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Studies on Cyanex-272 Complexes of Mg (II), Ca (II) and Fe (III)

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Abstract

Certain complex compounds were synthesized by the interaction of Mg(II), Ca(II) and Fe(III) halides with the solvent extracting reagent, Cyanex-272 i.e. bis (2,4,4-trimethylpentyl) phosphinic acid as ligand. All the prepared complexes have been characterized on the basis of their molar masses, conductivity, magnetic measurements and infrared and electronic spectral studies. The other physico-chemical properties e.g. colour, decomposition temperature have also been ascertained.

Key words: Chanex-272

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 in biological, biomedical, environmental, industrial transformations (Winterton, 2000, Ford, 1999, Ali *et al.*1997).

As a new ligand Cyanex-272 is a phosphinic acid. Although Cyanex272 is selective for cobalt in the presence of nickel, a variety of other cations can also be extracted depending upon the solution pH (Rickelton *et al.*1984). In coordination chemistry, studies on these new ligands are of great importance for the extractive metallurgy. However, metal complexes of Fe(III), Mg(II) and Ca (II) with Cyanex 272 are not known. These metal ions have been extensively used for various purposes. Literature studies (Nahar *et al.* 1992) show that complexes of various transition metals with different ligands are of great importance, because many of them are efficient stoichiometric and catalytic reagents. In the therapeutic, analytical, bio

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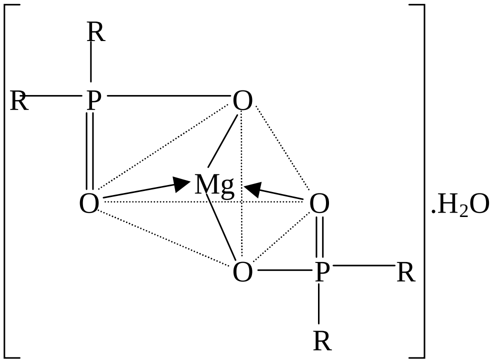
logical and industrial fields and in coordination chemistry, these complexes have been extensively used.

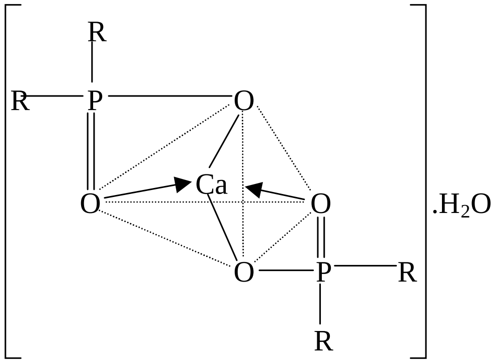
It is reported (Islam *et al*. 1997) that Cyanex -272 may form water insoluble complexes with different metal ions. Therefore, the study of complexing behaviour of Ca (II), Mg (II) and Fe (III) ions with extracting reagent, Cyanex 272 will be of much value for their various solvent extracting processing (Lever, 1984). It was therefore, thought appropriate to synthesize and characterize the new complexes of Cyanex 272 with such common metal ions in order to investigate the complexing behaviour of the extracting reagent acting as a uninegative bidentate ligand. Thus the present investigation with the said solvent extracting reagent which contribute to the knowledge of solvent extraction/separation of the metals.

So, efforts have been made to prepare some new complexes of common metals viz, calcium, magnesium and iron with the newly introduced solvent extracting ligand, Cyanex 272 and their characterization based on some physical methods e.g. conductivity, solubility, magnetic measurements and infrared and electronic spectroscopic studies. The complexes are shown in scheme 1. The details of the work are described in the present paper.



