New Trinuclear complexes of Co(II),Ni(II) ,Cu(II) and Zn(II) with Thiolato triazole, dithiocarbamate indium (III) and their biological study

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Abstract

Indium metal react with $(C_3H_4N_3S)_2$ (L^1) or $(C_5H_{14}N_3S_2)_2$(L^2)in refluxing toluene to give the compounds $[In(L^1)_3]$ and $[In(L^2)_3]$ through an oxidative addition reaction. Trinuclear complexes of general formulas $[In(L^1)_3(MCl_2)_2]$ and $[In(L^2)_3(MCl_2)_2]$ were prepared by a direct reaction of $MCl_2.6H_2O$, (M=Co, Ni) or $CuCl_2.2H_2O$ and $ZnCl_2.XH_2O$ with the above indium compounds. The prepared compounds and complexes were characterized by IR and UV/Vis spectra, conductivity measurement, magnetic measurements , metal content were determined spectrophotometrically and their biological activity were also determined.The electronic spectra and magnetic measurements indicate that the Co and Ni complexes have square plan and octahedral geometry, while the Cu complexes show the presence of tetrahedral and octahedral geometry.

الخلاصة

يتفاعل فلز الانديوم مع الليكاندات (L^1) $(C_3H_4N_3S)_2$ و(L^2) $(C_5H_{14}N_3S_2)_2$ في التولوين لتعطي المركبات ذوات الصيغ $[In(L^1)_3]$ و $[In(L^2)_3]$ خلال تفاعل الاكسدة المضافة. كذلك تم تحضير المعقدات ثلاثية النوى الجديدة ذوات الصيغ العامة$[In(L^1)_3(MCl_2)_2]$و$[In(L^2)_3(MCl_2)_2]$ (M=Co , Ni,Cu and Zn) خلال تفاعل الاضافة المباشرة مع مركبات الانديوم أعلاه .

تم تشخيص المركبات والمعقدات بواسطة أطياف الأشعة تحت الحمراء وفوق البنفسجية والتوصيلية الكهربائية والقياسات المغناطيسية. كذلك تم تقدير المحتوى الفلزي بالطريقة الطيفية وكذلك تم دراسة الفعالية البايولوجية لبعض المركبات المحضرة.

بينت القياسات المغناطيسية والطيف الالكتروني بان معقدات Ni,Co تمتلك بنية ثمانية السطوح واما النحاس فتمتلك بنية رباعية السطوح وكذلك ثمانية السطوح.

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Introduction

Studies involving reaction of non-transition elements and thiuram sulfide have been limited to a handful of reports(1). The stability of high oxidation state in dithiocarbamate complexes seems to be restricted to transition metals, where empty d orbitals can behave as π acceptors (2).

Selenium and bismuth metals reacts with di-2-pyridyl disulphide (Py_2S_2) in refluxing toluene to give the compounds $Se(Spy)_4$ and $Bi(Spy)_3$ in high yield. Reactions of selenium or bismuth, Py_2S_2 and iodine in different molar ratios was carried out in refluxing toluene led to the formation of $Se(Spy)_3I$, $Se(Spy)_2I_2$, $Bi(Spy)_2I$ and $Bi(Spy)I_2$, respectively (3).Their antibacterial activity were studied.

Copper and nickel powders react directly with sodium dithiocarbamates in organic solvents and produce the corresponding metal complexes. The results showed that the copper powder reacts in chloroform more readily than any other system examined. This reaction has been successfully applied in the determination of copper content in brass and bronze powders (4).

Tin powder is oxidized by $Et_2P(S)SS(S)PEt_2$ to tin (II) diethyldithiophosphinate , the reaction involve the insertion of the metal into the S-S bond (5).

Tetraethylthiuram disulfide (DTS), an inhibitor of nephrotoxicity of Pt(II) drugs, an efficient agent in the treatment of chronic alcoholism , in treatment of HIV infections, (AIDS) and heavy metal toxicity, fungicide and herbicide, the reactions of tetraethylthiuram disulfide with $K_2[PtCl_4]$, in ratio 1:1 and 1:2 gave the compounds $[PtCl_2DTS]$ and $[Pt(S_2CNEt_2)_2]$ respectively,were described by (6).They showed that the complexes have higher biological activity that at the ligands.

Reaction of silver (I) halide with PPh_3 and pyridine-2-thion or dipyridin- disulfide in (1:1:1) has yielded sulphur bridge dimmer of general formula $[AgX_2(PySH)_2(PPh_3)_2]$ (X=Cl,Br), the complexes have been determined by x-ray crystallography (7). Their cytotosity were also determined.

