

Synthesis, Spectral and XRD Studies on Isomeric Chelates of Strontium(II) and Barium(II) with Phthiocol and Plumbagin

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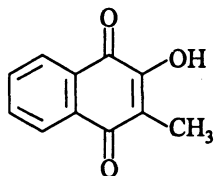
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Metal chelates of strontium(II) and barium(II) with isomeric phthiocol (3-methyl-2-hydroxy-1,4-naphthalene dione) and plumbagin (2-methyl-5-hydroxy-1,4-naphthalene dione) have been synthesized. Molecular structures of these isomeric chelates are investigated with the help of thermogravimetry, infrared and electronic spectroscopy and XRD. The results of structural investigations are employed to explore the nature and consequences of ring isomerism on the physical and structural characteristics of these isomeric chelates.

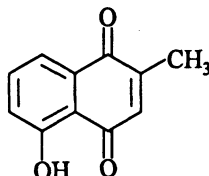
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INTRODUCTION

Among the alkaline earth metals, the coordination chemistry of strontium and barium is relatively much less investigated¹⁻³ as compared to beryllium, magnesium and calcium. The probable reasons behind this include (a) the poor complexing ability of Sr(II) and Ba(II), (b) absence of unpaired 'd' or 'f' valence electrons which play a predominant role in structural investigations, (c) lack of useful applications of the synthesized Sr(II) and Ba(II) complexes. Therefore, synthesis and chemical as well as structural characterization of new complexes of Sr(II) and Ba(II) along with some kind of their utility will be appreciated in promoting the coordination chemistry of these two alkaline earth metal ions.



(I) Phthiocol



(II) Plumbagin

Phthiocol (I) and plumbagin (II) are the two powerful chelating agents whose metal chelates^{4,5} are found to be extremely interesting in the field of structural, analytical and biological chemistry. From the structural point of view, these

isomeric ligands are specially attractive due to the formation of two series of isomeric chelates, one formed by phthiocol involving a five-membered ring and the other formed by plumbagin involving a six-membered ring. This results in an interesting type of isomerism caused exclusively due to the difference in the size of the ring which may be recognized as 'ring isomerism'. Exploration of the nature and consequences of such ring isomerism is an important area of our current interest. In this communication, we are reporting some of the significant observations and results of synthetic and structural investigations of isomeric phthiocolates and plumbaginate of Sr(II) and Ba(II).

EXPERIMENTAL

Syntheses: All reagents, chemicals and solvents used were of AR grade.

Ligands: Phthiocol was prepared from 2-methyl-1,4-naphthalene dione (Fluka, A.G. Switzerland) by following the method suggested by Fieser⁶, while plumbagin was the commercial product obtained from Bio Organics, Madra (India). The purity of both these ligands was checked, after recrystallization from ethanol by m.p. (phthiocol 173°C and plumbagin 76°C) and TLC.

Chelates: Methanolic solutions of the ligands (2 mmol 0.38 g phthiocol or plumbagin) and aqueous solution of strontium nitrate (1 mmol 0.212 g) and barium nitrate (1 mmol 0.261 g) were used. Aqueous ammonia solution (10%) prepared in distilled water was used to adjust the required pH.

The Sr(II) and Ba(II) phthiocolates and plumbaginate were precipitated by mixing the corresponding metal ion solution and ligand solution taken in the proportion of about 1 : 2 (with a slight excess of ligand solution) in a three-necked flask provided with a magnetic stirrer. After adjusting the pH to 4–5 for phthiocolates and 6–7 for plumbaginate by aqueous ammonia solution, the reaction mixtures were kept stirring for 1 h at room temperature and then kept in a refrigerator overnight. The products were filtered under suction, washed thoroughly with small quantities of ice-cold water and then with methanol and finally dried in a vacuum desiccator.

The chelates were analysed microanalytically using the Hosli-Holland analyzer for obtaining the percentages of carbon, hydrogen and residue (as metal oxide MO). Determination of the percentage of water molecules and confirmation of the percentage of metal oxide were also done through thermogravimetry by recording the thermograms of the chelates on Natus simultaneous thermo-analyzer STA-490 model. The solid state infrared spectra were recorded in nujol mulls on a Perkin-Elmer FTIR infrared spectrophotometer model 1600 in the range 4000–450 cm⁻¹. The electronic spectra of ligands as well as their chelates were recorded in distilled water on a Shimadzu UV-300 double beam spectrophotometer in the range 200–700 nm using 1.0 cm matched quartz cells. The XRD patterns were recorded on a Rigaku (Geigerflex RB RU 200) X-ray diffractometer using CuK_α radiation filter by a nickel foil over the range of diffraction angle 3.0–50.0°, the wavelength used being 1.542 Å.

RESULTS AND DISCUSSION

The molecular composition of the chelates, which has been established on the basis of elemental analysis and thermogravimetry, and their general physical properties are given in Table-1.

