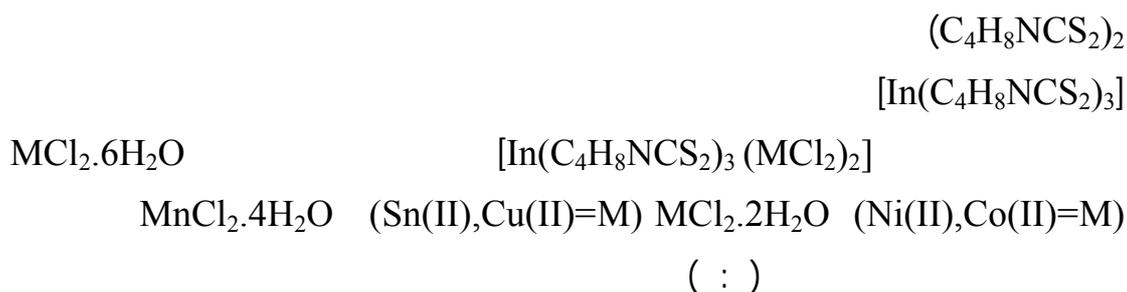


Synthesis and characterization of trinuclear complexes of Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , and Sn^{2+} with indium dithiocarbamate

N. H. Buttrus W. T. Al-Kattan S. A. Al-Sabaawi
Department of Chemistry / College of Science
University of Mosul

Received
03 / 02 / 2011

Accepted
26 / 06 / 2011



CHN

Sn(II) Cu(II) Mn(II)

Ni(II) Co(II)

Abstract:

Indium metal is reacted with dipyrrolidine disulfide ($C_4H_8NCS_2$)₂ in refluxing toluene, to give the compound [In($C_4H_8NCS_2$)₃] through an oxidative addition reaction. Trinuclear complexes of the general formula [In($C_4H_8NCS_2$)₃ (MCl₂)₂] were prepared by the direct reaction of metal salt with the above indium compound.

Additives of the new complexes with bipyridyl have been synthesized by the direct reaction between of the trinuclear complexes and the neutral ligand. The prepared compounds, complexes and adducts were characterized by using electric spectra, IR, electrical conductivity measurements, magnetic measurements, metal contents and CHN microanalysis.

The electronic spectra study and magnetic moment measurements indicate that Mn(II), Cu(II), Sn(II) complexes have tetrahedral geometry while their adducts have octahedral geometry and that, the Co(II) and Ni(II) complexes have square planer geometry and their adducts have octahedral geometry.

Introduction:

Dithiocarbamates own special significance due to their wide application as vulcanization additives, stabilizer for PVC, fungicides and anticancer agents^[1-3]. The recognition of the importance of Sn-S bond in biology has led to the study of organotin compounds with dithiocarbamates^[4]. They are given importance due to their use as chemoprotectants in platinum based chemotherapy^[5].

Novel transition metal dithiocarbamates of the types $[M_2(\text{etdtc})_2]$ and $[M'(\text{etdtc})Cl]_2$, where $M=Co(II)$, $Ni(II)$, $Cu(II)$, $Zn(II)$, $Cd(II)$, $Hg(II)$, $M'=Cr(III)$, $Fe(III)$ and $\text{etdtc}=(S_4N_4C_{11}H_{18})$ (which derived from the condensation reaction between acetylacetone, ethylenediamine and carbon disulfide in 1:2:2 molar ratio respectively), were synthesized by the use of self-assembly technique^[6].

The reaction of $[Ni_3(\text{dppm})_3(\mu_3-I)_2]$ where (dppm)= bis (diphenyl - phosphenomethane) with sodium trichlorostannate affords the first tin capped cluster $[Ni_3(\text{dppm})_3(\mu_3-I)(\mu_3-SnCl_3)](1)$. A site of coordinative unsaturation at tin can be introduced by the reaction of (1) with $Tl[PF_6]$ yielding the stannylene -capped cluster $[Ni_3(\text{dppm})_3(\mu_3I)(\mu_3-SnCl_2)]^+(2)$. Clusters, (1) and (2) were characterized by $^{31}PNMR$, X-ray diffraction and cyclic voltametry^[7].

