5-(1-PHENYL-2, 2-DICYANOETHYL) BARBITURIC ACID (PDCEB) AS CHELATING LIGAND: COMPLEXES WITH IRON(III) AND DIOXOURANIUM (VI)

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The new coordination complexes of iron(III) and dioxouranium(VI) with a ligand drived from benzalmalononitrile and barbituric acid has been synthesized and characterized by, elemental analysis, electronic absorption spectra, infrared spectra, and ·potentiometric equilibrium measurements. The ligand behaves as monoprotic bidéntate NO donor forming complexes of the type $FeL_3.H_2O$ and $UO_2L_2.H_2O$ (where HL=ligand). The use of PDCEB as analytical reagent for determination of U(VI) and Fe(III) ions spectrophotometrically and as metallochrom indicator in the complexometric titration of Fe(III) ion is discussed. IR spectra reveals the existance of PDCEB in the closed tautomeric form.

Key words: Barbituric acid, Chelating ligand, Iron.

INTRODUCTION

Barbiturates are widely used medicinally and are among the most frequently encountered toxic drugs. They are, usually, determined via colour reaction with a metal ion in presence of base such as ammonia, pyridine, picoline, imidazole, and quinoline. Numerous workers have reported determination methods of barbiturates and thiobarbiturates through their complex formation with Hg(II) [1-3]. The formation of mixed complexes of metals with base and barbiturates has been reported as a method of drug determination [4-5].

A survey of literature reveals that no work has been carried out on the syntheses of 5-(1-phenyl 2,2-dicyanoethyl) barbituric acid (PDCEB)(I), and metal complexes of (I) which undergoes keto-enol tautomerism. The compound (I) has five potential donor sites (N_2O_3) with different coordinating abilities which may lead to varied bonding and stereochemical behaviour in complexes with different metal ions. In the present paper the syntheses and characterization of compound (I) and its metal complexes with iron (III) and dioxouranium (VI) are explained.

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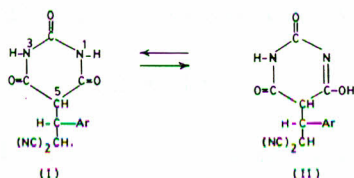
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EXPERIMENTAL

(i) *Preparation of the solid legand and its metal chelates*
A mixture of 6.4 g(0.05 mole) barbituric acid in 100 ml absolute ethanol in the presence of 1 ml piperidine. 7.7 g (0.05 mole) benzalmalononitrile was added and reaction mixture was refluxed for 3 hours, and concentrated. The solid obtained was filtered, dried and recrystallized from ethanol as colourless crystals, m. p. 224°, molecular formula; $C_{14}H_{10}N_4O_3$.

Analysis:	C	H	N
calculated:	59.57	3.54	19.85
Found:	60.00	3.80	19.80

The iron chelate was prepared by adding aqueous ligand (0.03 mole) solution to an aqueous solution of ferric perchlorate (0.01-mole). The mixture was refluxed, for one hour, cooled and concentrated. The reddish brown precipitate obtained was filtered off, washed with water and dried under vacuum. Similar procedure was used for uranyl chelate except that, the mixture used was 0.03 mole ligand to 0.015 mole uranyl nitrate, and orange crystals were separated on cooling. The analysis of the species prepared agrees with the molecular formulae; $FL_3.H_2O$, and $UO_2L_2.H_2O$, where $L = C_{14}H_9N_4O_3$.

(ii) *Reagents and materials.* Stock solutions of ferric perchlorate and uranyl nitrate were prepared and standardized using EDTA in the presence of suitable indicator [6].

(iii) *Procedures.* Potentiometric titrations and the experimental conditions were essentially the same as des-

cribed previously [7]. The temperature was 30° and the ionic strength was maintained at 0.10M with KNO_3. The value of the activity coefficient, ν, for hydrogen ion in water at 0.10M ionic strength was taken as 0.78.

