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Physico-Chemical Characterization and Biological Screening of bis(2,4,4-trimethylpentyl) Monothiophosphinic Acid Complexes

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Abstract

Several new complexes of Cr(III), Mn(II), Fe(II), Co(II) and Cu(II) containing Cyanex 302 [bis(2,4,4-trimethylpentyl) monothiophosphinic acid] were synthesized and characterized by elemental analysis, molar conductance, molecular mass determination, magnetic, UV-Visible and IR studies. The prepared metal complexes has the compositions: **2**. $[CrL_3].H_2O$, **3**. $K[MnL_3].H_2O$, **4**. $[FeL_2].H_2O$, **5**. $K[CoL_3]$ and **6**. $K[CuL_3].H_2O$ (Where, L means anion of bis(2,4,4-trimethylpentyl) monothiophosphinic acid). The complexes **2**, **3, 5** and **6** are assumed to have octahedral geometries, but the complex **4** is tetrahedral based on experimental data. From magnetic measurements all the complexes are found to be paramagnetic. Measured molar conductance showed that the complexes **2** and **4** are non-electrolytes and complexes **3, 5** and **6** are electrolytes. Besides, some metal complexes have shown very good antibacterial and antifungal activities.

Keywords: Bis(2,4,4-trimethylpentyl) monothiophosphinic acid; Biological activity.

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1. Introduction

Studies on the extracted complexes of some common transition metal ions with various proprietary extracting reagents by solvent extraction method are of recent interest. These complexes (usually chelates) displaying distinctive coordination chemistry and characteristic physical properties, may have industrial as well as biological significance [1]. Cyanex 302 *i.e.,* bis(2,4,4-trimethylpentyl) monothiophosphinic acid is the sulfur substitution of organophosphorous extracting reagent. This reagent should therefore be beneficial for the extraction of metal ions [2]. The significantly lower electronegativity of sulfur renders it more polarizable than oxygen. Electrons are more readily shared in a

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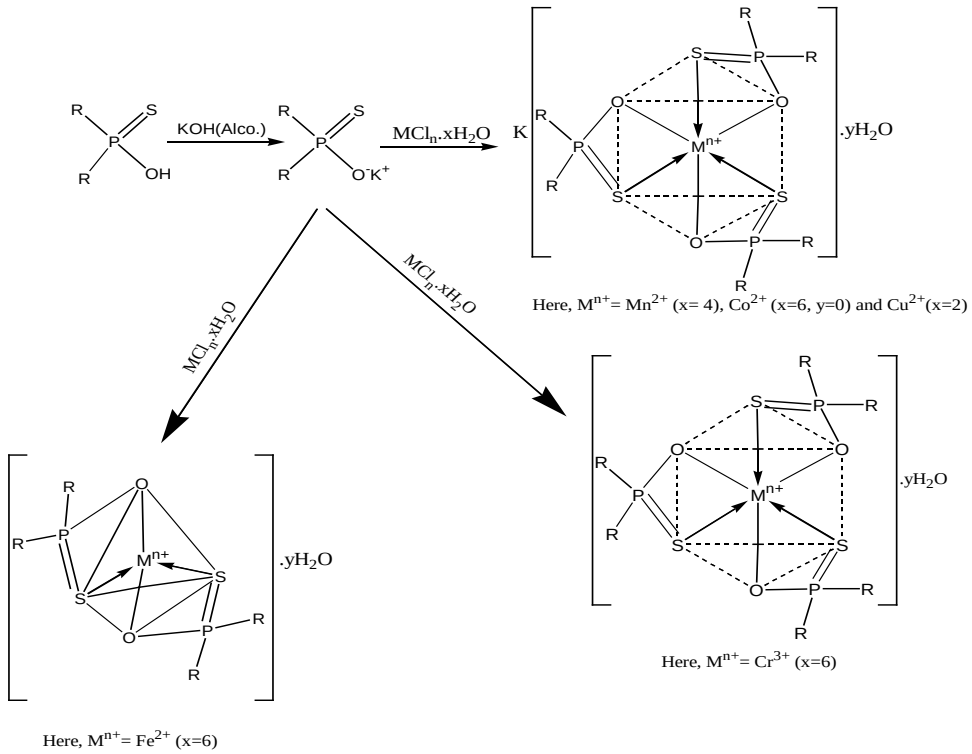
metal-sulfur bond than in a metal-oxygen bond, introducing a greater degree of covalency and increasing the strength of the bond [3]. Therefore, Cyanex 302 was examined in terms of their capability and selectivity in extracting metals from photographic wastes, fly ash, phosphate industrial waste water, rayon waste and different aqueous medium using the method of solvent extraction [4, 5]. The extracted complexes of transition metals with Cyanex 302 may have similar significances and studies on these complexes are expected to be helpful in extractive metallurgy. But no report on such complexes is available. A study has, therefore, been made to synthesize and characterize some complexes of Cr(III), Mn(II), Fe(II), Co(II) and Cu(II) ions with bis(2,4,4-trimethylpentyl) monothiophosphinic acid as ligand in order to get information about their compositions and structures. Here in we report synthesis of five new complexes and also investigation of their antibacterial and antifungal activities.