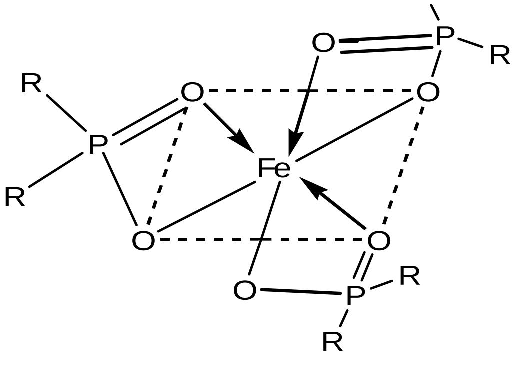
$[Mg(L)_2].H_2O$, Tetrahedral

Where, R= CH_3—$C(CH_3)_2$—CH_2 —$CH(CH_3)$—CH_2—



$[Ca(L)_2].H_2O$, Tetrahedral

Where, R = CH_3—$C(CH_3)_2$ — CH_2 — $CH(CH_3)$—CH_2—



$[Fe(L)_3]$, Octahedral

Where, R = CH_3—$C(CH_3)_2$—CH_2—$CH(CH_3)$—CH_2—

Materials and Methods

Except Cyanex-272, all the chemicals used in this investigation were of reagent grade. Absolute alcohol was purified by refluxing the 99% crude with magnesium turnings and iodine, and finally distilled and stored over molecular sieves.

Melting points were determined using Gallenkamp AZ 6512 apparatus and are uncorrected. IR Spectra (KBr) were recorded by a pye-Unicam SP3 Spectrophotometer. TLC checked purity of the compounds on silica gel GF_{254} plates and the spots were visualized by exposure to iodine vapour.

Preparation of [Mg (Cyanex-272)$_2$] H_2O complex:

To a solution of KOH (0.56g; 0.01 mol) in absolute alcohol was added a solution of Cyanex-272 (4.35g; 0.015 mol) in absolute alcohol in a 250 mL beaker and stirred. The resulting mixture was heated on a water bath for 1 hour. Then the mixture was allowed to stand at room temperature for several hours.

A solution of magnesium (II) chloride ($MgCl_2$. $6H_2O$) (1.01655g, 0.005 mol) in absolute alcohol was mixed with the above K-Cyanex-272 solution in absolute alcohol. The mixture was stirred well with a glass rod. Then the mixture was warmed in the water bath for half an hour and allowed to stand at room temperature for few minutes. The colourless precipitate found were collected by filtration, washed several times with alcohol and finally dried in a vacuum desiccator over P_4O_{10} for a fortnight.

Preparation of [Ca(Cyanex-272)$_2$] H_2O complex:

An ethanolic solution of Cyanex 272 (4.35g; 0.015 mol) (60 mL) was added to a solution of KOH (0.56g; 0.01 mol) in the same solvent (30 mL) in a 250 mL beaker and stirred. The resulting mixture was heated on a water bath for 1 hour. Then the contents of the beaker were allowed to stand at room temperature for several hours.

A solution of calcium (II) chloride (0.55495g, 0.005 mol) was added to the above solution. The mixture was stirred well with a glass rod. The colourless precipitate found were collected by filtration, washed several times with alcohol and finally dried in a vacuum desiccator over P_4O_{10} for a fortnight.

Preparation of [Fe (Cyanex-272)$_3$] complex:

A solution of KOH (0.56g; 0.01mol) in absolute ethanol (20 cm^3) was mixed with a solution of Cyanex 272 (4.35g; 0.015mol) in the same solvent (50cm^3) into a 250 mL beaker and stirred. The resulting mixture (K-Cyanex-272 salt solution) was heated on a water bath for 1 hour. Then it was allowed to stand at room temperature for several hours.

A solution of 0.005 mol (1.365g) ferric (III) chloride ($FeCl_3$. $6H_2O$); in absolute alcohol was added with the above K-Cyanex 272 solution in absolute alcohol.

The mixture was stirred well with a glass rod. Then the beaker with contents was warmed in the water bath for half an hour and allowed to stand at room temperature for few minutes. The yellow coloured precipitate found was filtered off and washed several times with absolute ethanol. This product was air dried and finally dried in a vacuum desiccator over P_4O_{10} for a fortnight.

Results and Discussion

The synthesized cyanex-272 complexes of Mg(II), Ca(II) and Fe(III) have been characterized on the basis of their conductance and magnetic measurements, molar masses, infrared and electronic spectral studies and their other physical properties.