The electronic spectra of solutions were recorded at 25° with a Perkin-Elmer 552 spectrophotometer using 1 cm matched stoppered quartz cells. IR spectra were recorded on a Pye Unicam SP 2000 spectrophotometer (200-4000 cm^{-1}) using potassium bromide discs.

RESULTS AND DISCUSSION

Potentiometric results. The pH-metric titration curves for the free ligand and complex B(B stands for the ligand anion) are shown in Fig. 1. Between a=0 and a=1 and in presence of different metal ions, only one proton dissociates (a moles of base added per mole of ligand present). This suggest that under these experimental conditions the ligand behaves as monoprotic species, with the dissociation of the NH or the enolic OH-group proton. The acid dissociation constant, pK^H, was calculated by using the relationship;

$$\log K^H = \log \frac{aC_L - [H^+] + [OH^-]}{(1-a)C_L + [H^+] - [OH^-]} + pH \qquad (1)$$

The titration curve for a system containing 1:2 molar ratio of U(VI) and PDCEB is similar to 1:5 titration curve wich exhibits one long buffer region from a=0 to a=2, indicating the formation of mono & bis-binary complexes. The inflection point at a=2 in 1:5 titration curve (Fig. 1) indicates that 1:2 chelates is higher complex type formed in U(VI)-PDCEB system.

The titration curve of 1:10 molar ratio of Fe(III) to PDCEB (Fig. 1), shows one long buffer region between a=0 and a=3, corresponding to the formation of FeL^{++} FeL_2^+, and FeL_3 complexes.

The average number of ligand bound per metal ion, $\overline{n}$ and the free ligand concentration [L], were calculated by the formula given by Irving and Rossotti [8]. The values of $\log K_1$, $\log K_2$. and $\log K_3$ were calculated with the help of the expressions:

$$\text{Log} \frac{\overline{n}}{1 - \overline{n}} = \text{Log} K_1 - pL \qquad (2)$$

$$\text{Log} \frac{\overline{n} - 1}{2 - \overline{n}} = \text{Log} K_2 - pL \qquad (3)$$

$$\text{Log} \frac{\overline{n} - 2}{3 - \overline{n}} = \text{Log} K_3 - pL \qquad (4)$$
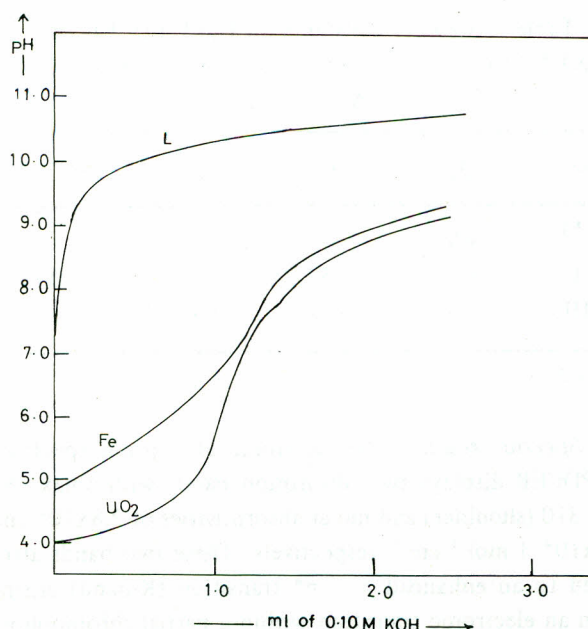

Fig 1. Potentiometric titration curves of PDCEB and its complexes with UO_2^{2+} and Fe (III) ions at 30° in water solvent.
(1) Free ligand = [PDCEB] = 0.0033 M.
(2) [PDCEB] = 0.0133 M + [Fe(III)] = 0.00133 M.
(3) [PDCEB] = 0.00833 M + [UO_2^{2+}] = 0.00167 M.