Selenium and bismuth metals react with di-2-pyridyl disulfide (Py_2S_2) in refluxing toluene to give the compounds $Se(\text{Spy})_4$ and $Bi(\text{Spy})_3$ in high yield. Reactions of selenium or bismuth, with Py_2S_2 and iodine in different molar ratios led to the formation of $Se(\text{Spy})_3I$, $Se(\text{Spy})_2I_2$, $Bi(\text{Spy})_2I$ and $Bi(\text{Spy})I_2$, respectively. Their antibacterial activity was studied^[8].

Trinuclear complexes of the general formula $[Sn(SC_6H_4NH_2-o)_4(MCl_2)_2]$, $M=Ni(II)$, $Pd(II)$ or $Pt(II)$ were prepared by a direct reaction of $NiCl_2 \cdot 6H_2O$, Na_2PdCl_4 or K_2PtCl_4 with the tin compound $[Sn(SC_6H_4-NH_2-o)_4]$ ^[9]. The prepared compound and complexes were characterized by physico-chemical feature.

In view of these interesting results and as a continuation of our studies on transition and non-transition metal complexes with sulfur containing ligands^[10-12], we have prepared the indium compound $\text{In}(\text{C}_4\text{H}_8\text{NCS}_2)_3$ and the trinuclear complexes of general formula $[\text{In}(\text{C}_4\text{H}_8\text{NCS}_2)(\text{MCl}_2)_2] \text{M}=\text{Co}(\text{II}), \text{Ni}(\text{II}), \text{Cu}(\text{II}), \text{Sn}(\text{II})$, as well as their adducts by their reaction with the neutral ligand (bipyridyl).

Experimental:

All the chemicals used were of high purity according to the supplier (Fluka)

IR spectra were recorded on Tensor 27 Co. Bruker (FT-IR) spectro- photometer at the range $(200-4000) \text{ cm}^{-1}$ range using CsI disc. The metal content was estimated spectrophotometrically using Shimadza AA670. Analysis of the ligand and complexes was carried out using CHN elemental analyzer model Perkin 2400 at Al-al-Bayt University (Jordan). Melting point or decomposition temperature was determined on a Buchi 510 melting point apparatus and was uncorrected. Electronic spectra were obtained with a Shimadzu UV/Vis recording UV160 spectrophotometer at room temperature. The measurements were recorded using a concentration of 10^{-3} M of the complexes in DMSO. The magnetic moments were carried out at 25°C on the solid state, by Faraday's method using Bruker B.M.6 apparatus. Room temperature conductivity measurements were performed for 10^{-3} M solutions in DMSO using a conductivity meter model PCM3-Jenway.

Starting Material:

Indium metal (Fluka) was available in the form of 0.6cm diameter rods, toluene and 1-pyrrolidinedithionyl acid were used as supplied (Fluka). Dipyrrolidine disulfide was synthesized by standard methods^[13].

Synthesis:

Preparation of $\text{In}(\text{C}_4\text{H}_8\text{NCS}_2)_3$:

A mixture of finely cut indium metal (1.14g, 10mmol) was refluxed vigorously with the ligand (pyrrolidine disulfide) $(\text{C}_4\text{H}_8\text{NCS}_2)_2$ (4.37g, 15mmol) in toluene (25 cm^3) for 10 h., during this 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 ($2 \times 10 \text{ cm}^3$) and dried under vacuum.

Preparation of $[\text{In}(\text{C}_4\text{H}_8\text{NCS}_2)_3(\text{MCl}_2)_2]$ complexes: (M=Mn(II), Co(II), Ni(II), Cu(II) or Sn(II)).

A clear solution of $\text{In}(\text{C}_4\text{H}_8\text{NCS}_2)_3$, (0.54 g, 1 mmol) in methanol (10 cm^3) was added to a solution of $\text{MCl}_2 \cdot 6\text{H}_2\text{O}$ $\text{M}=\text{Co}(\text{II}), \text{Ni}(\text{II}),$

$CuCl_2 \cdot 2H_2O$, $MnCl_2 \cdot 4H_2O$ or $SnCl_2 \cdot 2H_2O$ (2 mmol) in ethanol ($10cm^3$). The reaction mixture was stirred under reflux for 4h., the formed precipitate, was filtered off, washed with ethanol and diethylether and then dried under vacuum.