TABLE-1
ANALYTICAL DATA

Sr. No.	Empirical formula	Colour	Yield (%)	Elemental analysis: Found (Calcd.)		
				C	H	M (as MO)
1.	Sr(PH) ₂ ·4H ₂ O C ₂₂ H ₂₂ O ₁₀ Sr	Orange	66.25	49.68 (49.27)	4.16 (4.12)	16.50 (16.41)
2.	Sr(PH) ₂ ·2H ₂ O C ₂₂ H ₁₈ O ₈ Sr	Red brown	65.24	53.24 (53.05)	3.51 (3.61)	17.54 (17.96)
3.	Ba(PH) ₂ ·5H ₂ O C ₂₂ H ₂₄ O ₁₁ Ba	Dark orange	69.08	43.87 (43.90)	3.83 (3.99)	22.60 (22.83)
4.	Ba(PL) ₂ ·H ₂ O C ₂₂ H ₁₆ O ₇ Ba	Red brown	66.58	49.64 (49.87)	3.18 (3.02)	29.03 (28.96)

Note: PH = Phthiocol, PL = Plumbagin

An attractive feature of these chelates is their intense visible colours in solid state, which are quite stable. The phthiocolates possess intense orange colour while plumbaginates possess dark brown shades. All these chelates are partially soluble in water but the solubility of phthiocolates is relatively more than the corresponding plumbaginates. Similarly in polar solvents such as methanol, ethanol, acetone, DMF and DMSO, these chelates are partially soluble, the solubility trends being similar to that in water for the two series. In non-polar solvents such as hexane, heptane, chloroform, the solubility is very poor but here the plumbaginates are slightly more soluble than phthiocolates. This difference in physical properties such as colour and solubility trends may be attributed to the effect of ring isomerism on the molecular structures of the two series in solid state.

The thermal decomposition curves recorded in air show a two to three step weight loss pattern. In the initial step that occurs in the temperature range 0–180°C the weight loss corresponds to loss of water molecules that varies from one to five. In the subsequent steps, involving temperatures up to 530°C, oxidative decomposition of the ligands takes place resulting in the final product and alkaline metal oxide MO.

The significant IR peaks of the ligands and their chelates are shown in Table-2. These peaks are examined particularly to assess the effect of chelation and ring isomerism on their peak position and peak intensity leading to the following important conclusions.

TABLE-2
SIGNIFICANT IR PEAKS (cm⁻¹)

Sr. No.	Compound	ν(O—H)	ν(C=O)		ν(C—O)
			Chelated	Free	
1.	Phthiocol (PH)	3332	1635	1658	1208
2.	Plumbagin (PL)	—	1645	1662	1229
3.	Sr(PH) ₂ ·4H ₂ O	3386	1587	1642	1232
4.	Sr(PL) ₂ ·2H ₂ O	3455	1613	1641	1247
5.	Ba(PH) ₂ ·5H ₂ O	3374	1585	1641	1232
6.	Ba(PL) ₂ ·H ₂ O	3450	1607	1642	1232

- (i) The Sr(II) and Ba(II) phthiocolates as well as plumbaginates are strongly hydrated as indicated by the presence of characteristic bands due to O—H stretching frequency in the region 3600–3300 cm⁻¹.
- (ii) The chelated as well as unchelated C=O stretching frequencies^{7,8} are shifted to the lower frequency region for both the series. The large and red shift of the chelated C=O frequency by an amount of *ca.* 40 cm⁻¹ units indicates that the bonding is through carbonyl oxygen⁹. Here also the differential nature of the peak position and peak intensity for the two series is indicative of the effect of ring 'isomerism'.
- (iii) The C=O stretching frequency is shifted to the 'higher frequency' region for phthiocolates (1220–1230 cm⁻¹) as well as for plumbaginates (1255–1256 cm⁻¹) indicating that the C—O bond becomes stronger in the chelates which is consistent with the previous reports^{10, 11}.

Electronic spectra of phthiocol and plumbagin in organic solvents are recorded by previous workers¹²⁻¹⁴ which are conveniently described in terms of benzenoid electronic transitions (BET), quinonoid electronic transitions (QET) and $n \rightarrow \pi$ transitions.

In the present work, the spectra of both these ligands as well as their Sr(II) and Ba(II) chelates are recorded in water, in the region 200–700 nm. A comparative study of these spectra is expected to provide some useful information regarding the effect of chelation and ring size on the electronic energy levels of the ligands. The major absorption peaks are given in Table-3 and the results of the comparative study are summarized below.

TABLE-3
SIGNIFICANT ABSORPTION MAXIMA (nm) IN WATER

Sr. No.	Compound	Absorption Maxima λ_{\max} (nm)		
		BET	QET	$n \rightarrow \pi$
1.	Phthiocol (PH)	208	268	418
2.	Plumbagin (PL)	212	270	468
3.	Sr(PH) ₂ ·4H ₂ O	—	272	482
4.	Sr(PL) ₂ ·2H ₂ O	208	268	418
5.	Ba(PH) ₂ ·5H ₂ O	—	272	482
6.	Ba(PL) ₂ ·H ₂ O	208	268	422

Due to the partial solubility of these compounds in water, it was not possible to prepare transparent solutions of known concentration. Therefore, ϵ_{\max} values could not be calculated.