As part of our studies into the chemical and biological properties of dithiocarbamate complexes , we recently reported the synthesis , characterization, and biological activity of several, Ni^{+2},Cu^{+2} and Se^{+4} complexes (8) .

Here with we have used both compound $[In(L^1)_3]$ and $[In(L^2)_3]$ for the synthesis of new trinuclear complexes of the formula $[In(L^1)_3(MCl_2)_2$ and $In(L^1)_3(MCl_2)_2]$ and study their biological activity.

Experimental

All chemicals were reagent grade, indium metal and $MCl_2.6H_2O$, (M=Co,Ni), $CuCl_2.2H_2O$ and $ZnCl_2.XH_2O$ were used as supplied from Fluka A.G.The disulfide was synthesized by a standard method (9).

The compounds were analyzed for their metal content by Shimadzu AA670 spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer 580. infrared spectrophotometer in the range 200-4000 cm^{-1} range using CsI pellets, UV/Vis. spectra were recorded on a Shimadzu UV/Vis recording spectrophotometer of type UV-160 for 10^{-3}M solution of the compounds and complexes in dimethylsulfoxide (DMSO) at 25ºC using 1 cm quartz cell. Conductivity measurements were carried out at room temperature in DMSO solution (10^{-3}M) using a Jenway 4070 conductivity meter.

Synthesis of the compounds

1) [In(L^1)$_3$] tri(1-amino-3,4-diazole 2-thiolato)indium(III)

A mixture of finely cut indium metal chips (1.14 g ,10 mmol) were refluxed vigorously with the ligand (L^1)$_2$ (3.40 g, 15mmol) in toluene (25 cm^3), for 8hr., during which time the metal gradually dissolved and the solid precipitated. The mixture was allowed to cool to room temperature and the product collected, washed with diethylether (2 × 10cm^3) and dried in vacuum .

2) [In(L^2)$_3$] tri(diethylene diamine dithiocarbamato)indium(III)

Indium metal chips (1.14g, 10mmol) and ($C_5H_{14}N_3S_2$)$_2$ (5.34g, 1.5mmol) were refluxed in toluene (30 cm^3), for 8hr., by which time the metal was completely dissolved and the colour of indium is charged. A white solid was precipitated, refluxing was stopped at this stage and the stirred mixture was cooled to ambient temperature, petroleum ether (60-80ºC) (20 cm^3) was then added. The solid product was collected by filtration washed twice with (10 cm^3) portion of petroleum ether and dried in vacuum.

3) Preparation of [In(L^1)$_3$(MCl_2)$_2$] complexes

(M=Co,Ni,Cu or Zn)

A clear solution of [In(L^1)$_3$] (1 mmol) in methanol (10 cm^3) was added to a solution of $MCl_2.6H_2O$,M=Co,Ni, $CuCl_2.2H_2O$ or $ZnCl_2.6H_2O$ (2 mmol) in distil water (10 cm^3). The reaction mixture was stirred under reflux for 4hr., the formed precipitate, was filtered off, washed with methanol and diethylether then dried in vacuum.

4) Preparation of [In(L^2)$_3$(MCl_2)$_2$] complexes

(M=Co,Ni,Cu or Zn)

These complexes prepared using similar procedure as above.

Biological Activity

The antibacterial activity of indium compounds and their complexes were selected for screening by disc diffusion technique (10,11). The test disc were containing 200 microgram per disc of the compounds.

The activity was shown against staph (SPP.) *E.coli* and Candida albicans. Pencillin and Nystative were used as standard drugs. The inhibition zone (in mm) for the indium compounds and their complexes tested for antibacterial activity are listed in Table 3.

Results and Discussion

1- General properties

The compounds [In(L^1)$_3$] and [In(L^2)$_3$] were prepared through an oxidative addition reaction. These reactions are noticeably simpler than those used for preparation [M(SPh)$_n$] compound of main group elements involving the reaction of MCl_n with NaSPh or LiSPh (12). The mechanism of these reactions involves the initial cleavage of the S-S bond of the ligands to form the thiolate ions and the oxidation of indium metal from In^0 to In^{+3} (13) . Treatment of the indium compounds in alcohol with aqueous solution of metal chloride in (1:2) molar ratio gave the trinuclear complexes of the types [In(L^1)$_3$(MCl_2)$_2$] and [In(L^2)$_3$(MCl_2)$_2$]. The coordination of the sulphur atoms of the dithiocarbamate and thiolate ions of indium compounds and in the prepared complexes the amino groups are also responsible for the formation of these new complexes. The physical properties of the compounds and complexes are listed in (Table 1).

