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Synthesis and characterization of trinuclear complexes of Co^{+2}, Ni^{+2} and Cu^{+2} with tetrakis (dithiophosphate) tin

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Abstracts: Tin metals react with bis (thiophosphoryl) disulfanes ($(RO)_2PS_2)_2$, R= Et , ^{i}Bu , ^{t}Bu in refluxing toluene to give the compounds $[Sn(S_2P(OR)_2)_4]$ through oxidative addition reaction . Trinuclear compounds of the general formula $[SnM_2\{S_2P(OR)_2\}_4Cl_4(PPh_3)_4]$ where prepared by direct reaction of $MCl_2(H_2O)_6$ M=Ni , Co,$CuCl_2$.$2H_2O$ and PPh_3 in(1:2:4) molar ratio (L:M: PPh_3) with above tin compounds. The prepared compounds and complexes were characterized by different physicochemical, spectra method (IR and UV/Vis) elemental analysis, metal content, conductivity measurement and magnetic measurements .The results electronic spectra and magnetic measurements indicate that the complexes contain an octahedral geometry.

Introduction

The structural chemistry of metal complex and organometallic dithiophosphates, dithio phosphinates and dithiophosphonates has been reviewed. The remarkable ability of the dithiophosphorus ligands to display abroad diversity of coordination patterns is very important [1-4]. A new organodithiophosphorns derivative , namely o-(1,3-bispiperidino – 2- propyl) -4- methoxy phenyl dithiophosphonate was synthesized and then the kinetic behavior of the transport process as a function of concentration , temperature , stirring rate and solvent was investigated [5] .Reaction of Fe (S)pS_2p(S)Fe with NaOR [R=Me , ^{i}pr] gives the non-symmetric phosphonodiothioato anions $[Fe(RO)PS_2]^-$ which can be complexed to arange of metals . The square planar $[NiL_2]$ complexes adopt two distinct configuration cis and trans, while the zinc and cadmium complexes adopt dimeric$[M_2L_4]$ structures. All new compounds have been characterized spectroscopically and seven X- ray structures are reported [6].

Selenium and bismuth reacts with di – 2 – pyridyl disufide (Py_2S_2) in refluxing toluene to give the compounds $Se(SPy)_4$ and $Bi(SPy)_3$ in high yield . Reaction of Selenium and bismuth , with Py_2S_2 and iodine in different molar ratio led to the formation of $Se(SPy)_3$ I , $Se(SPy)_2I_2$,Bi($SPy)_2I_2$ and Bi $(SPy)_3$ I respectively [8] .Trinuclear complexes of the general formula $[Sn(SC_6H_4X)_4 (MCl_2)_2]$ X=NH_2-o , H , M = Ni(II), Pd(II) or Pt(II) were prepared by a direct reaction of $NiCl_2.6H_2O$, Na_2PdCl_4 or K_2PtCl_4 with the tin compound $[Sn(SC_6H_4X)_4]$ .The prepared compounds and complexes were characterized by physico-chemical analysis [9] .In view of these interesting results and due to the importance of metal complexes with dithiophosphate in different fields , we have prepared the tin compounds$[Sn(S_2P(OR_2)]_4$ and its trinuclear complexes of general formula $[SnM_2\{S_2P(OR)_2\}_4Cl_4(PPh_3)_4]$ where M=Co^{+2}, Ni^{+2} , Cu^{+2} , R= Et , ^{i}Bu , ^{t}Bu.

Experimental

General

All reagent used were either analytical or chemically pure , were purchased from commercial source (BDH or Fluka). Preparative work was carried out under dry nitrogen gas using standard schlenk techniques.

Physical measurements

Infrared spectra were recorded on Brucker Tensor 27CO.FTIR spectrophotometer in the 200-4000 cm^{-1} range using CsI discs. Elemental analysis (CHS) were carried out using microanalytical techniques perkin Elmer 2400 at AL-Albait University (Jordan). Metal content were determined spectrophotometrically using AA670 atomic absorption. Conductivity measurement were carried out on 10^{-3}M solution of the complexes in DMSO using conductivity meter PCM3 Jenway at ambient temperature. The electronic spectra were recorded on a Shimadzu UV-Visible spectrophotometer UV/160 for 10^{-3} M solution of the complexes in DMSO at 25°C. The magnetic moments were carried out at °C on the solid state by Farady's method using Brucker BM6 apparatus.