2. Experimental

IR spectra (4000-400 cm^{-1}) were recorded on a Nicolet 310 FTIR (Belgium) spectrometer with a KBr disk and UV-Visible spectra were recorded on a 1650 PC, Shimadzu spectrophotometer in DMSO. Magnetic susceptibility measurements were obtained with a Sherwood Scientific Magnetic Susceptibility Balance at room temperature. The electrical conductivities of 10^{-3} M solution in DMSO were carried out on a heavy-duty conductivity/temperature meter (USA), Extech Instruments, model No. 407303. Elemental analysis (C, H) was carried out with a Perkin Elmer 2400 II, organic elemental analyzer, Japan. The antibacterial and antifungal activities also carried out against the bacteria viz. *Escherihia coli, Staphyloccocus aureus* and *Salmonella typhi* and the fungi viz. *Aspergillus niger, Fusarium oxysporum* and *Trichophyton sp.* by disc diffusion technique [5, 6].

2.1. *General procedure for the synthesis of metal complexes*

A solution of the ligand, Cyanex 302 (1 or 1.5 mmol) in absolute ethanol was added to a solution of potassium hydroxide (1 or 1.5 mmol) in absolute ethanol and the mixture was stirred well and heated on a water bath for 15-20 min to reduce the volume by half. The resulting mixture (potassium salt of ligand) was allowed to stand at room temperature. Then a solution containing 0.5 mmol of the required metal chloride salt in absolute ethanol was slowly added to the above potassium salt of ligand solution, with stirring at room temperature. The metal complex formed immediately. The mixture was stirred for several minutes. The product was removed by filtration, washed several times with cooled absolute ethanol, then with distilled water (to remove KCl formed) and finally washed with hot absolute ethanol. The compound was dried in a vacuum desiccator over anhydrous $CaCl_2$. The reaction scheme for the synthesis of metal complexes is given below:



Here, R = CH_3-$C(CH_3)_2$-CH_2-$CH(CH_3)$-CH_2-

Scheme 1. Reaction scheme of the synthesis of metal complexes.

3. Results and Discussions

The reaction of the Cyanex 302 with various metal ions [M= Cr(III), Mn(II), Fe(II), Co(II) and Cu(II)] led to the formation of the complexes **2-6**, in the presence of alcoholic potassium hydroxide. The Cyanex 302 can act as uninegative bidentate ligand by loosing a proton from the >P(=S)OH moiety in presence of base. All the complexes were formed through the deprotonation of the ligand in presence of base and subsequent formation of potassium salt.

