

STUDIES ON THE COMPLEXES OF SOME MONOPHOSPHAZENES WITH Fe(III), Co(II), Ni(II), Zn(II), AND Ag(I)

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A series of complexes of general formulae $MLCl_2$ for Co(II), Ni(II), Cu(II), and Zn(II), $AgLNO_3$ for Ag(I) and $FeLClCl$ for Fe(III) complexes where L = 1-*o*-tolyl-2,2-dianiline, 2-(N-phenyl-thiourea) monophosphazene (L_1) and 1-*o*-tolyl-2,2-di(*o*-tolyl),2-(N-tolylthiourea) monophosphazene (L_2) were investigated spectrophotometrically and conductometrically. The results indicate the probable formation of 1:1 chelates (metal:ligand). The values of the apparent stability constant of the different complexes have been determined by continuous variation, mole ratio, straight line and limiting logarithmic methods. Solid chelates have been isolated and their structures established by elemental analysis and IR spectral data. It is concluded that the ligands are generally NS bidentate.

INTRODUCTION

The coordination properties of 1,2,2,2-monophosphazene derivatives have not yet been studied in spite of the importance of these compounds from biological standpoints. Since some of these complexes showed the most potent effect especially silver complex of L_2 . This is actually due to its broad action on different micro-organisms such as *B. subtilis*, *B. mycoides*, *B. cereus*, *E. coli* and *S. typhosa*. The aim of the present work is to study the complexes of 1-*o*-tolyl-2,2-dianiline, 2-(N-phenylthiourea) monophosphazene (L_1) and 1-*o*-tolyl-2,2-di(1-*o*-tolyl),2-(N-*o*-tolylthiourea) monophosphazene (L_2) with some transition metal ions viz Fe(III), Co(II), Ni(II), Zn(II) and Ag(I). The preparation and characterization of the solid chelates and their structures in solution as well as their stability constants are reported.

MATERIALS AND METHODS

All the materials used in this investigation were of the reagent grade (E. Merck or B.D.H.).

1-*o*-Tolyl-2,2-dianiline,2-(N-phenylthiourea)-(L_1) and 1-*o*-tolyl-2,2-(*o*-tolyl),2-(N-*o*-tolylthiourea)-(L_2) monophosphazenes were synthesised according to the method of Ibrahim and Lashien[1]. The compounds formed were purified by recrystallization from ethanol and dried *in vacuo* over silica gel.

Stock solutions (10^{-2} M) of the ligands and the metal salts were prepared by dissolving the appropriate amount of the solid in absolute ethanol. The metal ion concentrations were determined by conventional methods[2].

The electronic spectra of solutions were recorded on a PYE UNICAM SP 8000 spectrophotometer using 1 cm matched silica cells. Conductometric measurements were carried out using a YSI conductivity bridge model 31 and a dipping-type conductivity cell at 25°C.

The solid complexes were prepared by adding an ethanolic solution of the metal salts ($FeCl_3 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, $ZnCl_2$ and $AgNO_3$) to an ethanolic solution of the ligand in 1:1 molar ratio and refluxing the mixture on a water bath for about 3 hours. The solids were filtered off, washed with ethanol, dried and analysed for carbon, nitrogen, chlorine and molecular weights.

The IR spectra of the organic ligands as well as those of the solid chelates were recorded in KBr matrix on a UNICAM SP 1100 Spectrophotometer.

RESULTS AND DISCUSSION

The electronic absorption spectra of L_1 and L_2 in ethanol exhibit maximum absorption at 248 nm. The bands undergo an apparent red shift (50-100 nm) on adding the metal ion solution. This is presumably due to the electron acceptor character of the central positively charged ion which results in an enhanced charge transfer.

The calculated values of the molar absorptivity for copper and silver ions were 9500 and $12750 \text{ mol}^{-1} \text{ cm}^{-1}$

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respectively. These high values would suggest the validity of the method for the micro-determination.

The stoichiometry of the complexed ligands in solutions was determined by Job's continuous variation method [3] and also by applying molar ratio [4], straight line [5] slope ratio [6] and limiting logarithmic [7] methods. The continuous variation and mole ratio methods indicate the formation of one type of complexes for the metal ions investigated with stoichiometric ratio 1:1 (M:L); (Figs. 1 and 2).