Preparation of $[In(C_4H_8NCS_2)_3(MCl_2)_2(Bipy)_2]$

A clear solution of $[In(C_4H_8NCS_2)_3(MCl_2)_2]$ (1 mmol) in dimethylformamide ($10 cm^3$) was added to a solution of bipyridyl (0.31g, 2mmol) in ethanol ($10cm^3$). The mixture was stirred under reflux for 2h., the formed precipitate, was filtered off, washed with ethanol and diethyl ether and then dried under vacuum.

Results and discussion:

The direct reaction of the ligand dipyrrolidine disulfide with indium metal in refluxing toluene in a (1:1.5) metal to ligand molar ratio afforded the compound $In(C_4H_8NCS_2)_3$ through an oxidative addition reaction^[14]. The mechanism of the reaction involves oxidation of indium metal from In^0 to In^{+3} and the initial cleavage of $-S-S-$ bond to form the dithiocarbamate ion and affords the indium dithiocarbamate compound. Treatment of the above indium compound with alcoholic solution of metal chloride in (1:2) molar ratio gave the trinuclear complexes of the type $[In(C_4H_8NCS_2)_3(MCl_2)_2]$.

The nucleophilicity of CS_2^- group of the dithiocarbamate in indium compound is responsible for the formation of these new complexes.

Adducts of the prepared complexes with bipyridyl were prepared through the reaction of these new complexes with bipyridyl in (1:2) molar ratio. The physical properties of the compound, trinuclear complexes and their adducts are listed in (Table 1).

The complexes are quite stable in dry air and melt or decompose at a degree above $200^\circ C$. They are insoluble in most organic solvents but soluble in dimethyl formamide (DMF) or dimethylsulfoxide (DMSO).

The most important IR assignment of indium compound and its complexes are listed in Table 2. The IR bands of the free disulfide exhibit bands due to $\nu(S-S)$, $\nu(C=S)$, $\nu(C-S)$, $\nu(C-N)$ and $\nu(C-H)$ at 452, (997-1035), 874, 1460 and $2972 cm^{-1}$. In the indium compound, the $\nu(C-N)$ band observed at higher frequency due to the increase of bond order, the $\nu(C=S)$ bond appeared at the same position, while the $\nu(C-S)$ band observed at lower frequency which indicates that it was shared in coordination with indium. Further support for this coordination is provided by the appearance of new bands at $360cm^{-1}$ which tentatively attributed to $\nu(In-S)$ ^[15]. The trinuclear complexes display bands characteristics of coordinated dithiocarbamate ions, strong absorption in the (814-853), (932- 1023), and (1467-1489) cm^{-1} region, due to $\nu(C-S)$,

$\nu(\text{C}=\text{S})$, and $\nu(\text{C}-\text{N})$ ^[16] respectively. A shift to higher frequency in the $\nu(\text{C}-\text{N})$ band in the complexes when compared with dithiocarbamate ion indicates increase of the double bond order of the $\nu(\text{C}-\text{N})$ ^[17]. The shift to lower frequency in the $\nu(\text{C}=\text{S})$ band indicates involvement of sulfur atoms of the indium compound, in coordination with Mn(II), Co(II), Ni(II), Cu(II) and Sn(II) metal ions. The bands occurring at 370-390 cm^{-1} and 280-320 cm^{-1} have been assigned to the $\nu(\text{M}-\text{S})$ and $\nu(\text{M}-\text{Cl})$ modes, while the $\nu(\text{M}-\text{N})$ for pyridyl ligand are in good agreement with the reported values of Nakamoto ^[18] which fall in the 480-510 cm^{-1} .