The complexes **2**, **3**, **5** and **6** were formed in a ligand to metal ion molar ratio of 3:1 whereas complex **4** was formed in 2:1 molar ratio. All the complexes were comparatively stable in air and insoluble in most common solvents except benzene and dimethylsulphoxide. The elemental analyses and metal estimation data were in good agreement with their proposed (as listed in Table 1) formula. The molecular mass determination of the complexes also supported their proposed molecular formula (Table

1). The room temperature molar conductance values of the complexes suggested that the complexes **2** and **4** are non-electrolyte [7, 8], while complexes **3**, **5** and **6** are electrolyte in nature [9, 10].

Table 1. Analytical and physical data of the ligand and complexes.

No.	Ligand/ Complex	M.P. (±2 ºC)	Colour	yield (%)	Elemental analyses Expt. (calc.)			Λ_M ($\Omega^{-1}cm^2mol^{-1}$)
					C	H	M	
1	$C_{16}H_{35}POS$	-	-	-	-	-	-	-
2	$[Cr(C_{16}H_{34}POS)_3].H_2O$	256	Light brown	45	58.45(58.44)	10.64(10.63)	5.20(5.27)	3.00
3	$K[Mn(C_{16}H_{34}POS)_3].H_2O$	329	Dark brown	39	55.98(56.05)	10.20(10.19)	5.28(5.34)	54.16
4	$[Fe(C_{16}H_{34}POS)_2].H_2O$	260	Brownish red	43	55.79(56.12)	09.98(10.30)	8.10(8.15)	3.09
5	$K[Co(C_{16}H_{34}POS)_3]$	243	Orange	51	56.76(56.83)	10.08(10.13)	6.00(5.81)	49.03
6	$K[Cu(C_{16}H_{34}POS)_3].H_2O$	320 (d)	Brown	47	55.50(55.59)	10.00(10.11)	6.08(6.13)	48.10

L means anion of Cyanex 302.

3.1. *Infrared spectra*

The significant IR bands for the ligand as well as for its metal complexes and their tentative assignments are compiled and represented in Table 2. The free ligand showed two strong bands at 2955 and 2868 cm^{-1} respectively due to the asymmetric and symmetric ν(CH) modes of the alkyl group [5, 11].

In the spectra of all the metal complexes, the characteristic bands of ν(CH) are almost unperturbed, as expected, which indicated that it is not involved in the coordination. The band at 634 cm^{-1} due to the P=S moiety [12, 13] of the ligand underwent a shift to lower frequency (73-48 cm^{-1}) after complexation, indicated the coordination of thiophosphoryl group's sulphur atom to metal ions. This can be explained by the donation of electrons from sulphur to the empty d-orbitals of the metal ions. A strong band observed at 2343 cm^{-1} in the IR spectrum of the ligand assigned to ν(OH) [14] (included P-OH) was found to have disappeared in all the respective complexes, indicated its coordination with the metal ions *via* deprotonation. The low frequency skeletal vibrations due to M-O and M-S stretching provided direct evidence for the complexation. The complexes contained two weak bands at 510-523 cm^{-1} and at 407-418 cm^{-1} corresponding to the ν(M-O) [15, 16, 17]

and ν(M-S) bonds [18, 19, 20] respectively. The appearance of broad band at around 3357-3438 cm^{-1} in the spectra of Cr(II), Mn(II), Fe(II) and Cu(II) complexes, has been assigned to associated water molecules [19, 21]. Besides, the water containing complexes did not show any weak band at nearly 860 cm^{-1} indicating the absence of coordinated water molecule in the complexes [22, 23].

Table 2. The most important bands in the IR spectra of the ligand and complexes, cm^{-1}.

No.	Ligand/Complex	ν(O-H)[1]	ν(O-H)[2]	ν(P=S)	N(M-O)	ν(M-S)
1	$C_{16}H_{35}POS$	-	2343	634	-	-
2	$[Cr(C_{16}H_{34}POS)_3].H_2O$	3370	-	584	510	416
3	$K[Mn(C_{16}H_{34}POS)_3].H_2O$	3438	-	581	514	407
4	$[Fe(C_{16}H_{34}POS)_2].H_2O$	3385	-	586	508	409
5	$K[Co(C_{16}H_{34}POS)_3]$	-	-	579	523	418
6	$K[Cu(C_{16}H_{34}POS)_3].H_2O$	3357	-	561	519	412

