARACTERIZATION OF SOME NEW AZO COORDINATION POLYMERS

Mohammed Khalil Younis

Chem. Department, Faculty of Science, University of Zakho, Kurdistan Region, Iraq.

ABSTRACT

The synthesis of the ligand 2,2'-(4,4'-(1-methyl-3,4-phenylene bis(diazene-2,1-diyl)) bis(4,1-phenylene)) bis(azanediy) bis(oxomethylene) dibenzoic acid (L) and its coordinated polymers with six metals (Cu+2, Co+2, Ni+2, Pt+2, Th+4 and U+6) are characterized by elemental analysis, IR, electronic spectra and magnetic susceptibility. The geometries of the complexes diver between octahedral and square planer except for Th+4 and U+6 complexes which are eight coordinated number. All the complexes have a well considerable biological activity against different organisms.

Key Words: Coordination polymers, Azo dye, Phthalamic acid, Biological activity

1. INTRODUCTION

Coordination polymers were mentioned and developed nearly 50 years ago¹. Since that time, they witnessed much progress as their properties focus on waste water treatment in metal recovery, antifouling paints, anti-bacterial, anti-fungal properties, sensing and gas storage²⁻⁵. Azodyes are considered to be one of the famous class of organic chemical family characterized with wide properties and attracted the attention of researchers since that time. The diversity of their colors turns the application towards pigments and dyes for a long time.^{6,7} Furthermore, their superior optical and thermal properties have been studied widely⁸ in optical recording medium⁹, nonlinear optical elements and printing systems¹⁰.

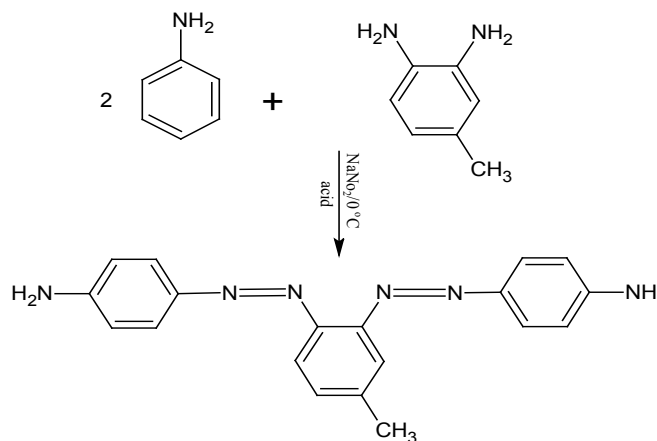
In this work, bisazo dye is synthesized with phthalamic acid group in order to investigate its coordinated bonding with six elements. This approves that this compound acts as a good metal chelating agent.

2. MATERIALS AND METHODS

3,4 toluene diamine (fluka), cobalt(II) chloride dihydrate (Carl Roth), nickel(II) chloride dihydrate (Carl Roth), Copper(II) chloride dihydrate (fluka) (Carl Roth), potassium tetrachloroplatinate(II) (fluka), thorium(IV) nitrate hydrate (fluka), uranyl(VI) acetate dihydrate (fluka), all the other chemicals were used as received without any purification and were of analytical grade.

Synthesis of 2,2'-(4,4'-(1-methyl-3,4-phenylenebis(diazene-2,1-diyl)) bis(4,1-phenylene)) bis(azanediy) bis(oxo methylene) dibenzoic acid (L):

The ligand was prepared as described earlier by diazotization and coupling classical procedures^{11,12}, as seen in scheme 1.