These expressions were solved by the graphic relation in the plots of $\log (\overline{n}/1-\overline{n})$ vs. pL; $\log(\overline{n}-1/2-\overline{n})$ vs. pL; and $\log (\overline{n}-2/3-\overline{n})$ vs pL. These representation were plotted in Fig. 2. The accurate values of $\log K_1$, $\log K_2$, and $\log K_3$ were determined by the method of least squares. A summary of the constants obtained is given in Table 1. In this Table it can be seen that the ratio of successive stability constants, $\log(K_1/K_2)^2$ is positive for UO_2^{2+}-PDCEB, and Fe^{3+}-PDCEB chelates and equals to 0.50, and 0.66 respectively. These lower values indicate that the 2:1 complex is predominant and forms at the start of titration [9].
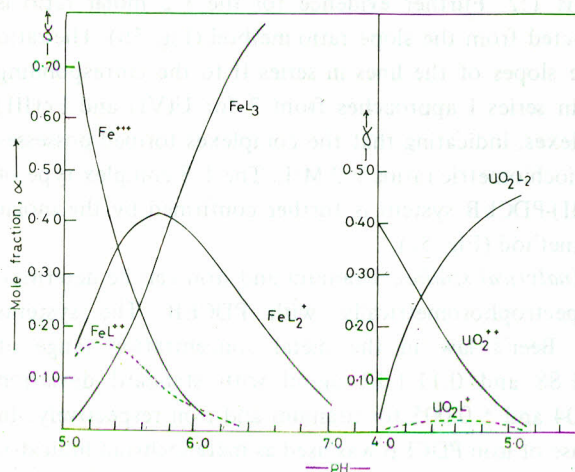

Fig. 2. Metal-ligand formation constants of Fe(III)-PDCEB and U(VI)-PDCEB by linear plot method.

Table 1. Stability constants for U(VI)-PDCEB, and Fe(III)-PDCEB complexes. T=30°, ionic strength = 0.10 M(KNO$_3$).

Cation	logK$_1$	logK$_2$	logK$_3$	log(K$_1$/K$_2$)
H$^{+(*)}$	9.97			
U(VI)	8.07	7.57		0.50
Fe(III)	6.84	6.18	5.48	0.66

(*) ± 0.06

Spectral results. The electronic absorption spectrum of PDCEB displays two absorption bands with λmax 286 and 310 (shoulder) and molar absorptivities of 2.8x10^3 and 4.8x10^2 1.mol^{-1}.cm^{-1} respectively. These two bands attributed to an enhanced $\pi - \pi^*$ transition (K-band) arising from an electronic transition within a partial chromophore and an enhanced n $- \pi^*$ transition (R-band) of carbonyl, respectively.

When ligand solution is mixed with Fe(III) or U(VI) (in water) violet and orange colour was detected respectively. These colours are stable for 24 hours and reach maximum intensity within 5-15 minutes. The optimum pH is 4.0 and 5.0 for U(VI) and Fe(III) complexes respectively. In the case of U(VI)-PDCEB mixture maximum absorbance is reached at an U(VI): PDCEB molar ratio of 1:2, whereas, in the case of Fe(III)-PDCEB system a maximum is observed at molar ratio of 1:3. (See Figs. 3 & 4).

The composition of the complexes obtained in these systems is determined using Job's, slope ratio, and molar ratio methods. The variation of the absorbance with Fe(III), and U(VI) mole fractions is shown in Fig. 5a, which indicates that the Fe (III)-PDCEB and U(VI)-PDCEB molar ratio is 1:2. Further evidence for the 1:2 molar ratio is abstracted from the slope ratio method (Fig. 5b). The ratio of the slopes of the lines in series II to the corresponding lines in series I approaches from 2 for U(VI) and Fe(III) complexes, indicating that the complexes formed possesses the stiochiometric ratios 1:2 M:L. The 1:3 complex type of Fe (III)-PDCEB system is further confirmed by the molar ratio method (Fig. 5c).