The electronic spectra of the ligand, indium compound and their complexes were recorded as 10^{-3} M solution DMSO and the results were presented in Table 3. The bands observed at 35714 cm^{-1} and 32467 cm^{-1} are due to disulfide ligand which may be assigned as $n-\pi^*$ or $\pi-\pi^*$ transition respectively. The UV spectral bands of the ligand were shifted to higher region upon formation of the indium compound, which are observed at 33112 cm^{-1} and 27027 cm^{-1} respectively. This can be attributed to the charge transfer from filled ligand orbitals to the vacant indium orbital ^[19].

The high spin tetrahedral Mn(II) complexes exhibit spin forbidden transition unlike their octahedral analogues which show both spin forbidden as well as parity forbidden bands ^[20]. This accounts for extreme pale colour in case of the octahedral complexes. The pale yellow coloured Mn (II) complex (2) shows a solitary d-d band at 22935 cm^{-1} assigned to ${}^6\text{A}_1\text{g} \longrightarrow {}^4\text{T}_1\text{g}(\text{G})$ transition. It also exhibits a broad strong charge transfer band centered at 25641 cm^{-1} . The magnetic moment of 5.82 B.M which is in proximity with the calculated spin-only value of 5.9 B.M indicates high spin tetrahedral arrangement of Mn (II) ion.

However, the Mn (II) complex (3) depicts two weak intensity bands at 21459 cm^{-1} and 25380 cm^{-1} which have been assigned to ${}^6\text{A}_1\text{g} \longrightarrow {}^4\text{T}_1\text{g}(\text{G})$, ${}^6\text{A}_1\text{g} \longrightarrow {}^4\text{T}_2\text{g}(\text{P})$ transitions, respectively ^[21]. The low magnetic moment (5.69 B.M) might be due to distortion from regular high spin octahedral field ^[22].

The magnetic values of Co (II) complexes (4,5) are (2.45 and 4.99 B.M). These values correspond to low spin square planer geometry for complex (4) and high spin octahedral environment for complex (5). The electronic spectra for complex (4) show a band at 15432, 25510 cm^{-1} which may be assigned to ${}^2\text{A}_1\text{g} \longrightarrow {}^2\text{B}_1\text{g}(\nu_2)$ and ${}^2\text{A}_1\text{g} \longrightarrow {}^2\text{E}_\text{g}(\nu_3)$ transitions in square planer geometry and a band at 30674 cm^{-1} which may be assigned as charge transfer ^[23].

The Co (II) complex (No.5) shows the presence of three bands in the region 12500 cm^{-1} , 17301 and 34722 cm^{-1} which are assigned to ${}^4\text{T}_1\text{g}(\text{F}) \longrightarrow {}^4\text{A}_2\text{g}(\text{F})(\nu_2)$, ${}^4\text{T}_1\text{g}(\text{F}) \longrightarrow {}^4\text{T}_1\text{g}(\text{P})(\nu_3)$ and charge transfer transitions, respectively. This shows that the position of the electronic

spectral band have changed from square planar to octahedral environment [24].