Molar conductance data of the prepared metal-Cyanex-272 complexes are given in Table I. The measured electrical conductance of 10^{-3} M solution in carbon-tetrachloride, cyclohexane, benzene and chloroform indicate that the complexes 1, 2 and 3 are non electrolytes. The result is satisfactory and conforms to the conductance of other complexes of same metals (Geary 1971). All other parameters like, colour, decomposition temperature, molar mass of the prepared complexes were determined and shown in Table I.

The IR spectrum for the ligand Cyanex-272 and that of its metal complexes are shown in Table II. In the infrared spectrum of Cyanex-272, CH-stretching (methyl, methylene) appears as a very strong band at 2950 cm^{-1} and other ν (C - H) stretching (symmetric and antisymmetric) bands at 2910 and 2871 cm^{-1}. The bonded OH vibration gives bands at 2700 and 2300 cm^{-1}, where as the very broad bands occurring at 1720 - 1635 cm^{-1}

Table I. Color, molar mass, decomposition temperature and molar conductance of the prepared complexes

Compound (No.)	Color	Molar mass, g mol^{-1}		Decomposition temperature, °C	Molar conductance, ohm^{-1} cm^2 mol^{-1}
		Exptl.	Theo.		
[Mg(Cyanex-272)$_2$] H_2O (1)	Yellow	624	620	>300	0
[Ca(Cyanex-272)$_2$] H_2O (2)	Colorless	628.141	636	>300	0
[Fe(Cyanex-272)$_3$] (3)	Colorless	--	--	290	0

Table II. IR absorption maxima in cm^{-1} of Cyanex-272 and M-Cyanex-272 complexes (Nahar *et al.* 1992)

Wave numbers for the IR absorption of Cyanex-272, cm^{-1}	Wave numbers for IR absorption of Ca(II)-Cyanex-272 complex, cm^{-1}	Wave numbers for IR absorption of Mg(II)-Cyanex-272 complex, cm^{-1}	Wave numbers for IR absorption of Fe(III) -Cyanex- 272, cm^{-1}
--	3400 (vb)	3386 (vb)	2952-2902 (vs)
2950-2910 (vs)	2954-2902 (vs)	2954 (vs) 2902	2868 (sh)
2871 (sh)	2869 (sh)	2869 (sh)	--
2638 (wb)	--	--	--
2293 (vb)	--	--	1635 (b)
1683 (vb)	--	--	1477 (ms)
1469 (ms)	1477 (ms)	1465-1477 (ms)	1363 (ms)
1394-1365 (m)	1365-1394 (ms)	1363-1394 (ms)	1238 (m)
1286 (vb)	1288-1240 (sh)	1240 (vw)	--
1168 (vb)	1166 (vs)	1164 (vs)	1029 (vs)
1049 (b)	1085 (vs)	1085 (vs)	--
954-912 (b)	968-912 (vs)	910 (vw)	821 (m)
860-817 (ms)	821 (ms)	819 (ms)	709 (b)
763-734 (m)	736 (vw)	736 (vw)	--
665 (vw)	--	--	
	553-499 (sh)	--	
	449 (m)	453 (m)	

represent OH deformation. The ν(P - O) stretching band for Cyanex-272 is found at 1286 cm^{-1}. The ν(P - O) antisymmetric stretching band appears as a broadband at 1049 and ν(P - O) symmetric stretching band at 734 cm^{-1}. Further, the IR spectrum of Cyanex-272 shows a broad band at 1180 - 1150 cm^{-1} for C - C - C antisymmetric stretching.

Symmetric and antisymmetric stretching bands of methyl and methylene C - H occurring in Cyanex-272 at 2950, 2910 and 2871 cm^{-1} are also present in all the M-Cyanex-272 complexes as expected. However, the OH stretching bands appears at 2700 and 2300 cm^{-1} are missing in all the spectra of the prepared metal Cyanex-272 complexes. This indicates deprotonation of the P - OH before complexation which signifies the normal cation exchange behaviour of the ligand Cyanex-272. Therefore, the metal ions are assumed to form strong complexes with the ligand Cyanex-272.