Analytical studies. Uranium and iron can be determined spectrophotometrically with PDCEB. The systems obeys Beer's law in the metal concentration-range of 0.06-1.88 and 0.11-1.12 μg/ml with standard deviation ± 0.004 and ± 0.005 for uranium and iron respectively. In the case of iron PDCEB was used as metallochrom indicator in the complexometric titration of iron. The addition of few crystals of the solid ligand to Fe(III) solution (0.02-
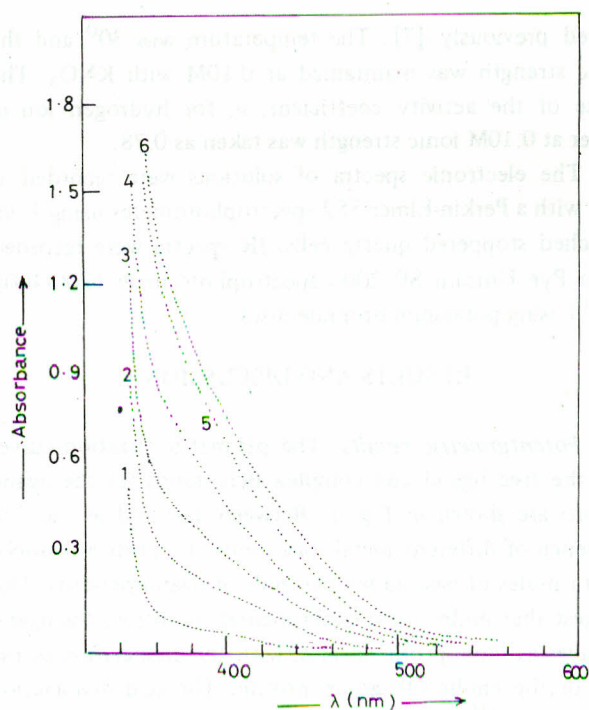
Fig. 3. Electronic absorption spectra of U(VI)-PDCEB chelates at optimum pH.

(1)	[U(VI)] = 0.005 M	+	[PDCEB]	=	0.00213	M.
(2)	[U(VI)] = 0.005 M	+	[PDCEB]	=	0.00398	M.
(3)	[U(VI)] = 0.005 M	+	[PDCEB]	=	0.00540	M.
(4)	[U(VI)] = 0.005 M	+	[PDCEB]	=	0.00795	M.
(5)	[U(VI)] = 0.005 M	+	[PDCEB]	=	0.01020	M.
(6)	[U(VI)] = 0.005 M	+	[PDCEB]	=	0.01500	M.

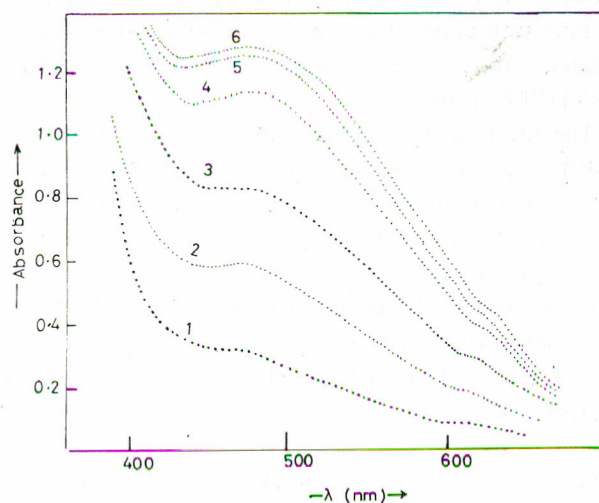Fig. 4. Electronic absorption spectra of Fe(III)-PDCEB chelates at optimum pH.