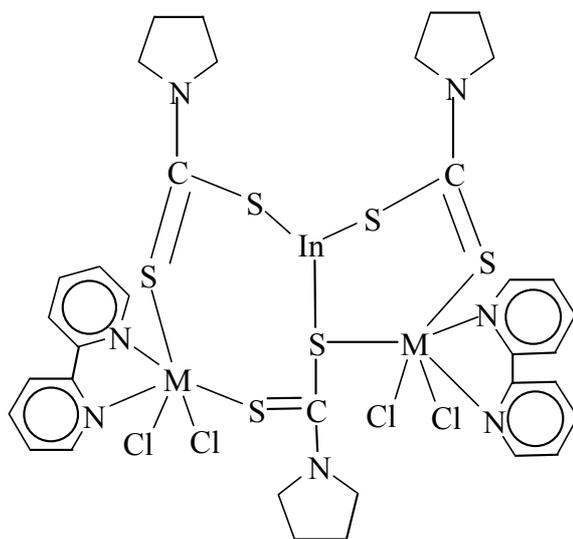
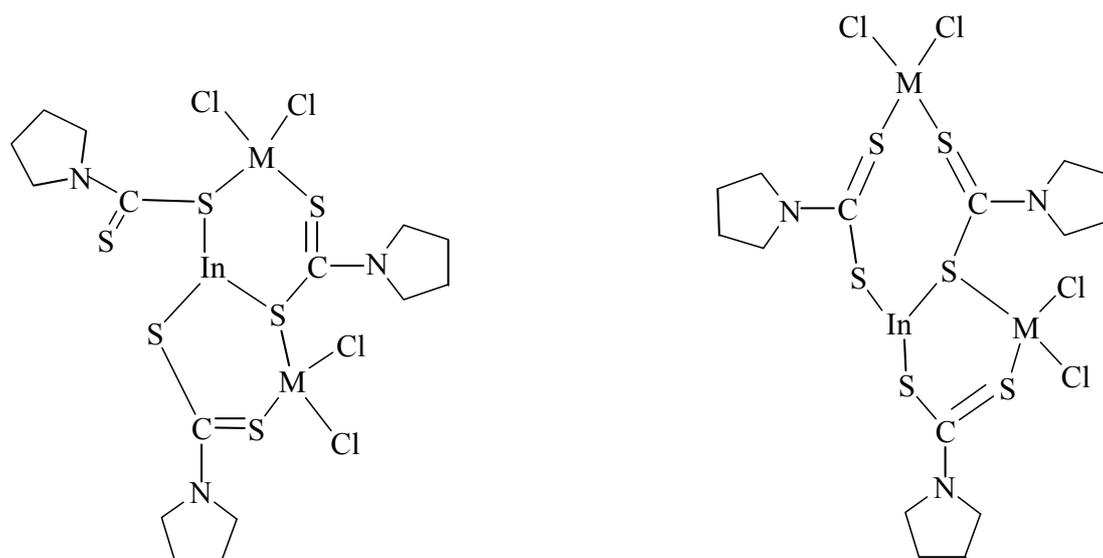
The magnetic measurement indicates that the Ni(II) complex (6) is diamagnetic while the magnetic moment of the complex(7) is 2.92 B.M which suggest a square planner and octahedral geometry of these complexes respectively.

The electronic spectra of Ni(II) complex (6) showed two bands at 15625cm^{-1} and 20746cm^{-1} . These bands were assigned to ${}^1A_{1g} \longrightarrow {}^1A_{2g}(\nu_1)$ and ${}^1A_{1g} \longrightarrow {}^1B_{1g}(\nu_2)$ transition. These results suggest a square planar geometry around the nickel ion [23]. The Ni(II) complex(7) show the presence of three bands in the region 10224cm^{-1} , 15151cm^{-1} and 25641cm^{-1} which were assigned to ${}^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F)(\nu_1)$, ${}^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F)(\nu_2)$ and ${}^3A_{2g}(F) \longrightarrow {}^3T_{1g}(P)(\nu_3)$ respectively. This show that the geometry of the complex is octahedral [25].

The magnetic moment of Cu(II) complexes (8,9) has been found to be (1.71, 2.01 B.M) which indicate the presence of one unpaired electron. The electronic spectra of Cu(II) complexes (8) showed a band at 13315cm^{-1} which was assigned to ${}^2T_2 \longrightarrow {}^2E$ transition in tetrahedral environment. Two bands appear at 14306cm^{-1} and 28089cm^{-1} in Cu(II) complex (9) which assigned to the three combined d-d transitions (${}^2B_{1g} \longrightarrow {}^2A_{1g}$, ${}^2B_{1g} \longrightarrow {}^2B_{2g}$, ${}^2B_{1g} \longrightarrow {}^2E_g$) and a charge transfer band respectively. This shows that the Cu(II) complex as have octahedral geometry [26].

The electronic spectra of Sn(II) complexes (10,11) showed bands at 37878cm^{-1} and 34013cm^{-1} respectively, these bands were assigned to the transfer transitions. Physico-chemical data for (10,11) complexes suggest that they based on stoichiometry Sn(II) four and six coordination respectively.