In the case of M-Cyanex-272 complexes, the shifting of ν(P - O) vibrational bands has been found occurring at 1286, 1049 and 734 cm^{-1} in pure Cyanex-272. The ν(P-O) vibration band at 1286 cm^{-1} shifts towards lower frequencies (1240 cm^{-1}) in all of the M-Cyanex-272 complexes. The antisymmetric ν(P - O) stretching band at 1049 cm^{-1}1 shifts to lower frequencies (1029 cm^{-1}) in Fe(III)-Cyanex-272 complex, whereas in the Mg(II) and Ca(II) complexes it shifts towards higher frequencies (1085 cm^{-1}). However, except Fe(III)- Cyanex-272 complex, the symmetric ν(P = O) stretching band in Cyanex-272 at 734 cm^{-1} shifts (736 cm^{-1}) towards higher frequencies in the spectra of all other metal-Cyanex-272 complexes. These shifts in ν(P - O) vibration indicate that strong chelate complexes are formed with the phosphoryl-oxygen coordination to the metal ion. For Mg(II) and Ca(II) complexes a broad absorption band at 3400 - 3386 cm^{-1} indicates the presence of water molecule outside the coordination sphere. Moreover, a ν(M – O) band found at 420 - 480 cm^{-1} is also indicative of M←O bond formation in the IR spectra of the complexes (Singh 1983). The band broadening at 420 - 480 cm^{-1} is tentatively attributed to the presence of n(Fe - O) and ν(Fe - O) axial and equatorial stretching modes in the complex of Fe (III)- Cyanex 272.

The magnetic susceptibilities and other magnetic data of the prepared metal- Cyanex-272 complexes were also measured and shown in Table III. From Table III, it is evident that the complex Fe(III)- Cyanex-272 is paramagnetic having five unpaired electrons per atom. But, complexes Mg(II)- Cyanex-272 and Ca(II)- Cyanex-272 are diamagnetic as also apparent from their negative susceptibility values besides their repulsion by applied magnetic field. Using the magnetic data, the structure or steriochemistry of the metal-Cyanex-272 complexes may be suggested. The Fe(III) ion has d^5 configuration and since the magnetic moment measurement of Fe(III)- Cyanex-272 complex indicates the presence of five unpaired electrons for each

Table III. Detailed magnetic date of the metal complexes of Cyanex-272 (Temperture=301 K)

Complexes (No.)	Susceptibility of empty tube Ro	Susceptibility of complex with tube R	Mas susceptibility $X_g \times 10^6$ in C.G.S. unit	Molar mass M, g mol^{-1}	Molar susceptibility, $\chi_M \times 10^3$ in C.G.S. unit	Diamagnetic correction $\chi_L \times 10^6$ in C.G.S unit	Corrected molar susceptibility χ_M^{Coor} $\times 10^3$ in C.G.S unit	μ_{eff} B.M.
1	-38	-42	-0.744	624	-0.4643	-279.66	-0.185	dia
2	-41	-59	-1.9732	628.141	-1.2395	-279.66	-0.96	dia
3	-79	-8	12.14	--	11.2155	-382.66	11.5982	5.32

atom, this Fe(III)- Cyanex-272 complex with coordination number six, may have octahedral structure.

Again, the measured values of magnetic moment indicate that the complexes Mg(II) Cyanex-272, Ca(II)- Cyanex-272 are diamagnetic. Molecular weight determination of Mg(II)-Cyanex-272 complex and gravimetric mass determination of Ca for Ca(II)-Cyanex-272 complex indicate that the Mg(II) and Ca(II)complexes of Cyanex-272 are tetrahedral with sp^3 hybridization.