(1)	[Fe(III)] = 0.008 M	+	[PDCEB] = 0.0045 M.
(2)	[Fe(III)] = 0.008 M	+	[PDCEB] = 0.0105 M.
(3)	[Fe(III)] = 0.008 M	+	[PDCEB] = 0.0165 M.
(4)	[Fe(III)] = 0.008 M	+	[PDCEB] = 0.0210 M.
(5)	[Fe(III)] = 0.008 M	+	[PDCEB] = 0.0240 M.
(6)	[Fe(III)] = 0.008 M	+	[PDCEB] = 0.0600 M.

Fig. 5 (A) Job's method; (B) Slope ratio method; (C) Molar ratio method. Scale between brackets for Fe(III) chelates.

Table 2. Ultraviolet and visible absorption spectra of the ligand and metal chelates in DMF.

Species	λ nm	log ϵ	Assignment
PDCEB	280	3.455	$\pi - \pi^*$ (K-band)
	310	2.681	$n - \pi^*$ (R-band)
U(VI)-chelate	270	4.061	$\pi - \pi^*$
	320	4.634	$n - \pi^*$
	485	3.846	$\Sigma g^+ \rightarrow {}^3\pi_u$
	550	3.778	CT
Fe(III)-chelate	280	4.947	$\pi - \pi^*$
	300	4.916	$n - \pi^*$
	480	4.978	$4T_{2g} \leftarrow {}^6A_{1g}$
	620	4.653	$4T_{1g} \leftarrow {}^6A_{1g}$

first two corresponding to the complexing agent if shifted to lower wavelengths. This shift can be ascribed to the polarization suffered by the ligand as a consequence of the coordination around uranium central atom. The band located at 480nm which is assigned to the $1 \Sigma g^+ \rightarrow {}^3\pi_u$ transition typical of OUO symmetric stretching frequency for the first excited state. This band is expected at 420nm [10]. The shift of this band towards longer wavelength could be due to the withdrawing effect of the two CN

0.10 M) produces violet colour which turns to yellowish at equivalent point when titrated with standard EDTA solution. The results obtained are in excellent agreement with those obtained following the spectrophotometric titration method and other standard procedures.

The electronic spectra of $UO_2B_2.H_2O$ complex show four bands at: 270, 320, 480, and 550nm (Table 2). the

Fig. 6.

groups in PDCEB. The band at 550nm is charge transfer band, such transfer takes place from the oxygens of the uranyl group to the central uranium ion.

The Fe(III) complexes reported reveal four bands at: 280, 300nm these bands were ascribed previously to the ligand. The other two bands at 480, and 620nm assignable to $^4T_{2g} \leftarrow {}^6A_{1g}$ and $^4T_{1g} \leftarrow {}^6A_{1g}$ transitions [11].

IR spectra of PDCEB and their complexes with U(VI) and Fe(III) ions. Since the ligand under investigation are polyfunctional and possess different sites, infrared spectra of the ligand and those of the complexes were compared in order to decide the bonding sites. Owing to the extensive mixing of δ (NH), ν (C=C). ν (C-O), ν (C=N) and τ (NH) modes. The infrared spectra were characterised by the presence of IR bands. Complications also arose by the presence of the ligand in different tautomeric forms included open (I and II) and closed (III and IV) structures;
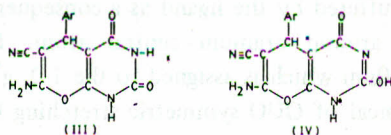
The ν (C=o) vibrational modes are present in the free ligand spectrum as a broader band at 1690 cm^{-1} of B$_1$ type, which contains two shoulders at 1735 cm^{-1} and 1705 cm^{-1} of A$_1$ type [12]. The ν N-H stretching is also possible for the band at 1685 cm^{-1}. The broad band appearing in the region 1580-1630 cm^{-1} in the ligand is due to ν (C=N) and partial overlapping of ν C=N + ν C=C and ν NH bending modes. In U(VI) complex two broad bands appearing at 1720-1675 and 1660-1570 cm^{-1}. Fe(III) complex shows three bands at 1690 (weak), 1680 (weak) and a strong one at 1620 cm^{-1}. These bands could be due to the uncomplexed C=O, and NH groups, beside the stretching vibrations of ν C=C and ν C=N groups (see Table 3).