The ligand used in this study was coordinated to indium metal through the sulfur atoms only but for the complexes, the coordination of the metal ions occur through the uncoordinated C=S and the nucleophilicity sulfur atoms attached to indium, as shown in Fig 1:



Complexes No. (3, 5, 7, 9, 11)
 $M = Mn^{+2}, Co^{+2}, Ni^{+2}, Cu^{+2}, Sn^{+2}$

Fig 1 : Suggested structure for the prepared complexes

Table 1: Some physical properties of the ligand and its complexes

No.	Complexes	Colour	M.P (°C)	Analysis Cal. (Found) %				M% Obs. (calc.)	Cond. Λ $Ohm^{-1}.cm^2.mol^{-1}$
				C	H	N	S		
	$(C_4H_8NCS_2)_2$	Pale yellow	133-134	41.01 (41.32)	5.47 (5.61)	9.57 (9.65)	43.75 (43.81)	----	----
1.	$[In(C_4H_8NCS_2)_3]$	Grey	200*	32.51 (32.75)	4.33 (4.61)	7.59 (7.62)	34.67 (34.72)	----	3.0
2.	$[Mn_2In(C_4H_8NCS_2)_3Cl_4]$	Pale yellow	275*	22.35 (22.44)	2.98 (3.09)	5.21 (5.36)	23.84 (23.89)	----	5.7
3.	$[Mn_2In(C_4H_8NCS_2)_3(bip)_2]$	Yellowish	300	37.57 (37.64)	3.58 (3.83)	8.77 (8.91)	17.18 (17.23)	----	13.5
4.	$[Co_2In(C_4H_8NCS_2)_3Cl_4]$	Pale green	200	20.33 (20.53)	2.71 (2.93)	4.74 (4.79)	21.69 (21.71)	6.66 (6.36)	1.9
5.	$[Co_2In(C_4H_8NCS_2)_3(bip)_2]$	Brown	300	35.07 (35.16)	3.34 (3.42)	8.18 (8.21)	16.03 (16.15)	4.93 (4.85)	5.2
6.	$[Ni_2In(C_4H_8NCS_2)_3Cl_4]$	Dark yellow	250	22.14 (22.27)	2.95 (3.12)	5.17 (5.23)	23.612 (23.83)	7.22 (7.12)	5.5
7.	$[Ni_2In(C_4H_8NCS_2)_3(bip)_2]$	Yellowish green	300*	37.32 (37.54)	3.55 (3.63)	8.71 (8.91)	17.06 (17.25)	5.22 (5.01)	3.7
8.	$[Cu_2In(C_4H_8NCS_2)_3Cl_4]$	Dark grey	300	21.88 (21.92)	2.92 (2.99)	5.11 (5.34)	23.34 (23.93)	7.78 (7.57)	5.0
9.	$[Cu_2In(C_4H_8NCS_2)_3(bip)_2]$	Dark brown	300	37.01 (37.08)	3.52 (3.63)	8.63 (8.80)	16.92 (16.99)	5.64 (5.33)	5.4
10.	$[Sn_2In(C_4H_8NCS_2)_3Cl_4]$	Pale yellow	240	19.30 (19.43)	2.57 (2.64)	4.50 (4.62)	20.58 (20.61)	----	15.3
11.	$[Sn_2In(C_4H_8NCS_2)_3(bip)_2]$	Beije	300	33.73 (33.88)	3.21 (3.29)	7.87 (7.95)	15.42 (15.66)	----	34.7