The electronic spectra of Cyanex-272 and its metal complexes are shown in Figs. (1-4). The absorption spectrum of Cyanex-272 (taken in cylohexane) shows two bands at 245 nm and 310 nm which are assigned to the $\pi \longrightarrow \pi^*$ and $n \longrightarrow \pi^*$ transitions of -P = O group. The electronic spectra of complexes 1 and 2 exhibit two characteristic bands at 280 nm and 290 nm respectively. Since, Mg (II) and Ca (II) are spin paired so charge transfer bands obscure their ligand field (large) bands. Therefore, they do not show d-d transitions. Generally, charge transfer transition occurs in the region 200 - 400 nm (Srivastava *et al.* 1967)

The complex Fe (III) -Cyanex-272 shows three characteristic bands at 560 nm, 595 nm and 640 nm, which are indicative of the octahedral geometry (Lever 1984).

Electronic spectrum of Cyanex-272 and M-Cyanex-272 complexes

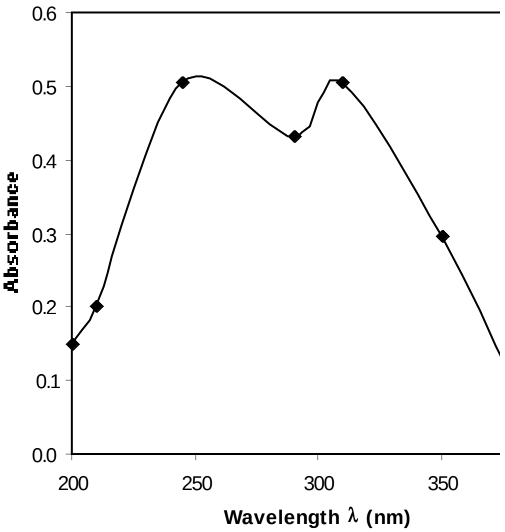


Fig. 1. Cyanex-272 ligand.

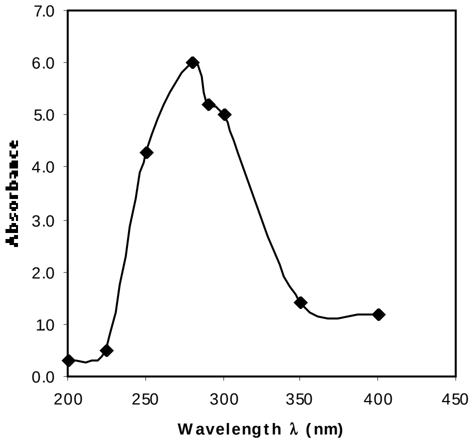


Fig. 2. [Mg(Cyanex-272)$_2$] H$_2$O complex

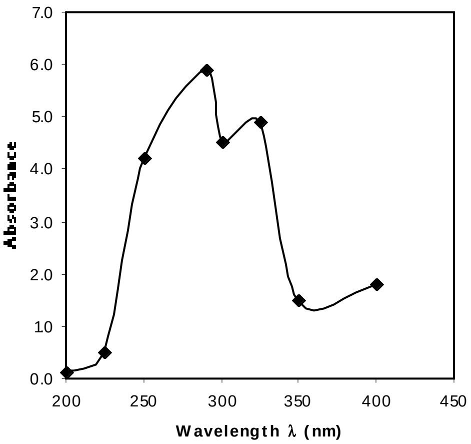


Fig. 3. [Ca(Cyanex-272)$_2$] H_2O complex

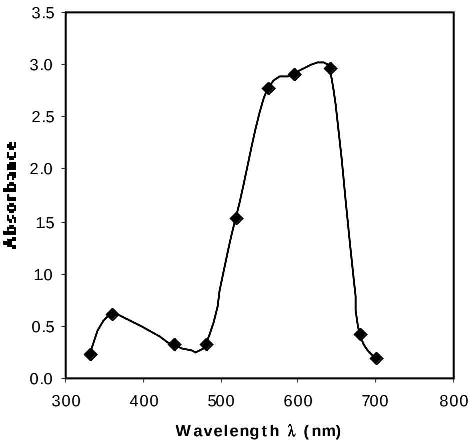


Fig. 4. [Fe(Cyanex-272)$_3$] complex.

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