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# Spectrophotometric Determination Of Cobalt(II) With 5- (4-Hydroxy-3,5-Dimethylbenzilidene)Thiazolidine-2,4-Dione

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***Abstract*—The possibility of using 5-(4-hydroxy-3,5-dimethylbenzylidene)thiazolidine-2,4-dione (HDBT) for spectrophotometric determination of cobalt(II) has been studied. Structure of ligand was confirmed by using NMR and IR spectra. The cobalt(II) complex is formed in the pH range 5.7-6.9. The best results were observed by using methanol as a proper solvent. The optimal condition for the formation and extraction of the complex is 5× $10^{-4}$ mol / L concentration of HDBT. The maximum analytical signal for the complexation of cobalt with HDBT is observed at 517 nm. Bathochromic shift is 181 nm. The molar absorption coefficient is $2.10\times10^{4}$. The ratio of components in the complex is Co:HDBT=1:2. These data were utilized to calculate stability constant of complex (lgβ). The complex of cobalt with HDBT is stable in aqueous and organic solvent and does not decom-pose for two days. It was found that the complexing form of cobalt is $Co^{2+}$.The structure of the complex was studied by spectrophotometry, IR spectroscopy and thermogravimetry. Obedience to the basic law of light absorption is observed at a cobalt concentration of 0.5-14 µg / mL. Based on the results of spectrophotometric studies of cobalt(II) with HDBT, methods for determining cobalt in different objects have been developed.**

***Keywords—cobalt, 5-(4-hydroxy-3,5-dimethylbenzylidene)thiazolidine-2,4-dione, spectrophotometric method***

## 1.INTRODUCTION

Cobalt is one of the chemical factors that are ecologically important for the body. Cobalt belongs to the group of micronutrients, that is, it is vital for the functioning of living organisms. Together with them, in excess, as and many other micronutrients for the body are toxic and may even be destructive. Cobalt can contribute to the development of tumors, it is even included in the list of carcinogenic agents. İt play an important role in biological processes in the body, and are an indicator of some diseases. For example, the absence of cobalt in the body causes acobaltosis [1].This requires continuous monitoring of industrial pollutants and the migration of toxic substances in the environment and creates the need for the implementation of operational and reliable control of the content of heavy metals with toxic properties.

For the photometric determination of cobalt, reagents with an *o*-nitrosophenol group or a similar structure with an oxime group are rather selective [2,3]. The most widely used methods are those that use organic reagents derived from nitrosonaphtoles, pyridine azocompounds, of which 4-(2-pyridylazo)resorcinol is widespread [4]. The optimal experimental conditions for the quantitative sorption of Co(II)-4-(2-pyridylazo) resorcinol were found. The proposed method has been applied to determine cobalt in various water samples [5].

A spectrophotometric method for the determination of Co(II) using N-(*o*-hydroxybenzylidene)pyridin-2-amine is proposed. The developed method is used to determine Co(II) in pharmaceutical samples [6].

Mixed ligand complexes of cobalt with dithiophenols and hydrophobic amines [7,8], with 4-(2-pyridylazo) resorcinol and 1,4-diphenyl-3-(phenylamino)-1H-1,2,4-triazole [9], with 4-(2-pyridylazo)resorcinol and tetrazolium salts [10] were used for the extraction-photometric determination of cobalt in various natural and industrial objects.

We have studied the possibility of using 5-(4-hydroxy-3,5-dimethylbenzyli-dene) thiazolidine-2,4-dione (HDBT) for the photometric determination of cobalt(II).

## Experimental part

### Instruments

The absorbance of the extracts was measured using a Shimadzu UV1240 spectrophotometer (Japan) and KFK-2 photocolorimeter (USSR). Glass cells with optical path of 10 or 5 mm were used. pH of aqueous phase was measured using an I-120.2 potentiometer with a glass electrode.

Muffle furnace was used for dissolution of the samples. IR spectra were recorded using a Specord M-80 spectrophotometer (Germany). $^{1}$H-NMR spectra were recorded on "Bruker" Fourier Transform (300,18 MHz) in $C_6D_6$.

### Reagents and Solutions

Standard solution (1 mg/ml) of Co(II) was prepared by dissolving an exact sample of $CoSO_4 \cdot 7H_2O$ in water containing 2 ml of conc. $H_2SO_4$, and diluted with water to 1 l [2]. The working solutions were prepared just be-fore use by dilution of the standard solution with redistilled deionised water. HDBT were synthesized according to the procedure [11]. The reagent solution (0.002 M) was prepared by dissolving accurately weight of pure reagent in sodium hydroxide (1 M). Freshly prepared solutions were used for all experiments. To create the optimal pH, 1M solutions of KOH and NaOH or Britton-Robinson buffer were applied (pH 5-12).