4,4'-(1-methyl-3,4-phenylenebis(diazene-2,1-diyl)) dianiline

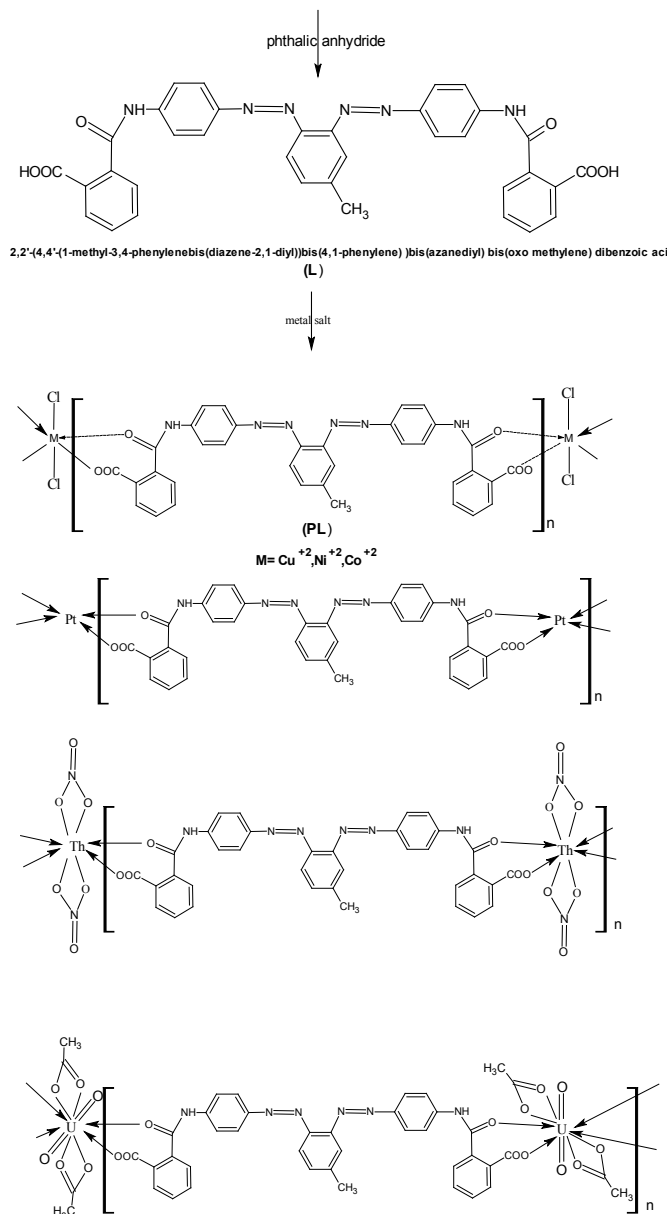
Scheme 1: Synthesis of 2,2'-(4,4'-(1-methyl-3,4-phenylenebis(diazene-2,1-diyl)) bis(4,1-phenylene)) bis(azanediy) bis(oxo methylene) dibenzoic acid [L] and their polymeric complexes

Corresponding Author:

Mohammed Khalil Younis, Chem. Department, Faculty of Science, University of Zakho, Kurdistan Region, Iraq.

E-mail: polymeryounis@yahoo.com

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Scheme 1: continue.....

2.1. Synthesis of Coordination Polymers

(0.001 mol) of metal salt is dissolved in formic acid (50 ml) and mixed with (0.001 mol) of ligand L solution in (50 ml) formic acid. The mixture is refluxed for 8hs. In order to complete the precipitation of the polymeric complex, the solution must be alkalized with dilute ammonia solution and heated for 3 hr. The complex is filtered and washed several times with water accompanied with acetone and dried at 45 °C for 24 hr.

2.2. Physical Measurements

Analysis of the ligand L and its complexes are carried out using C.H.N.S elemental analyzer model 2400 Perkin Elmer. IR spectra are measured at room temperature using Perkin-Elmer spectrum one B FTIR spectropho-

tometer equipped with potassium bromide (KBr). Conductivity meter JENWAY 4510, is used to measure the conductivity of the complexes. These measurements are carried out using $10^{-3}M$ of absolute ethanol. The magnetic susceptibility measurements of coordination polymers are carried out at room temperature by Faraday's method using Bruker BM6 instrument. The electronic spectra of coordination polymers are recorded by Unicam HEIOS UV-VIS 2000 spectrophotometer using 10^{-3} absolute ethanol solution at room temperature.

2.3. Antibacterial Activity

Biological activity of the prepared complexes are screened against five isolated organisms (*Klebsiella pneumonia*, *Escherichia coli*, *Enterococcus faecalis*, *Pseudomonas aeruginosa* and *Staphylococcus aureus*) at $10^{-3}M$ concentration in DMSO on Muller-Hinton agar plates by disk diffusion method²⁵. These agars are incubated for 24 hs at 37 °C. The inhibition zone is measured in mm as well.