2- Physical properties

The compound and complexes are quite stable in dry air and melt or decompose over 159ºC. They are isoluble in most organic solvents but soluble in dimethyl formamide.

3- IR spectra

The most important IR assignment of indium compounds , and their complexes are listed in Table 2. The infrared spectra of the free disulfide were included here for comparison. The IR spectrum of the disulfide exhibit four bands due to the υ(C-S), υ(C=S), υ(C=N), υ(NH_2), and υ(S-S), at 990,1040,1595,3390 and 470 cm^{-1}. In the indium compounds the υ(NH_2) band appear at the same positions, indicating that this band was not shared in coordination, while the υ(S-S) band disappeared due to the cleavage of this bond as discussed before. The υ(C-S) band observed at lower frequency which indicate it was shared in coordination with indium. Further support of this coordination is provided by the appearance of new band at 340 and 360 cm^{-1} which tentatively attributed to υ(In-S) (9). The complexes display bands characteristic of coordinated dithiocarbamate ions, strong absorption in the 960-970, 1015-1026, 1460-1550, 3390-3400 cm^{-1} region due to υ(C-S), υ(C=S), υ(C-N), and υ(NH_2) (14). A shift to higher frequency in the υ(C-N) band in the complexes comparable to the dithiocarbamate ions indicating increase in the double bond order of the υ(C-N) (15). The shift to lower frequency in the υ(C=S) band indicating the involvement of sulphur atom of the compounds in the corrdination with Co(II),Ni(II),Cu(II) and Zn(II) metal ion, the band occurring near 380-390 cm^{-1} and 280-320 cm^{-1} have been assigned to the υ(M-S) and υ(M-Cl) modes. Also in complexes No.(1-5 and 7-10) the υ(NH_2) was shifted to a lower frequency by 90-110 cm^{-1} which indicate the nitrogen of the NH_2 group was shared in coordination with metal (II) ions (16). Furthermore, the IR spectra of the complexes (7-10), show the presence of a band at 840 cm^{-1} further suggests the presence of coordinated water molecules (17) . The appearance of two additional low frequency bands in the region 460-480 and 525-540 cm^{-1} is assignable to υ(M-N) and υ(M-O) respectively, further supporting our observation through nitrogen atom of the amine group and oxygen atoms of water molecules.

4- Electronic spectra and magnetic measurments

The electronic spectra of the compounds and their complexes were recorded as 10^{-3}M solution in DMSO and the results were presented in Table 3.

The bands observed at 39700,251nm -33222 cm^{-1},301nm (Table 3) due to disulfide ligands which may be assigned as n-π* or π-π* transitions respectively. The U.V spectral bands of the ligand were observed at higher region upon formation of the compounds which are observed at 28818-26809 cm^{-1} ,347-373nm. This can be attributed to the charge transfer from filled ligand or orbitals to the vacant indium orbitals (18).

The magnetic values of Co(II) complexes (No.2,7) are (2.3 and 4.61 B.M) these values correspond to low spin squre planar geometry for complexes (2) and octahedral environment for complex (7) (8). The electronic spectra of Co(II) complex (2) show a band at 15790 cm^{-1},(633nm) which may be assigned to $^2A_1g \longrightarrow {}^2Eg$ transition in square planar geometry and band at 26520 cm^{-1} , (377nm) which may be assigned as charge transfer.

The Co(II) complexes (No. 7) show the presence of two band in the region 13889,(719nm) and19379cm^{-1},(516nm) which are assigned to $^4T_1g(F) \longrightarrow {}^4A_2g(F)$ ($υ_2$) $^4T_1g(F) \longrightarrow {}^4T_2g(p)$($υ_3$) transition respectively .This shows that the positions of the electronic spectral band have changed from square planar to octahedral environment.

The magnetic moments of Ni(II) complexes (3 and 8) are (0.3 and 3.08 B.M) which suggest a square planar and octahedral geometry of these complexes .

The electronic spectra of Ni(II) complex (3) showed two bands at 11500cm^{-1}(869,5nm) and 25000cm^{-1}(400nm) (Table 3). These bands were assigned to $^1A_1g \longrightarrow {}^1B_2g$ and $^1A_1g \longrightarrow {}^1Eg$ transition . These results suggested a square planar geometry around the nickel ion (19).The Ni(II) complex (8) show the presences three bands in the region10384,(963nm)15898,(629nm) and21929cm^{-1},(456nm) which were assigned to $^3A_2g \longrightarrow {}^3T_2g(\upsilon_1)$, $^3A_2g \longrightarrow {}^3T_1g(F)(\upsilon_2)$ and $^3A_2g \longrightarrow {}^3T_1g(p)$ respectively . This show that the geometry of the complex is octahedral.