* Decomposition temperature

Table 2: Infrared spectral data of the ligand and its complexes

No.	Complexes	IR spectral bands (cm ⁻¹)						
		ν (C=S)	ν (C-S)	ν (C-N)	ν (C-H)	ν (M-S)	ν (M-Cl)	ν (M-N)
	(C ₄ H ₈ NCS ₂) ₂	997 _s , 1035 _s	874 _m	1460 _s	2972 _m	----	----	----
1.	[In(C ₄ H ₈ NCS ₂) ₃]	997 _s , 1034 _s	863 _m	1475 _s	2942 _m	360 _m	----	----
2.	[Mn ₂ In(C ₄ H ₈ NCS ₂) ₃ Cl ₄]	947 _s	830 _m	1483 _s	2976 _m	375 _w	320 _w	----
3.	[Mn ₂ In(C ₄ H ₈ NCS ₂) ₃ (bip) ₂]	1013 _s	819 _m	1472 _s	2975 _m	380 _m	285 _w	490 _s
4.	[Co ₂ In(C ₄ H ₈ NCS ₂) ₃ Cl ₄]	1023 _s	838 _m	1469 _s	2971 _m	370 _w	291 _w	----
5.	[Co ₂ In(C ₄ H ₈ NCS ₂) ₃ (bip) ₂]	1023 _s	835 _m	1472 _s	2959 _m	383 _w	295 _w	480 _m
6.	[Ni ₂ In(C ₄ H ₈ NCS ₂) ₃ Cl ₄]	946 _s	823 _m	1468 _s	2980 _m	390 _w	315 _m	----
7.	[Ni ₂ In(C ₄ H ₈ NCS ₂) ₃ (bip) ₂]	1019 _s	853 _m	1468 _s	2963 _m	385 _w	300 _w	502 _w
8.	[Cu ₂ In(C ₄ H ₈ NCS ₂) ₃ Cl ₄]	946 _s	844 _m	1467 _s	2964 _m	378 _m	305 _w	----
9.	[Cu ₂ In(C ₄ H ₈ NCS ₂) ₃ (bip) ₂]	1021 _s	830 _m	1489 _s	2957 _m	382 _m	280 _s	510 _w
10.	[Sn ₂ In(C ₄ H ₈ NCS ₂) ₃ Cl ₄]	932 _s	814 _m	1488 _s	2976 _m	372 _w	298 _w	----
11.	[Sn ₂ In(C ₄ H ₈ NCS ₂) ₃ (bip) ₂]	1005 _s	842 _m	1480 _s	2970 _m	381 _m	282 _w	496 _m

s= strong, m= medium, w=weak

Table 3: Magnetic moments and the electronic spectral data of the ligand and its complexes.

No.	Complexes	μ_{eff} (B.M)	Assignment	Band maxima λ (cm^{-1})
	$(C_4H_8NCS_2)_2$		$n \longrightarrow \pi^*$ $\pi \longrightarrow \pi^*$	35714, 32467
1.	$[In(C_4H_8NCS_2)_3]$	Diamagnetic	C.T	33112, 27027
2.	$[Mn_2In(C_4H_8NCS_2)_3Cl_4]$	5.82	${}^6A_{1g} \longrightarrow {}^4T_{1g}(G)$ C.T	22935, 25641, 37313
3.	$[Mn_2In(C_4H_8NCS_2)_3(bip)_2]$	5.69	${}^6A_{1g} \longrightarrow {}^4T_{1g}(G)$ ${}^6A_{1g} \longrightarrow {}^4T_{2g}(P)$ C.T	21459, 25380, 35971
4.	$[Co_2In(C_4H_8NCS_2)_3Cl_4]$	2.45	${}^2A_{1g} \longrightarrow {}^2B_{1g}$ ${}^2A_{1g} \longrightarrow E_g$ C.T	15432, 25510, 30674
5.	$[Co_2In(C_4H_8NCS_2)_3(bip)_2]$	4.99	${}^4T_{1g}(F) \longrightarrow {}^4A_{2g}(F)$ ${}^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$ C.T	12500, 17301, 34722
6.	$[Ni_2In(C_4H_8NCS_2)_3Cl_4]$	Diamagnetic	${}^1A_{1g} \longrightarrow {}^1A_{2g}$ ${}^1A_{1g} \longrightarrow {}^1B_{1g}$ C.T	15625, 20746, 32258
7.	$[Ni_2In(C_4H_8NCS_2)_3(bip)_2]$	2.92	${}^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F)$ ${}^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F)$ ${}^3A_{2g}(F) \longrightarrow {}^3T_{1g}(P)$	10224, 15151, 25641
8.	$[Cu_2In(C_4H_8NCS_2)_3Cl_4]$	1.71	${}^2T_{2g} \longrightarrow {}^2E$ C.T	13315, 36764
9.	$[Cu_2In(C_4H_8NCS_2)_3(bip)_2]$	2.01	$B_{1g} \longrightarrow {}^2A_{1g}$ C.T	14306, 28089
10.	$[Sn_2In(C_4H_8NCS_2)_3Cl_4]$	Diamagnetic	C.T	37878
11.	$[Sn_2In(C_4H_8NCS_2)_3(bip)_2]$	Diamagnetic	C.T	34013

