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Short Communication

Synthesis and Antimicrobial Screening of the Metal Complexes with Cyanex 302

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Abstract

The synthesis and characterization of metal complexes of the Cyanex 302 [bis(2, 4, 4-trimethylpentyl) monothiophosphinic acid] are reported. The complexes have been characterized by elemental analyses, molar conductivity, molecular mass determination and magnetic measurements, infrared and electronic spectral studies. The antibacterial and antifungal activities of the ligand and metal complexes have also been investigated. They have the stoichiometry of the type **1**. $[MgL_2].H_2O$, **2**. $[Ca\ L_2].H_2O$, **3**. $[ZrOL_2].H_2O$, **4**. $[FeL_3]$ and **5**. $[NiL_2]$. Electronic spectral data and the magnetic moment values suggested the complexes **1** and **2** are tetrahedral geometry, while the complexes **3**, **4** and **5** are square pyramidal, octahedral and square planar geometry around the central metal ions, respectively. Besides, magnetic susceptibility measurements of the complexes also revealed that complexes **1-3** and **5** are diamagnetic in nature, except complex **4**, which is paramagnetic. The metal complexes showed stronger antibacterial and antifungal activities than the ligand.

Keywords: Antibacterial, antifungal; Bis(2, 4, 4-trimethylpentyl) mothiophosphinic acid; Cyanex 302.

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1. Introduction

The chemistry of metal complexes is now the most active research field of inorganic chemistry. Today coordination chemistry stands as landmark in the area of scientific advancement embracing most diverse branches of science, engineering and technology. In the rapidly developing field of Hydrometallurgy, the metal complexes have large utility in the metallurgical operations, great practical importance in dying and textile industries, in analytical chemistry, in engineering technology, and also have important functional values

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in biological, biomedical, environmental, industrial transformations [1]. Coordination compounds, generally known as inorganic complexes, are of great practical importance in industries and also have important functional values in nature [1, 2]. The ligand (Cyanex 302) has been used in hydrometallurgy for the extraction of a few very useful metals *viz.* copper from different aqueous media [3, 4], lead from fly ash, Cd(II) and other heavy metals from phosphate industrial waste water and zinc from rayon waste using the method of solvent extraction. But the chemistry of the extraction processes as well as the elucidation of the structures of the extracted complexes and antimicrobial studies has not yet been studied. Complexing behaviour of the Cyanex 302 ligand with useful metal ions is also lacking. So we report here the results of our studies on chelating property of the ligand, characterization and antimicrobial activities of their corresponding Mg(II), Ca(II), ZrO(II), Fe(III) and Ni(II) complexes.

2. Materials and methods

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 407303. Elemental analysis (C, H) was carried out with a Perkin Elmer 2400 II, organic elemental analyzer, Japan. The metal content of the complexes were determined after the decomposing the organic matter with a mixture of $HClO_4$, H_2SO_4 and HNO_3 (1: 1.5: 2.5). Magnesium, calcium, iron and zirconium were estimated gravimetrically [5], while nickel was estimated complexometrically using EDTA [5]. The antibacterial and antifungal activities also carried out against some pathogenic organisms by disc diffusion technique [6].

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

Cyanex 302 (1 mmol or 1.5 mmol) was dissolved in absolute ethanol (25 mL) in a beaker and KOH (1 mmol or 1.5 mmol) was dissolved in absolute ethanol (35 mL) in another beaker. These two solutions were mixed together in a 250 mL beaker and shaked well. The resulting solution was heated on a water bath for 30 minutes and allowed to stand at room temperature.

A solution of metal chloride (0.5 mmol) in absolute ethanol (20 mL) was added to the above solution of K-salt of Cyanex 302 (Metal: Cyanex 302 of 1:2 or 1:3). The solution was stirred well with a glass rod, warmed in the water bath and then allowed to stand at room temperature for 10 minutes. The precipitate of metal complex was obtained, which was filtered off, washed with cooled absolute ethanol for several times and then distilled water (to remove KCl formed) and finally washed with hot absolute ethanol. The compound was dried in a vacuum desiccator over anhydrous $CaCl_2$.

2.2. *Biological activity technique*

The biological screening of the ligand and its Mg(II), Ca(II), ZrO(II), Fe(III) and Ni(II) complexes was undertaken against the bacteria *E. coli, S. aureus* and *S. typhi* by the disc diffusion technique [6] using nutrient agar as medium. In a typical procedure, molten nutrient agar kept at 45°C was then poured into Petridishes and allowed to solidify. Then holes of 4 mm diameter were punched carefully using a sterile cork borer and these were completely filled with the test solutions (40 μg/disc). The plates were incubated for 24h at 37°C. The diameter of the zones of inhibition for all the test compounds was measured and the results were compared with the standard drug ciprofloxcin of the same concentration as that of the test compound under identical conditions. The antifungal activity of the test compounds was evaluated against the *A.. niger, F. oxysporum* and *T. species* by disc diffusion technique cultured on potato-dextrose agar (PDA) medium adapting similar procedure described above. The plates were incubated for 48h at 28°C. The compounds were measured and the results were compared with the standard drug griseofulvin of the same concentration as that of the test compound under identical conditions. Since all test compounds and standard drugs were prepared in freshly DMSO, its zone of inhibition was found to be very negligible and taken as zero mm.