3. RESULTS AND DISCUSSION

3.1. Infrared of the Ligand and its Polymeric complexes

The ligand 2,2'-(4,4'-(3-methyl-1,2-phenylenebis(diazeno-2,1-diyl))bis(4,1-phenylene))bis(azanediyl) bis(oxomethylene)dibenzoic acid (L), isolated in pure form (dark brown color). The important spectral bands for this ligand and its coordination polymers in IR spectrum are recorded as KBr disks and are shown in (Table 2). The main functional bands for the prepared ligand are as follow,

a broad band at 3326cm^{-1} and 3441cm^{-1} of $\nu(\text{COO-H})$ and $\nu(\text{NH})$ respectively. The bands at 1708cm^{-1} and 1637cm^{-1} are of $\nu(\text{C=O})$ for the carboxylic and amide groups as follow. The band around 1505cm^{-1} are attributed the azo $\nu(\text{N=N})$ group, all the other groups at their expected regions¹³. This confirm the successful synthesis of the ligand.

As a result of comparing the spectrum of the ligand with its polymeric complexes, it is found that there are many shifts and differences which can be illustrated as follows, The broad band at 3336cm^{-1} of the ligand is disappeared in the spectrum of the polymeric complexes. This confirms the bonding at (-OOH). The $\nu(\text{C=O})$ band of amide are shifted to lower frequencies ($18\text{-}24\text{cm}^{-1}$) except the complexes of Th^{+4} and U^{+4} which shifted to higher one ($4\text{-}9\text{cm}^{-1}$). These shifts give us an idea about the type of coordination bonding occurred at (C=O and COOH) groups respectively¹⁴. Also the weak stretching bands at 1268cm^{-1} and 1278cm^{-1} for (C-O) in the ligand are shifted to lower frequencies in their complexes. These results indicate the formation of C-O-M stretching bond¹⁵. The

uranyl complex exhibits two bands at 937 and 874 cm^{-1} , which are assigned to the asymmetric stretching frequency and symmetric stretching frequency, respectively of the dioxouranium ion¹⁶.

3.2. Electronic Spectra and Magnetic Susceptibility

The magnetic moment (μ_{eff}) of the complexes are given in (table 1). The electronic spectrum of the Co^{+2} complex gives three bands at 318, 359, 484 nm (broad in nature) with transitions ${}^4\text{A}_2\text{g}(\text{F}) \rightarrow \text{T}_2\text{g}(\text{F})$, ${}^4\text{T}_1\text{g}(\text{F}) \rightarrow {}^4\text{A}_2\text{g}(\text{F})$, ${}^4\text{T}_1\text{g}(\text{F}) \rightarrow {}^4\text{T}_1\text{g}(\text{P})$. These bands with its magnetic moment value indicate the high spin octahedral geometry with orbital contribution¹⁶. Cu^{+2} complex also gives three bands at 311, 354 and 473 nm mainly of ${}^2\text{B}_{1\text{g}} \rightarrow {}^2\text{A}_{1\text{g}}$. A transition typically suggests a distorted octahedral geometry enhanced by a high value of magnetic moment 2.1 (μ_{eff})¹⁷. Ni^{+2} complex also gives three bands at 306, 365 and 477 nm assigned as ${}^3\text{A}_2\text{g} \rightarrow {}^3\text{T}_2\text{g}(\text{F})$, ${}^3\text{A}_2\text{g} \rightarrow {}^3\text{T}_1\text{g}(\text{F})$, ${}^3\text{A}_2\text{g} \rightarrow {}^3\text{T}_1\text{g}(\text{P})$ transitions respectively. These bands with magnetic moment 4.8 (μ_{eff}) suggest octahedral geometry with orbital contribution¹⁸. Platinum⁺² complexes show strong band at 306 nm and two weak bands at 399 and 498 nm. These two bands are assigned as ${}^1\text{A}_{1\text{g}} \rightarrow {}^1\text{A}_{2\text{g}}$ transition in square planar geometry^{19,20}, with diamagnetic property as enhanced with magnetic moment value 0.981 (μ_{eff}). Uranyl(VI) complex gives three bands, the first two peaks at 311 and 355 nm are of charge transfer, while the last band at 475 nm can be definitely assigned as oxygen to f transition with almost eight coordinate geometry^{21,22}. Thorium (IV) complex also gives four bands, the first three one at 306, 360, 398 nm which assigned as charge transfer while the fourth one at 503 nm, as in

uranyl complex, with almost ten coordinate geometry^{23,24}.