Starting materials

The ligands of the type $(RP)_2P(S)SS(S)P(OR)_2$, R=Et, ^{i}Bu, ^{t}Bu was synthesized by using standard methods [10].

Synthesis

Preparation of $[Sn\{S_2P(OR)_2\}_4]$

A mixture of finely eat tin metal (1.19 g, 0.01 mol) was refluxed vigorously with the ligand diethyldithiophophoryl disulfide (7.40g,0.02 M) or disobutyl dithiophosphoryl disulfide(9.64g,0.02M) or ditertiary butyl dithiophosphoryl disulfide (0.02 mol) in toluene ($30cm^3$) was refluxed for 10h. The reaction mixture was filtered off through cellite and the resultant solution was reduced to $10cm^3$ of its volume by evaporation. The solid thus obtained after cooling at room temperature , was washed with petroleum ether (60-80°C) and dried under vacuum for several hours.

Preparation of $[SnM_2\{S_2P(OR)_2\}_4Cl_4(PPh_3)_4]$ complexes

A clear solution of $[Sn\{S_2P(OR_2)_2\}_4]$ (1mmol) in methanol (10 cm^3) was added to a solution of $MCl_2.6H_2O$, $M=Co^{+2},Ni^{+2}$(0.02 M) or $CuCl_2.H_2O$ (0.02 M) in ethanol ($10cm^3$) and PPh_3 (9.16g,0.04 M) in ethanol (15 cm^3). The reaction mixture was stirred under reflux for 4h., the formed precipitate , was filtered off, washed with ethanol and diethyl ether then dried under vacuum.

Results and Discussion

The direct reaction of the ligand bis (thiophosphoryl) disulfide with tin metal in refluxing toluene using a (1:2) metal to ligand molar ratio afforded the compounds $[Sn\{S_2P(OR)_2\}_4]$ through an oxidative addition reaction [11]. The mechanism of the reaction involves the oxidation of tin metal from Sn^0 to Sn^{+4} and the initial cleavage of –S-S- bond to from the $-S_2P(OR)_2$ions, then to give the tin compounds. Treatment of the above tin compounds with $MCl_2.6H_2O$ (Co^{+2},Ni^{+2}) or $CuCl_2.2H_2O$ and triphenylphosphine in (1:2:4) molar ratio gave the trinuclear complexes of the types $[SnM_2\{S_2P(OR)_2\}_4Cl_4(PPh_3)_4]$, M= Co^{+2},Ni^{+2},Cu^{+2}. The nucleophilicity of PS_2- of dialkyldithiophosphate in the tin compounds are responsible for the formation of these new complexes. The physical properties of the compound and trinuclear complexes are listed in Table 1. All complexes are thermally stable and insoluble in organic solvent, however fair solubility in DMSO and DMF. The molar conductivities of 10^{-3}M solution of tin compounds and their trinuclear complexes (Table1) indicate that they are non electrolytes[12].

The most important IR assignment of tin compounds and the trinuclear complexes are listed in Table2. The IR spectra of the disulfide ligands exhibitbands due to υ(S-S), υ(P=S),υ(P-S),υ(P-C) at 440-480,700-727,529-556 sym., 600-630 asy. , and 1100-1150 cm^{-1}. In the tin compounds the band due to (P=S) appear at the same position, while the υ(P-S) band observed at lower frequencies which indicate that it was shared in coordination with tin metal. Further support of this coordination is provided by the appearance of new bands at 350-370 cm^{-1}, which tentatively attributed to υ(Sn-S)[13]. The trinuclear complexes display bands characteristic of coordinated dialkyldithiophosphate ion, showing absorption in the (502-609) and (653-695)cm^{-1} region due to υ(P-S) and υ(P=S)[14] respectively. The shift to lower frequency in the υ(P=S) bond indicate the involvement of sulfur atoms of the tin compounds in coordination with Co(II), Ni(II),Cu(II) and Zn(II) metal ions, the band occurring at (460-390)cm^{-1} and (290-320)cm^{-1} have been assigned to υ(M-S) and υ(M-Cl) modes[15]. The electronic spectra of the ligands, tin compounds and their complexes were recorded as 10^{-3} M solution in DMSO and the results presented in Table 2. The bands observed at39100-42000 cm^{-1} are due to the disulfide ligands which may be assigned as n-π* or π-π* transitions respectively. The U.V spectral bands of the ligands were shifted to higher region upon formation of the tin compounds. which are observed at (37878-27100)cm^{-1} respectively. This can be attributed to the charge transfer from filled ligands orbitals to the vacant tin orbital[16].