3. Results and discussion

The reaction of Cyanex 302 with various metal ions [M= Mg(II), Ca(II), ZrO(II), Fe(III) and Ni(II)] led to the formation of the complexes **1-5**, in the presence of alcoholic potassium hydroxide. All the complexes were obtained *via* the formation of a potassium salt of the ligand. Among these complexes **1-3** and **5** were formed in a ligand to metal ion molar ratio of 2:1 where as complexes **4** was formed in 3:1 molar ratio. All the complexes were more air stable and insoluble in most common solvents except benzene and dimethylsulphoxide. The elemental analyses and metal estimation data were in good agreement with their proposed formulae (Table 1). The molecular mass determination of the complexes (by cryoscopic method) also supported their proposed molecular formulae (Table 1). The room temperature molar conductance values of the complexes suggested that the all complexes **1-5** are non-electrolyte in nature [7, 8]. The nature of complexes also suggested that, the Cyanex 302 was coordinated to metal ions as anion and no ions were present out side of the coordination sphere [9].

3.1. *Infrared spectra*

The IR spectra provided valuable information regarding the nature of functional group attached to the metal atom [10]. 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 bands at 2868 and 2955 cm^{-1}, which are assigned to ν(C-H) symmetric and asymmetric stretching respectively. In the spectra of all the metal complexes, the bands characteristic of ν(C-H) 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 [11, 12] of the ligand. This band shifted to lower frequency (58-46 cm^{-1}) after complexation, which suggested 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*-orbital of the metal ions.

Table 1. Analytical and physical data of the complexes.

Complex (No.)	M.P. (ºC)	Colour	Yield (%)	Elemental analyses Expt. (Calc.) C	H	M	Λ_M (ohm^{-1} cm^2 mol^{-1})
[MgL$_2$].H$_2$O (**1**)	288	Yellow	32	58.70 (58.55)	10.55 (10.50)	03.80 (03.72)	04.12
[CaL$_2$].H$_2$O (**2**)	270	Ash	49	57.07 (57.17)	10.12 (10.25)	06.03 (05.99)	01.97
[ZrOL$_2$].H$_2$O (**3**)	242	Yellow	50	52.00 (51.96)	09.36 (09.32)	12.50 (12.40)	03.25
[FeL$_3$] (**4**)	265	Brown	40	57.02 (56.81)	10.52 (10.14)	05.42 (05.51)	03.54
[NiL$_2$] (**5**)	251	Golden yellow	46	57.10 (57.37)	10.39 (10.24)	09.00 (08.77)	02.90

Table 2. The IR spectra of the ligand and complexes.

Ligand / Complex (No.)	ν(O-H)*	ν(O-H)**	ν(P=S)	ν(M-O)	ν(M-S)	ν(Zr=O)
Ligand (L)	-	2343 s	634 m	-	-	
[MgL$_2$].H$_2$O (**1**)	3389 b		588 m	520 w	411 w	
[CaL$_2$].H$_2$O (**2**)	3404 b		580 m	512 w	407 w	
[ZrOL$_2$].H$_2$O (**3**)	3423 b		578 m	512 w	406 w	768 m
[FeL$_3$] (**4**)	-		576 m	518 w	409 w	
[NiL$_2$] (**5**)	-		588 m	510 w	411 w	

* Water; ** include P-OH; b = broad, m= medium, w= weak.

A strong band observed at 2343 cm^{-1} in the IR spectrum of the ligand assigned to ν(O-H) (included P-OH) [13], which was found to have disappeared in all the respective complexes, which indicated the 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. Furthermore, in the present investigation, the absence of ν(O-H) band as well as the presence of new weak bands in the 510-520 cm^{-1} region have been assigned to ν(M-O) vibrations [14] and the bands observed in the 406-411 cm^{-1} region for ν(M-S) vibrations [15] respectively. These vibrations further suggested the coordination of the Cyanex 302 anion to metal ions *via* sulphur and oxygen atoms. The spectra of complexes **1-3** showed a broad and medium intensity band in the 3389-3423 cm^{-1} region, which is assigned to ν(O-H) vibrations of hydrated water molecule [7, 16]. However, ZrO(II) complex showed a medium band at 768 cm^{-1} assigned to ν(Zr=O) vibration [17].