[1]Water, [2]Include P-OH

3.2. *Magnetic susceptibility and electronic spectra*

The magnetic susceptibilities of the test complexes are included in Table 3. The magnetic moments of the Cr(III), Mn(II), Fe(II), Co(II) and Cu(II) complexes [23, 24, 25, 26, 27] were corresponded to three, five, four, three and one unpaired electron respectively. The electronic spectra data of the ligand and its Cr(III), Mn(II), Fe(II), Co(II) and Cu(II) complexes were recorded in DMSO solution as shown in the Table 3. The electronic spectrum of Cr(III) complex showed three absorption bands at 605, 465 and 410 nm. The three spin-allowed transitions for chromium(III) in an octahedral field are: $^4A_{2g} \rightarrow {}^4T_{2g}$ (F), $^4A_{2g} \rightarrow {}^4T_{1g}$ (F) and $^4A_{2g} \rightarrow {}^4T_{1g}$ (P) [23, 28]. The Mn(II) complex exhibited bands at 663, 478, 402 nm assigned to $^6A_{1g} \rightarrow {}^4T_{1g}$, $^6A_{1g} \rightarrow {}^4T_{2g}$ and $^6A_{1g} \rightarrow {}^4A_{1g}$, ^4E_g transitions, respectively, suggested spin-free manganese(II) complex with octahedral geometry [29, 30]. The tetrahedral high spin Fe(II) complex showed only one spin allowed d-d transition in the visible region. The brownish red iron(II) complex given only one spin allowed d-d bond at 440 nm assigned to $^5T_{2g} \rightarrow {}^5E_g$ transition [31, 32, 33]. The high spin octahedral cobalt(II) complex exhibited three electronic transitions in electronic spectrum from ground state $^4T_{1g}$ (F) to the excited states $^4T_{2g}$ (F), $^4A_{2g}$ (F) and $^4T_{2g}$ (P), due to three absorption bands at 700, 515 and 446 nm respectively [18, 24, 26]. The electronic spectrum of the Cu(II) complex showed two bands at 640 and 530 nm, are assigned to $^2B_1 \rightarrow {}^2B_2$ and $^2B_1 \rightarrow {}^2E$ transitions respectively, which suggested octahedral geometry [7, 23, 27].

Table 3. The molecular mass, magnetic moment and electronic spectra of the ligand and complexes.

No.	Lignad/ Complex	Molecular mass (g/mol) Expt.	Calc.	μ_{eff} (B. M.)	Band observed (nm)	Band assignment
1	$C_{16}H_{35}POS$	-	306.00	-	346	$n \rightarrow \pi^*$
2	$[Cr(C_{16}H_{34}POS)_3].H_2O$	987.00	985.9	3.68	605, 465, 410	$^4A_{2g} \rightarrow {}^4T_{2g}(F)$, $^4T_{1g}(F)$, $^4T_{1g}(P)$
3	$K[Mn(C_{16}H_{34}POS)_3].H_2O$	1026.50	1026.0	5.70	663, 478, 402	$^6A_{1g} \rightarrow {}^4T_{1g}$, $^4T_{2g}$, $^4A_{1g}$, ^4E_g
4	$[Fe(C_{16}H_{34}POS)_2].H_2O$	685.02	684.49	5.12	440	$^5T_{2g} \rightarrow {}^5E$
5	$K[Co(C_{16}H_{34}POS)_3]$	1014.60	1014.00	4.96	700, 515, 446	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, $^4A_{2g}(F)$, $^4T_{2g}(P)$
6	$K[Cu(C_{16}H_{34}POS)_3].H_2O$	1035.82	1036.60	1.80	640, 530	$^2B_1 \rightarrow {}^2B_2$, ^2E

3.3. *Biological activity*

The biological activities of the free ligand and its metal complexes were determined at a concentration of 40 μg/disc against three pathogenic bacteria and three pathogenic fungi. The standard drugs ciprofloxacin and grisofulvin were also tested for their antibacterial and antifungal activities at the same concentration under similar conditions for comparison. The results of biological activity tested for the free ligand and its complexes are given in Tables 4 and 5.