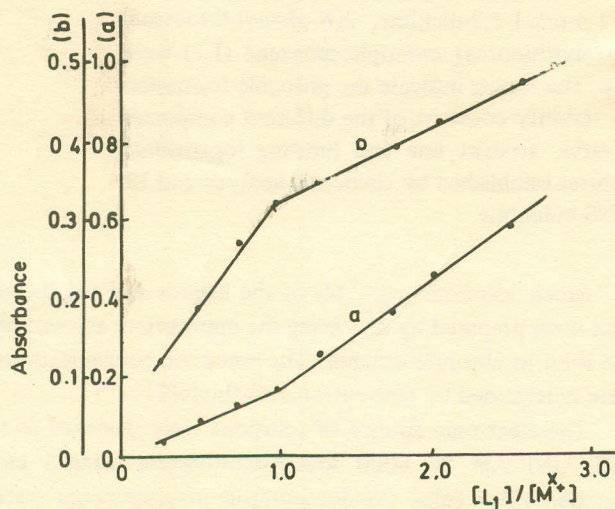


Fig. 1.

The apparent stability constant B_n is determined from the results of the molar ratio [4], straight line [5], continuous variation [6], and limiting logarithmic [7] methods using the relation:

$$B_n = \frac{A/A_m}{(1-A/A_m)n^2 C_{HL}^n}$$

where A = absorption, A_m - absorbance at saturation C_{HL} = concentration of the ligand and n = number of the ligand groups in complex.

For the straight line method the relation applied for the determination of B_n is as follows:

$$B_n = (\log C_m^{X+} \cdot C_{HL}) / (\log A - n \log V)$$

where V is the volume of the mixed solution and C_m^{X+} is the concentration of the metal ion.

The mean values of $\log B_n$ as well as the values of ΔG^* are given in Table 1. The results obtained indicated that the complexes of L_1 and L_2 exhibit moderate stability.

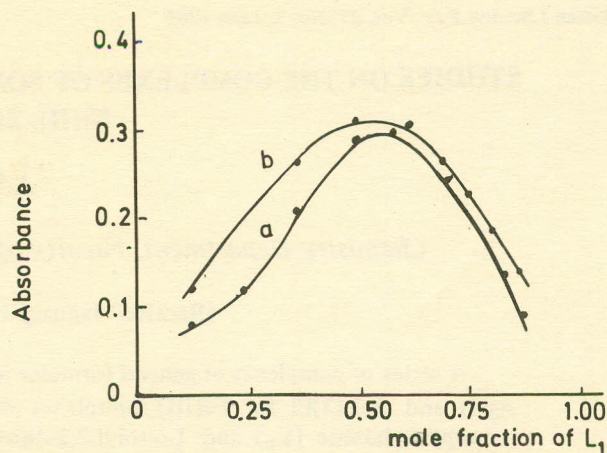


Fig. 2.

The composition of the complexes formed in solution were further confirmed by conductivity measurements, which show a progressive increase in specific conductance during the titration of metal ion solutions ($4 \times 10^{-4} M$) with that of the ligands ($2 \times 10^{-3} M$). The curves obtained are characterized by breaks at the molar ratio 1:1 (metal: ligand) (Fig. 3.).

The elemental analysis data of the solid complexes (Table 2) indicate that the ligand molecules under investigation are coordinated to the metal ion forming 1:1 complexes. The experimental values were in good agreement with those calculated from the stoichiometric formulae of the complexes under study. The general formula of the complexes of both L_1 and L_2 is $M(L)Cl_2$ Cl for Fe(III), $M(L)Cl_2$ for Co(II), Cu(II), Zn(II) and $M(L)NO_3$ for

Table 1. Values of $\log \beta$ and $-\Delta G^*$ for L_1 and L_2 complexes.

Complexes	$\log \beta$	ΔG^* Kcal/mole
Fe(III)- L_1	5.52	7.5
Co(II)- L_1	5.98	8.1
Ni(II)- L_1	5.85	8.0
Cu(II)- L_1	6.18	8.4
Zn(II)- L_1	5.79	7.9
Ag(I)- L_1	5.49	7.5
Fe(III)- L_2	5.30	7.2
Co(II)- L_2	5.50	7.5
Ni(II)- L_2	5.41	7.4
Cu(II)- L_2	5.89	8.0
Zn(II)- L_2	5.45	7.4
Ag(I)- L_2	5.07	6.9

Table 2. Analytical, colour, decomposition temperature and molar conductivity (Λ_M ohm⁻¹ cm² mole⁻¹) data of the monophosphazene complexes.