References:

- 1) G.Faraglia, S.Sitran and D. Montagner, Inorg. Chim. Acta. 358, 971 (2005).
- 2) O. Guzd and A. Salman, Biorg. Med. Chem., 14, 7804 (2006).
- 3) P. J. Heard, Prog. Inorg. Chem. 53, 1, (2005).
- 4) S. Ozkirimli, T. I. Apak,, M. Kiraz and Y. Yegenolglu, Arch. Pharm. Res., 28, 1213 (2005).
- 5) H. Imamura, N. Ohtak, H. Jona, A. Shmizu, M. Moriya, H. Sato, Y. Sugimoto, C. Ikeura, H. Kiyonaga, M. Nakamo, R. R. Nagano, S. Abe, K. Yamada, P. Hashizume and H. Morishima Bio-org. Med. Chem. 9, 1571 (2001).

- 6) K. S. Siddqi, S. A. A. Nami and L. Y. Chebude, *J. Braz. Chem. Soc.*, 17 (1), 1 (2006).
- 7) B. Breedlove, P. E. Fanwick and C. P. Kubiak, *Inorg. Chem.*, 41, 4306 (2002).
- 8) N. H. Buttrus, Z. U. Jassim and T. A. K. Al-Allaf, *J. J. Appl. Sci.*, 7(2), 92, (2005).
- 9) L. J. Al-Haylay, N. H. Buttrus, F. Tarq. and T. A. K. Al-Allaf. *J. J. Appl. Sci.*, 7(1), 64, (2005).
- 10) N. H. Buttrus, Z. U. Jassim, *J. Edu. And Sci.*, 22(2), 1, (2009).
- 11) N. H. Buttrus and W. T. Al-Kattan, *Orient, J. Chem.* 25(4), 885 (2009).
- 12) N. H. Buttrus, S. H. Al-Smaan and S. M. Al-Asalli, *International, J. Chem.*, 20(1), 37 (2010).
- 13) I. Haiduc and L. Y. Goh, *Coord. Chem-Rev.*, 224, 151, (2002).
- 14) N. H. Buttrus, *Synth. React. Inorg. Met-Org. Chem* 28(10), 1643, (1998).
- 15) R. K. Chadha, R. Kumar and D. G. Tuck, *Polyhedron*, 7, 1121 (1988).
- 16) N. Singh and L. B. Prashed, *Synt. React. Inorg., Met-Org. Chem.* 28(6) 929 (1998).
- 17) S. Khan, S. A. A. Nami and K. S. Siddiqi, *J. Organo-Met. Chem.*, 693, 1049 (2008).
- 18) N. Nakamoto, "Infrared and Raman spectra of Inorganic and coordination compounds". Wiley Intarsince, New York (1997).
- 19) N. H. Buttrus, A. F. Al-Omri and E. Yassin, *National J. Chem.*, 37, 101 (2010).
- 20) F. A. Cotton and G. Wilknozon, "Advance Inorganic Chemistry", Wiley & Sons, New York (1988).
- 21) L. K. Gupta and S. Chandra, *Spectrochim. Acta Part A* 65, 792, (2006).
- 22) K. S. Siddiqi, S. A. A. Nami and Y. C. Lufullah, *Synth. React. Inorg. Met-Org. Nano-Met. Chem*, 35, 445 (2005).
- 23) N. Bicak and T. Atay, *Turk. J. Chem.*, 22, 261 (1998).
- 24) K. S. Siddiqi, S. Khan, S. A. A. Nami and M. M. El-Ajaily, *Spectrochim. Acta Part A* 67, 995, (2007).
- 25) R. Gup and B. Kirtan, *Spectrochim. Acta Part A* 64, 809, (2006).
- 26) M. A. Zayed, F. A. Nour El-Dien, G. G. Mohamed and N. E. A. El-Gamal, *Spectrochim. Acta Part A* 60, 2843, (2004).