The experimental magnetic moment for each complex is listed in Table 1. The magnetic moment give an idea about the electronic state of the metal ion in the complex. The magnetic moment are (4.79-5.10)B.M for Co(II) complexes (1,4 and 7) respectively , while for Ni(II) complexes (2,5and8) are (3.09-3.49) B.M for Cu(II) complexes (3,6 and 9) are (1.89-2.09) B.M suggest the presence of one unpaired electron and Zn(II) complexes diamagnetic .

The electronic spectra of cobalt (II) complexes (1,4 and 7) shows two bands at (14727-14947 and 18050-21500) cm^{-1} these bands are assigned to

$^4T_1g(F) \longrightarrow {}^4A_2g(F)(\upsilon_2)$ and $^4T_1g(F) \longrightarrow {}^4T_2g(p)$ (υ_3) respectively. Further the dark blue to green colors of these complexes support the octahedral geometry[17].

Nickel complexes (2,5 and 8) exhibit three bands at (10718-10775) (1426-15384) and (22883-26581) cm^{-1} corresponding to the transitions $^3A_2g(F) \rightarrow {}^3T_2g(F)(\upsilon_1)$, $^3A_2g(F) \rightarrow {}^3T_1g(F)(\upsilon_2)$ and $^3A_2g(F) \rightarrow {}^3T_1g(P)(\upsilon_3)$ respectively. These finding and the magnetic moment values are in favour of an octahedral geometry for Ni(II)complexes [18]. The copper (II) complexes (3,6 and 9) shows abroad bands peaking at (14128-16526)cm^{-1} This bands may arise from the $^2Eg \rightarrow {}^2T_2g$ transition in octahedral field[19].

The ligands used in this study was coordinated to tin metal through the sulphur atom only, while for the complexes, the coordination of the metal ions occur through the uncoordinated υ(P=S) as shown in Fig 1.

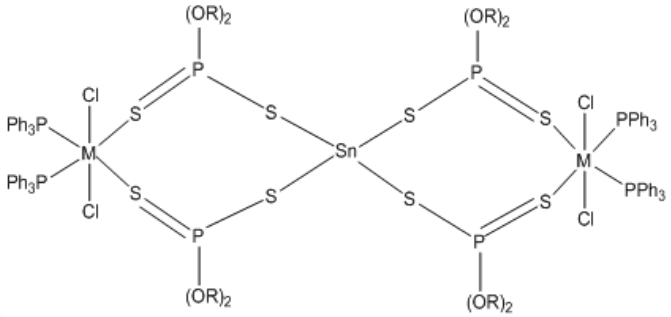

Fig 1: Suggest structures for the complexes

M= Co^{+2},Ni^{+2},Cu^{+2}, R= Et, ^{i}Bu or ^{t}Bu

Table 1: Analytical, conductance and magnetic data of the ligands and their complexes