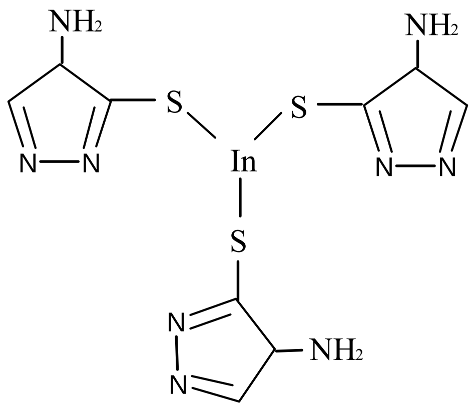
The magnetic moment of Cu(II) complexes (4 and 9) has been found (1.70 and 1.99 B.M) which indicate the presences of one unpaired electron. The electronic spectra of Cu(II) complex (No.4) showed band at 13300cm^{-1},(751nm) which are assigned to $^2T_2 \longrightarrow {}^2E$ transition tetrahedral environment (20). Three shoulder bands appear at 14300,(699nm)16600,(602nm) and 27700, cm^{-1},(316nm) in Cu(II) complex (No. 9) which may be assigned to $^2B_1g \longrightarrow {}^2A_1g$, $^2B_1g \longrightarrow {}^2B_2g$ and $^2B_1g \longrightarrow {}^2Eg$ transition respectively . This shows that the Cu(II) complex (9) have distorted octahedral geometry As the spectrum of Zn(II) complexes (5 & 10) are not well resolved, it is not interpreted, $\boldsymbol{\mu}_{\mathbf{eff}}$ values shows that they are diamagnetic as expected.

5- molar conductivity

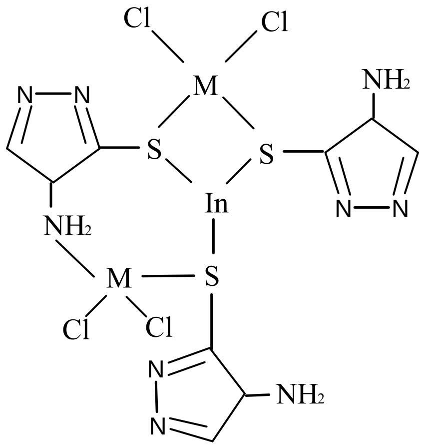
The molar conductivities of 10^{-3} M solution of compounds and complexes (Table 1) indicate that they are non-electrolyte in DMSO (21). From the above discussion, the following structures can be suggested for the compounds and complexes as in Fig 1.

6- Biological activity studies

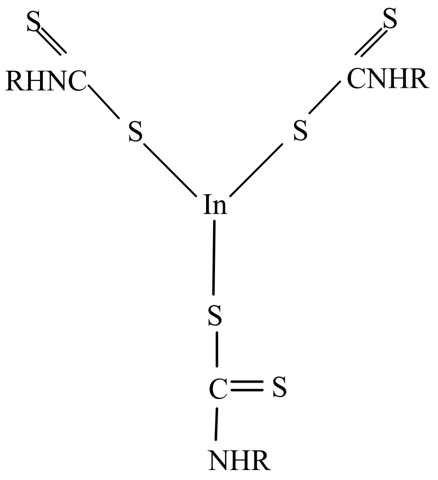
The biological studies revealed that the compounds and complexes (1-5) are effective against different microorganisms . The biological study (Table 4) indicate the indium compound $In(L^1)_3$ is the most active against all microorganism (22, 8), while the $[In(L^1)_3(MCl_2)_2]$, M=Ni, Co are the most effective toward *staphylococcus* as well as the complex $[In(L^1)_3(ZnCl_2)_2]$ is most effective toward candidia albicans also they showed to have better activity than standard reference (23) as shown in Fig 2.



(1)



(2-5)



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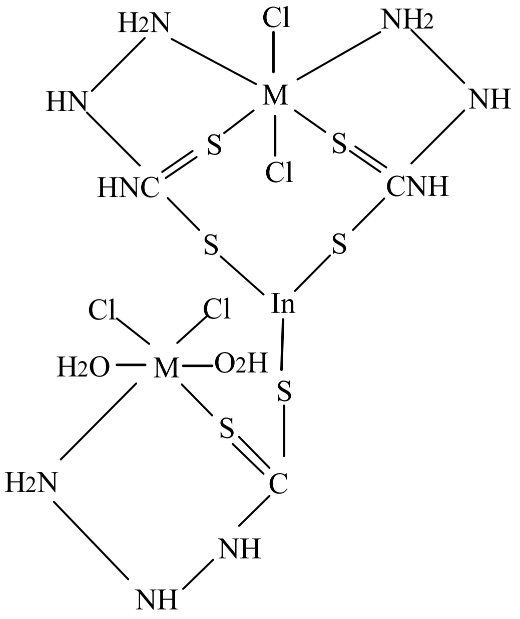