- (i) In general, this solution spectrum consists of three major bands observed in the regions 210–230 nm, 260–290 nm and 400–500 nm. These are respectively assigned to BET, QET and $n \rightarrow \pi$ transitions.
- (ii) For phthiocol, the BET band is observed distinctly at 208 nm, but it is totally missing in the spectra of its chelates; on the contrary, for plumbagin this BET band is observed at 212 nm as a weak and a broad band which becomes sharp and intense in the spectra of both of its chelates appearing at 208 nm.
- (iii) The second band due to QET, observed at 268 nm for phthiocol and at 270 nm for plumbagin, is present in the spectra of all the chelates, but shows opposite trends for both the series. Thus for phthiocolate, it shows a red shift and for plumbaginate it shows a blue shift. The amounts of these shifts however are small, *i.e.*, 2–4 nm.
- (iv) The third band due to $n \rightarrow \pi$ transition, observed in the region 400–500 nm, is very broad and weak but shows definite trends similar to those for QET. Thus for the phthiocolates, this band (at 418 nm) shows a red shift of 64 nm and appears at 482 nm while for plumbaginate, it shows the large blue shift due to which it is shifted from 468 nm to 418–422 nm.

The occurrence of red shifts for phthiocolates indicates the reduction in the energy gaps responsible for QET and $n \rightarrow \pi$ transitions while the blue shifts for plumbaginate indicate the increase in the corresponding energy gaps in the electronic energy levels of the ligands as a result of chelation. The opposite trends may be attributed to the effect of ring isomerism.

The powder X-ray diffraction patterns of the isomeric Sr(II) and Ba(II) are shown in Fig. 1. The indexing¹⁵ of these patterns has been done by using the computerized programme, powder diffraction package (PDP) prepared by M. Calligaris from Department di Science Chimiche University di Tries te Italy. From this, the lattice constants and crystal systems for the chelates are determined which are given in Table-4.

TABLE-4
LATTICE CONSTANTS AND CRYSTAL SYSTEMS OF THE CHELATES

Sr. No.	Compound	Lattice constant (Å)			Volume (Å) ³	Crystal systems
		a	b	c		
1.	Sr(PH) ₂ ·4H ₂ O	26.030	30.826	12.267	9843.050	Orthorhombic
2.	Sr(PL) ₂ ·2H ₂ O	22.974	25.497	14.967	8767.190	Orthorhombic
3.	Ba(PH) ₂ ·5H ₂ O	12.991	31.138	25.056	10135.497	Orthorhombic
4.	Ba(PL) ₂ ·H ₂ O	31.674	17.993	13.182	7512.557	Orthorhombic

PH = Phthiocol, PL = Plumbagin.

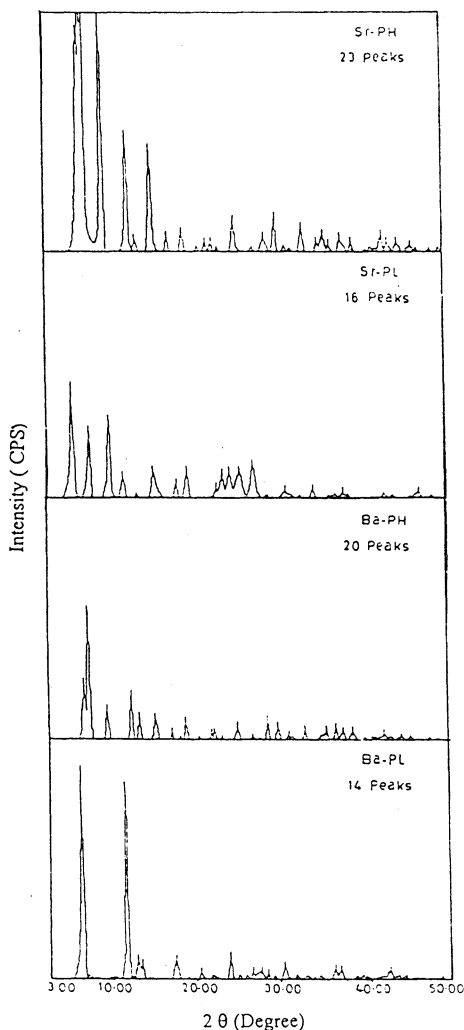


Fig. 1. XRD Patterns of isomeric chelates of Sr(II) and Ba(II)

The results and conclusions from the X-ray diffraction studies may be summarized as follows:

- (a) All the isomeric chelates are crystalline in nature as indicated from their X-ray patterns.
- (b) Same crystal system is adopted by Sr(II) and Ba(II) phthiocolates as well as plumbaginates which is orthorhombic. Therefore, it seems that there is no effect of 'ring size' on the lattice system.
- (c) There is, however, a significant difference in the volume of the unit cell of the two series. The volume of the phthiocolates is found to be greater than that of the corresponding plumbaginates.

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