The ligand exhibits several bands between 1490-1210 cm^{-1}. The most probable vibrations to be expected are C-N$_1$, C-N$_3$ stretching, δ N$_1$-H and δN$_3$-H inplane bending modes. Also the vibration of ν C-O enolic could be found in this region. The δ N$_1$-H and δN$_3$-H vibration is found at 1460 and 1370 cm^{-1}, while the bands at 1290 and 1210 cm^{-1} are assigned to ν C-N$_1$ and ν C-N$_3$ vibrations. In ligand PDCEB δ N$_1$-H disappears while δ N$_3$-H shifted to 1380 and 1400 cm^{-1} for U(VI) and Fe (III) chelates respectively. A new band is noticed in the complexes at 1150 and 1130 for U(VI) and Fe (III) chelates, this band can be assigned to the enolic ν C-O. This band as well as the observed disappearance of δ N$_1$-H vibration in the complexes can be explained by the conversion of the dilactam

Table 3. Selected band groups in the IR spectra and their tentative assignment, cm^{-1}

PDCEB	U(VI)-PDCEB	Fe(III)-PDCEB	Assignment
	3300 b	3330 b	νHOH
3140 b	–	–	νNH
3050 w	3020 w	3020 w	νCH
2960 w	2940 w	2990 w	
2250 m	2200 m	2200 s	νC≡N
1735 sh			
1710 sh			νC=O, νNH
1690 s	1690 b	1690 w	
1685 sh		1680 w	
1630 m	1630 b	1620 m	νC=C, νC=N
1600 b			
1460 s	–	–	δN$_1$-H
1370 b	1380 s	1400 s	δN$_3$-H
1290 s	1280 m	1280 w	νC-N$_1$
1210 s	1200 m	–	νC-N$_3$
	1150 s	1130 w	New band
1070 m	–	–	ν(C-O-C), Structure III & IV
	920 s	–	νas (U=O)
	410 m	480 w	νM-O
	385 m	350 w	νN-O
	365 m		

s = strong; m = medium; w = weak; b = broad; sh = shoulder

form (O=C-NH-) of barbitone to the dilactim form (O-C=N) of the ligated barbitone on coordination. This indicates the deprotonation of only one of the two NH groups (N$_1$-H). This is in good agreement with pH-metric studies that in presence of various metal ions only one proton is liberated during the titration.

The infrared spectra of U(VI) complex show a very strong band attributed to the antisymmetric ν_3 (O-U-O) at 912 cm^{-1}, and this is in the usual range (ν_{as}, 870-950 cm^{-1}) as reported for the majority of dioxouranium (VI) complexes [13-14].

The participation of nitrogen atom in N$_1$-H and oxygen in enolic OH groups are further confirmed from the following finding:

(a) The position of the band due to ν (NH) at 3140 cm^{-1} in PDCEB disappeared in the complexes and a new band appeared around 3300 cm^{-1} which may be a band due to coordinated water. This suggested the deprotonation of

N_1H group which was also indicated by the charge balance in the complexes.

(b) The appearance of new bands in the IR spectra of the complexes, at 410, 385 and 365 cm^{-1} for U(VI) complex, and at 480 and 350 cm^{-1} for Fe(III) complexes. These bands can be assigned to ν M–O, and ν M–N respectively.

The band observed at 1070cm^{-1} in the spectrum of the ligand may be assigned to the ν (C-O-C) mode of pyran moeity indicative of the closed tautomeric forms III and IV of the ligand. This band is not observed in the spectra of the complexes, and indicates the closed forms of the ligand participate in chelate formation. Such posibility could be remote due to the weak basicity of oxygen atom in pyran ring, and less stability of such ring. The disappearance of ν (C-O-C) band in the spectra of the complexes can be due to the presence of metal ions in closed structure of the ligand transferred to the open tautomeric form .

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