Complex	Colour	Λ_M	Decomp. Temp. °C	M.Wt.	Found (Calc.) %		
					C	N	Cl
<i>Metal Complexes of L₁</i>							
C ₂₆ H ₂₆ PN ₅ SCoCl ₂	skyblue	27	170	601.62 (601.70)	51.80 (51.92)	11.56 (11.64)	11.70 (11.79)
C ₂₆ H ₂₆ PN ₅ SNiCl ₂	green	20	180	601.40 (601.47)	51.90 (51.94)	11.90 (11.65)	11.85 (11.79)
C ₂₆ H ₂₆ PN ₅ SCuCl ₂	brown	21	194	606.75 (606.31)	51.70 (51.53)	11.40 (11.55)	11.60 (11.70)
C ₂₆ H ₂₆ PN ₅ SZnCl ₂	white	18	194	608.44 (608.15)	51.20 (51.37)	11.57 (11.52)	11.75 (11.66)
C ₂₆ H ₂₆ PN ₅ SAgNO ₃	brown	15	110	641.50 (641.73)	48.50 (48.68)	13.00 (13.10)	—
C ₂₆ H ₂₆ PN ₅ SFeCl ₂ Cl	brown	56	232	634.40 (634.07)	49.10 (49.27)	10.85 (11.05)	16.88 (16.78)
<i>Metal Complexes of L₂</i>							
C ₂₉ H ₃₂ SCoCl ₂	skyblue	23	160	643.22 (643.48)	54.00 (53.13)	10.80 (10.88)	11.10 (11.02)
C ₂₉ H ₃₂ PN ₅ SNiCl ₂	white-green	14	199	643.14 (643.25)	54.25 (54.15)	10.95 (10.89)	10.95 (11.02)
C ₂₉ H ₃₂ PN ₅ SCuCl ₂	brown	12	215	648.60 (648.09)	53.90 (53.74)	10.65 (10.80)	10.80 (10.94)
C ₂₉ H ₃₂ PN ₅ SZnCl ₂	white	22	171	649.55 (649.93)	53.50 (53.59)	10.90 (10.77)	11.00 (10.91)
C ₂₉ H ₃₂ PN ₅ SAgNO ₃	brown	26	104	683.58 (683.51)	50.80 (50.96)	12.15 (12.29)	—
[C ₂₉ H ₃₂ PN ₅ SFeCl ₂]Cl	brown	39	230	675.74 (675.85)	51.40 (51.53)	10.20 (10.36)	15.60 (15.74)

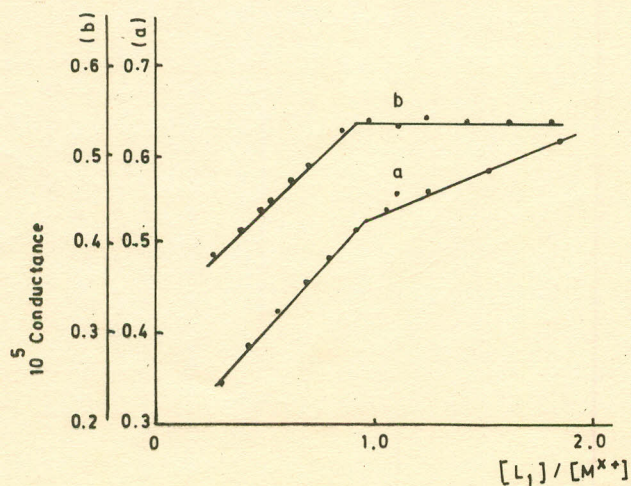


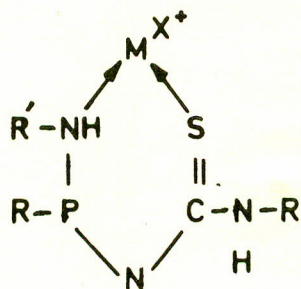
Fig. 3.

Ag(I) complexes.

The IR spectra of the ligands (in KBr) exhibit bands in the vicinity of 1350 and 3450 cm⁻¹ due to the stretching of both C=S[8] and NH groups. These bands are obviously shifted to lower frequencies when the ligands are bonded to the metal ions (10-55 cm⁻¹). This suggests that the ligands under investigation coordinate as bidentate where the two binding sites are the nitrogen and sulfur atoms of the N-H and C=S groups respectively. It should be noted also that, all the spectra of the metal chelates from S-M bonds which have a characteristic band at 395 cm⁻¹. Generally, the observed shift in the C=S and N-H to lower energy on complexation can be attributed to the electron acceptor character of the central positively charged metal ion resulting in decreasing the bond order of these bands.

It is worthy to mention that, the IR spectra of the free ligands do not display S-H band at 2570 cm^{-1} indicating that at least in the solid state they remain in the thione form.

From the foregoing results we can propose the mode of coordination of the metal ions used with the studied monophosphazenes (L_1 and L_2) in the 1:1 type complexes as represented in structure (I).



L_1 , $\text{R}' = \text{C}_6\text{H}_4\text{CH}_3\text{-O}$; $\text{R} = \text{Ph}$.

L_2 , $\text{R}' = \text{R} = \text{C}_6\text{H}_4\text{CH}_3\text{-O}$

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