(7-10)

$R = NH_2CH_2CH_2NHCH_2CH_2NHCS_2$

M= Co,Ni,Cu,Zn

Fig1 : Suggested studies of the compound and complexes

Table 1: Physical properties ,conductance of the complexes

No.	compound	colour	Yield %	m.p (ºC)	Analysis % Found(calc.)		Ω ohm^1.cm^2. mol^{-1}
					In%	M	
1	[In(L^1)$_3$]	white	90	159	22.01 (22.08)	---	5
2	[In(L^1)$_3$(CoCl$_2$)$_2$]	Olive	80	195^d	14.69 (14.73)	15.09 (15.12)	12
3	[In(L^1)$_3$(NiCl$_2$)$_2$]	Green	85	200^d	14.71 (14.78)	15.01 (15.07)	10
4	[In(L^1)$_3$(CuCl$_2$)$_2$]	Brown	83	220	14.51 (14.55)	16.08 (16.12)	20
5	[In(L^1)$_3$(ZnCl$_2$)$_2$]	White	79	201-203	14.52 (14.56)	16.03 (16.08)	19
6	[In(L^2)$_3$]	White	92	180	17.41 (17.45)	---	8
7	[In(L^2)$_3$(CoCl$_2$)$_2$]	Dark green	83	201^d	12.43 (12.31)	12.80 (12.85)	18
8	[In(L^2)$_3$(NiCl$_2$)$_2$]	Green	80	223	12.49 (12.52)	12.79 (12.80)	16
9	[In(L^2)$_3$(CuCl$_2$)$_2$]	Olive	85	260	12.31 (12.34)	13.65 (13.72)	21
10	[In(L^2)$_3$(ZnCl$_2$)$_2$]	white	80	240	12.31 (12.39)	13.60 (13.64)	15

d= decomposition , * per metal ion

Table 2: Infrared of the compounds and complexes

No.	IR band assignments (cm^{-1})							
	υ(C – S)	υ(C = S)	υ(C = N)	υ(NH_2)	υ(M–S)	υ(M– Cl)	υ(M– N)	υ(M– O)
L_1	990	---	1460	3390	---	---	---	---
1	975	---	1470	3292	340	---	---	---
2	960	---	1490	3290	380	290	---	---
3	970	---	1500	3290	385	310	---	---
4	965	---	1550	3290	390	320	---	---
5	960	---	1540	3290	380	300	---	---
L_2	990	1040	1460	3400	---	---	---	---
6	965	1026	1495	3990	380	320	480	540
7	970	1020	1540	3290	370	310	460	525
8	960	1015	1550	3300	390	320	470	530
9	972	1018	1525	3290	385	300	465	540
10	970	1015	1530	3300	380	320	480	525

Table 3 : **Electronic spectral bands and magnetic measurements of the compounds and complexes**

No.	**compound**	**UV.Visible band λ_{max}(cm^{-1})**	**μ_{eff} (B.M)**
1	$[In(L^1)_3]$	39700,34330	**---**
2	$[In(L^1)_3(CoCl_2)_2]$	28818,27100	**2.31***
3	$[In(L^1)_3(NiCl_2)_2]$	15790,26520	**0.3**
4	$[In(L^1)_3(CuCl_2)_2]$	15000,25000	**1.70***
5	$[In(L^1)_3(ZnCl_2)_2]$	13300	**---**
6	$[In(L^2)_3]$	18800	**---**
7	$[In(L^2)_3(CoCl_2)_2]$	38900,33222	**4.61***
8	$[In(L^2)_3(NiCl_2)_2]$	28800,26809	**3.08***
9	$[In(L^2)_3(CuCl_2)_2]$	13889,19379	**1.99***
10	$[In(L^2)_3(ZnCl_2)_2]$	10384,15898,21929	**---**
		14300,16600,27700	
		21200	

Table 4: The antimicrobial activities of the complexes (1-5)

Microorganism tested	**complexes**					**Antibiotics**	
	1	**2**	**3**	**4**	**5**		
Staphylococus	20	24	26	18	15	18	Pencillin
E.coli	20	20	17	13	17	19	Pencillin
Candida albicans	17	15	13	10	18	15	Nystatine

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