Diameter of inhibition zone (mm) including the disc diameter was measured for each treatment. The ligand presented no activity against the all tested microorganisms under identical experimental conditions. The antibacterial activity results revealed that complexes **2, 3** and **4** showed very weak activity with the zone of inhibition 10-12 mm against *Escherichia coli* as compared to standard drug ciprofloxacin, which showed 24 mm inhibition. The complex **5** has exhibited almost similar activity with the zone of inhibition 20 mm against *Escherichia coli*. The complexes **3, 4** and **5** displayed moderate activity with the zone of inhibition 13-15 mm against *staphylococcus aureus* as compared to the standard drug with 22 mm inhibition. The complexes **2, 3** and **5** showed very weak activity with the zone of inhibition 10 mm, except complex **6**, which exhibited almost similar activity with the zone of inhibition 20 mm against *Salmonella typhi* when compared to the standard drug, which showed 22 mm inhibition. The antifungal activity results revealed that the complexes **2, 3** and **4** have exhibited moderate activity with the zone of inhibition 14-16 mm against *Aspergillus niger* as compared to the standard drug

griseofulvin (24 mm). The complex **3** displayed moderate activity with the zone of inhibition 13 mm, but the complex **5** exhibited maximum activity with the zone of inhibition 22 mm against *Fusarium oxysporum* compared to the standard drug which showed 23 mm inhibition. Further, the complexes **2-6** showed moderate activity with 15-18 mm inhibition against *Trichophyton sp*. compared to the standard drug with 26 mm inhibition.

Table 4. Antibacterial activity of the ligand and its complexes.

No.	Ligand /Complex/ Standard drug	Antibacterial activity (zone of inhibition in mm)		
		E. coli (40 μg/disc)	*S. aureus* (40 μg/disc)	*S. typhi* (40 μg/disc)
1	$C_{16}H_{35}POS$	06	09	07
2	$[Cr(C_{16}H_{34}POS)_3].H_2O$	10	08	10
3	$K[Mn(C_{16}H_{34}POS)_3].H_2O$	12	13	10
4	$[Fe(C_{16}H_{34}POS)_2].H_2O$	10	13	04
5	$K[Co(C_{16}H_{34}POS)_3]$	20	15	10
6	$K[Cu(C_{16}H_{34}POS)_3].H_2O$	05	04	20
	Ciprofloxacin (40 μg/disc)	24	22	22

Table 5. Antifungal activity of the ligand and its complexes.

No.	Ligand /Complex/ Standard drug	Antifungal activity (zone of inhibition in mm)		
		A. niger (40 μg/disc)	*F. oxysp.* (40 μg/disc)	*Tricho. sp.* (40 μg/disc)
1	$C_{16}H_{35}POS$	06	08	10
2	$[Cr(C_{16}H_{34}POS)_3].H_2O$	16	04	18
3	$K[Mn(C_{16}H_{34}POS)_3].H_2O$	14	13	15
4	$[Fe(C_{16}H_{34}POS)_2].H_2O$	16	10	16
5	$K[Co(C_{16}H_{34}POS)_3]$	10	26	17
6	$K[Cu(C_{16}H_{34}POS)_3].H_2O$	10	10	15
	Griseofulvin (40 μg/disc)	24	23	26

4. Conclusion

The ligand, Cyanex 302 behaved as an uninegative bidentate agent coordinating through sulfur and oxygen atoms. Cr(III), Mn(II), Co(II) and Cu(II) ions have been found to form octahedral complexes, but the Fe(II) formed tetrahedral complex with the Cyanex 302. The ligand and its Cr(III), Mn(II), Fe(II), Co(II) and Cu(II) complexes were tested for antibacterial and antifungal activities and some compounds have shown very good antibacterial and antifungal activities against *Escherichia coli*, *Salmonella typhi* and *Fusarium oxysporum*.

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