3.2. *Magnetic susceptibility and electronic spectra*

The magnetic moment values give information on their probable geometries. The electronic spectral measurements were used to assign the stereochemistries of the metal ions in the complexes based on the positions and number of *d-d* transition peaks [18].The magnetic measurements at room temperature (Table 3) indicated that the Mg(II) and Ca(II) ions have 3d° configuration. Hence both complexes (**1-2**) are tetrahedral geometry [1]. The complex **3** is also diamagnetic, consistent with square pyramidal geometry [7] around ZrO(II) ion. The μ_{eff} value for the complex **4** is 6.02 B.M. indicating a slight ferromagnetic behavior and suggested distorted octahedral geometry of Fe(III) complex [19]. On the other hand, the complex **5** is diamagnetic showing square planar geometry around the Ni(II) ion [20]. The electronic spectrum of the ligand showed only one band at 346 nm assigned to the n → π^* transition. On complexation, this band is shifted to lower wave length, which suggested the coordination of the uncharged thiophosphoryl sulphur

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

Ligand/ Complex (No.)	Molecular mass in g/mol		μ_{eff} (B. M.)	Band observed (nm)	Band assignment
	Expt.	Calc.			
Ligand (L)	-	306.00	-	346	$n \rightarrow \pi^*$
$[MgL_2].H_2O$ (**1**)	652.70	653.00	Diam.	335	$n \rightarrow \pi^*$
$[CaL_2].H_2O$ (**2**)	667.90	668.70	Diam.	330	$n \rightarrow \pi^*$
$[ZrOL_2].H_2O$ (**3**)	734.60	735.80	Diam.	336	$n \rightarrow \pi^*$
$[FeL_3]$ (**4**)	1014.02	1013.93	6.02	576, 403	${}^6A_{1g} \rightarrow {}^4T_{1g}$, ${}^6A_{1g} \rightarrow {}^4T_{2g}$
$[NiL_2]$ (**5**)	668.86	669.31	Diam.	690, 570	${}^1A_{1g} \rightarrow {}^1B_{1g}$, ${}^1A_{1g} \rightarrow {}^1E_{1g}$

and oxygen atoms to the metal ions [21]. The complexes **1** and **2** exhibited only one band at 335 nm and 330 nm respectively assigned to the n → π^* transition. Since, complexes **1** and **2** are spin paired so charge transfer band obscured their ligand field bands. Therefore, they do not show *d-d* transitions [1]. The electronic spectrum complex **3** showed a single band at 336 nm, which can be assigned to n → π^* transition and is in accordance with its (n-1)d°ns° electronic configuration [22]. The complex **4** appeared two absorption bands at 576 nm and 403 nm which can be assigned to the $^6A_{1g} \rightarrow {}^4T_{1g}$ and $^6A_{1g} \rightarrow {}^4T_{2g}$ transitions respectively. The spectrum suggested distorted octahedral with D_{4h} symmetry [19]. While, the complex **5** showed two absorption bands at 690 nm and 570 nm due to $^1A_{1g} \rightarrow {}^1B_{1g}$ and $^1A_{1g} \rightarrow {}^1E_{1g}$ transitions respectively supporting the square planar geometry of nickel complex [20].

3.3. *Antimicrobial activity*

The ligand and its metal complexes were screened against some pathogenic organisms to study their antibacterial and antifungal activities. The ligand showed no activity against the all tested microorganisms under identical experiment conditions. The antibacterial activity results (Table 4) revealed that the complex **5** showed almost similar activity with the zone of inhibition 22 mm and the complex **4** displayed maximum activity with the zone of inhibition 18 mm against *E. coli* as compared to standard drug ciprofloxacin, which showed 24 mm inhibition. The complex **5** exhibited moderate activity with the zone of inhibition 16 mm against *S. aureus* as compared to the standard drug with 22 mm inhibition. The antifungal activity results (Table 5) revealed that the complex **2** showed very good activity with the zone of inhibition 19 mm against *A. niger* as compared to the standard drug griseofulvin. Besides, the complexes **2** and **5** exhibited moderate activity with 14-16 mm inhibition against *T. species* compared to the standard drug with 26 mm inhibition.

Table 4. Antibacterial activity of the ligand and complexes (inactive: 05 to 07 mm).

Ligand /Complex (No.)	Antibacterial activity (zone of inhibition in mm)		
	E. coli (40 μg/disc)	*S. aureus* (40 μg/disc)	*S. typhi* (40 μg/disc)
Ligand (L)	07	06	06
$[MgL_2].H_2O$ (**1**)	05	05	06
$[CaL_2].H_2O$ (**2**)	10	10	06
$[ZrOL_2].H_2O$ (**3**)	06	06	07
$[FeL_3]$ (**4**)	18	10	12
$[NiL_2]$ (**5**)	22	16	10
Ciprofloxacin	24	22	22
DMSO (Control)	05	05	05

Table 5. Antifungal activity of the ligand and its complexes (inactive: 05 to 07 mm).

Ligand /Complex (No.)	Antifungal activity (zone of inhibition in mm)		
	A. niger (40 μg/disc)	*F. oxysp.* (40 μg/disc)	*T. species* (40 μg/disc)
Ligand (L)	05	06	07
$[MgL_2].H_2O$(**1**)	07	13	06
$[CaL_2].H_2O$(**2**)	19	06	14
$[ZrOL_2].H_2O$(**3**)	05	06	10
$[FeL_3]$ (**4**)	10	06	06
$[NiL_2]$ (**5**)	10	11	16
Griseofulvin	24	23	26
DMSO (Control)	05	06	06

A comparative study of the ligand and its metal complexes indicated that some of the metal chelates exhibited higher antimicrobial activity than the free ligand. The increase in the antimicrobial activity of metal chelates is due to the presence of metal ions in the complexes.

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