3.3. Biological Activity Study

The antimicrobial activity examination of the polymeric complexes is carried out by disk diffusion method^{25,26}. The test solutions are prepared in dimethyl sulfoxide. The zone of inhibition is measured in mm and the values are summarized in (table 3). These values indicate that all the complexes have moderate activity towards the tested organisms. Thorium and uranium complexes have the highest activity and that has been explained on the basis of overtone's concept and chelating theory^{27,28}.

4. CONCLUSION

Bisazo dye with phthalamic acid shows a good chelating activity towards different metals, and act as a bidentate ligand. The geometry of the complexes vary as octahedral (copper, nickel and cobalt), square planar (platinum) and 8 to 12 coordination number (thorium and uranium) respectively. All the complexes show moderate biological activity towards different bacterial types.

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Table 1: Elemental analysis, magnetic moment value and physical properties of the prepared ligands and their complexes.

Compounds	Color	% Calculated (found)			(μ_{eff}) B.M.	Conductivity in ethanol $\text{ohm}^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$	m.p. $^{\circ}\text{C}$
		C	H	N			
L	Dark purple	67.09(67.03)	4.18(4.15)	13.41(13.17)	-	6.8	125
$[\text{CoLCl}_2]$	Dark red	55.72(55.70)	3.21(3.25)	11.14(11.16)	5.1	18.8	>270
$[\text{CuLCl}_2]$	Dark red	55.38(55.35)	3.19(3.12)	11.07(10.94)	2.1	15	>270
$[\text{NiLCl}_2]$	Pale yellow	55.74(55.70)	3.21(3.25)	11.14(11.09)	4.8	23.9	>270
$[\text{PtL}]$	Black	51.29(51.20)	2.95(2.92)	10.25(10.26)	0.98	12.2	>270
$[\text{Th}(\text{NO}_3)_2]$	Red brown	42.87(42.80)	2.47(2.49)	11.43(11.52)	-	9.9	>270
$[\text{UO}_2(\text{CH}_3\text{COO})_2]$	purple	46.25(46.23)	2.99(2.93)	8.30(8.10)	-	4.0	>270

Table 2: Infrared spectra (cm⁻¹) and electronic spectra (nm) for the ligands and their polymeric complexes.

Compounds	ν (-NH)	ν (COOH)	ν (C=O) amide	ν (-N=N-)	ν (C=O) carboxylic	UV-VIS absorption bands λ (nm)
L	3411	3336	1637	1505	1708	
[CoLCl ₂]	3405	-	1619	1506	1709	318, 359, 484
[Cu LCl ₂]	3369	-	1619	1503	1708	311, 354, 473
[Ni LCl ₂]	3429	-	1619	1507	1707	306, 365, 477
[PtL]	3414	-	1613	1501	1712	306, 399, 498
[Th(NO ₃) ₂]	3332	-	1646	1518	1722	306, 360, 398, 503
[UO ₂ (CH ₃ COO) ₂]	3422	-	1640	1519	1716	311, 355, 475

Table 3: Antibacterial activity (inhibition zone/mm) of chemicals complex (10⁻³M) Against Gram positive and Gram negative pathogen isolates.

Complex	E. coli	P. aeruginosa	S. aureus	K. pneumonia	E. faecalis
[CoLCl ₂]	11 mm	8 mm	10 mm	11mm	13 mm
[Cu LCl ₂]	14 mm	17 mm	-----	-----	14 mm
[Ni LCl ₂]	-----	13 mm	14 mm	12 mm	18 mm
[PtL]	15 mm	15 mm	17 mm	-----	14 mm
[Th(NO ₃) ₂]	20 mm	14 mm	-----	17 mm	15 mm
[UO ₂ (CH ₃ COO) ₂]	17 mm	14 mm	-----	13 mm	22 mm

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