No	Complexes	Color	m.p °C	Yield %	Elemental analysis /found (calc.)					μ_{eff} (B.M)	Λ_m
					C%	H%	S%	Sn%	M%		
L_1	($C_{16}H_{40}O_8P_4S_8Sn$)	Yellowish green	220-222	80	22.40 (22.35)	4.60 (4.65)	29.73 (29.81)	13.42 (13.80)	---	---	---
1	[$Co_2Sn(L_1)Cl_4(PPh_3)_4$]	Dark green	205[d]	74	48.69 (48.73)	4.54 (4.62)	11.75 (11.81)	5.37 (5.47)	5.18 (5.43)	4.79	11
2	[$Ni_2Sn(L_1)Cl_4(PPh_3)_4$]	Orange	105[d]	85	48.59 (48.74)	4.52 (4.61)	11.72 (11.81)	5.72 (5.49)	5.11 (5.10)	3.09	10
3	[$Cu_2Sn(L_1)Cl_4(PPh_3)_4$]	Green	230-232	71	48.49 (48.53)	4.50 (4.59)	11.70 (11.76)	5.14 (5.44)	5.51 (5.85)	1.85	6
L_2	($C_{32}H_{72}O_8P_4S_8Sn$)	Yellow	162-164	76	35.41 (35.47)	6.62 (6.65)	23.99 (23.64)	11.17 (10.98)	---	---	---
4	[$Co_2Sn(L_2)Cl_4(PPh_3)_4$]	Green	140-143	69	52.59 (52.90)	4.20 (4.24)	10.80 (10.85)	4.61 (4.96)	5.20 (4.92)	5.10	12
5	[$Ni_2Sn(L_2)Cl_4(PPh_3)_4$]	Pale green	251[d]	83	52.69 (52.91)	4.19 (4.24)	10.60 (10.51)	5.04 (5.44)	4.56 (4.91)	3.58	8
6	[$Cu_2Sn(L_2)Cl_4(PPh_3)_4$]	Brown	238[d]	78	52.55 (52.70)	4.19 (4.22)	10.41 (10.47)	11.26 (10.98)	5.55 (5.30)	2.09	11
L_3	($C_{32}H_{72}O_8P_4S_8Sn$)	Yellow	223-225	89	35.40 (35.46)	6.64 (6.65)	23.61 (23.64)	5.17 (4.96)	---	---	---
7	[$Co_2Sn(L_3)Cl_4(PPh_3)_4$]	Green	118[d]	76	52.61 (52.91)	4.19 (4.25)	10.79 (10.86)	4.60 (4.97)	4.62 (4.92)	4.89	20
8	[$Ni_2Sn(L_3)Cl_4(PPh_3)_4$]	Lemon	189[d]	70	52.71 (52.92)	4.20 (4.25)	10.60 (10.53)	5.04 (5.45)	4.51 (4.98)	3.19	7
9	[$Cu_2Sn(L_3)Cl_4(PPh_3)_4$]	Green	200[d]	75	35.40 (35.46)	6.60 (6.66)	23.60 (23.65)	5.18 (4.97)	5.51 (5.34)	1.91	17

d= decomposition temperature

Table 2 : IR and Electronic spectral data of the mono and trinuclear complexes

No.	υ(P=S)	υ(P-S)		υ(Sn-S)	υ(M-S)	υ(M-Cl)	Electronic spectra (cm^{-1})
		Sym.	Asym.				
L_1	$710_{(S)}$	$556_{(m)}$	$630_{(S)}$	$370_{(S)}$	---	---	34246,27100
1	$695_{(S)}$	$525_{(m)}$	$609_{(S)}$	$360_{(S)}$	$420_{(m)}$	$320_{(m)}$	14814,20449
2	$670_{(S)}$	$523_{(m)}$	$595_{(S)}$	$355_{(S)}$	$390_{(m)}$	$300_{(m)}$	10775,14260,22883
3	$680_{(S)}$	515	$585_{(m)}$	$350_{(S)}$	$430_{(m)}$	$310_{(m)}$	14124,16556
L_2	$690_{(S)}$	$529_{(m)}$	$600_{(m)}$	$355_{(m)}$	---	---	37878,27247
4	$653_{(S)}$	$510_{(m)}$	$575_{(m)}$	$360_{(m)}$	$390_{(m)}$	$290_{(m)}$	14727,21500
5	$662_{(S)}$	$512_{(S)}$	$570_{(m)}$	$370_{(m)}$	$410_{(m)}$	$320_{(m)}$	11545,14492,23640
6	$650_{(S)}$	$505_{(m)}$	$580_{(m)}$	$369_{(m)}$	$460_{(m)}$	$295_{(m)}$	16638
L_3	$717_{(S)}$	$525_{(m)}$	$620_{(S)}$	$350_{(m)}$	---	---	371741,28011
7	$670_{(S)}$	$495_{(m)}$	$600_{(S)}$	$370_{(m)}$	$399_{(m)}$	$298_{(w)}$	14780,19880
8	$682_{(S)}$	$500_{(m)}$	$602_{(S)}$	$365_{(m)}$	$400_{(m)}$	$310_{(m)}$	10718,15384,26581
9	$685_{(S)}$	$502_{(m)}$	$595_{(S)}$	$360_{(m)}$	$390_{(m)}$	$315_{(m)}$	16500

s= strong, m= medium, w=weak

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