Structure of ligand was confirmed by using NMR and IR spectra [12,13]. IR (KBr, $cm^{-1}$): 3364 (N-H); 2925 (Ar-H), 1674 (C=O), 1573 (C=N), 1449 (C=C), 1380 (C-N) 733 (C-S-C), $^1$HNMR (sDMSO-d6) d: 2.2 (6H, s), 7.18 (2H, s), 7.61 (1H, s), 9.16 (1H, s), 12.45 (1H, s).

The stock solution of various metal ions and anions were prepared by dissolving the appropriate metal salts in distilled water or with suitable dilute acids and making up to a known volume.

### General Procedure

### General procedure for the determination of cobalt(II)

In a 10 mL volumetric flask, 1 mL of the solution containing 5-100 μg $Co^{2+}$ and 2 mL of a 0.01 M 5-(4-hydroxy-3,5-dimethylbenzylidene) thiazolidine-2,4-dione reagent was added and the volume was adjusted to 10 mL with metha-nol. Absorbance was measured at 490 nm against the reagent blank (l=0.5cm). Calibration graphs were constructed by plotting the absorbance *vs.* $Co^{2+}$ concentration.

### Determination of cobalt in sewage water and bottom sediments

1*l* taken for analysis of waste water is evaporated to obtain a precipitate, do not boil. The precipitate was dissolved in 5 ml of conc.$HNO_3$, was transferred to a 50 ml flask and diluted to the mark with water. Cobalt was determined in aliquots of the solution using the procedure proposed by us.

### Determination of cobalt in plant samples

A portion of the plants (25-50 g ) were crushed and dried in a porcelain dish, first at 60-70° C, then at a temperature of 105°C. The dry residue was ashed in a muffle furnace at 500 °C. The ash was dissolved in diluted (1: 1) $HNO_3$ and evaporated to wet salts, which were then dissolved in water, filtered into a 100 ml volumetric flask and diluted with distilled water to the mark. Cobalt was determined in aliquots of the solution using the procedure proposed by us.

## RESULTS AND DISCUSSION

HDBT forms stable and red colored complex with Co(II) in some aqueous and non-aqueous solvents. A solvent which could dissolve both the HDBT reagent and the Co-HDBT complex would be a suitable solvent. On the other hand acceptable absorbance spectra for the formed complexes should be observed without the interference from the reagent. In this study, ethyl alcohol, methyl alcohol, water (basic media), chloroform, hexane, dichloromethane and acetonitrile were used. The best results were observed by using methanol as a proper solvent. The complex is formed in the range of pH 5.7-6.9. With a decrease in pH, light absorption gradually decreases, which is obviously associated with a decrease in the concentration of the ionized form of HDBT and, most likely, in solution it is in an undissociated form. At pH 8.5, the complex practically does not form, which, apparently, is associated with the hydrolysis of the cobalt ion. The beginning of the precipitation of cobalt hydroxide pH 7.6; The pH of complete precipitation is observed at 9.2. The optimal condition for the formation and extraction of the complex is the HDBT concentration of 5 × $10^{-4}$ mol / L.

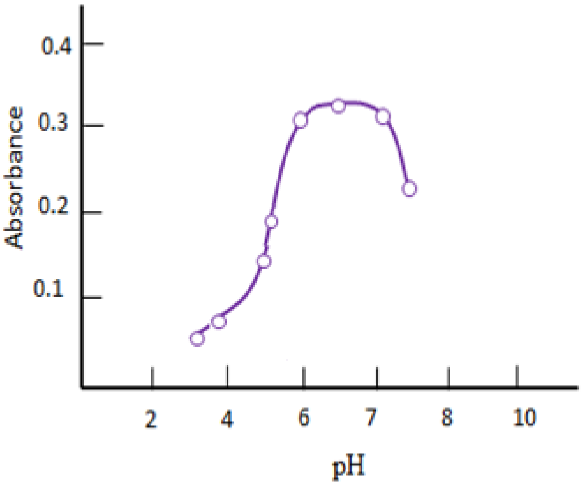


Fig.1. The dependence of the light absorption of the complex on the pH of the solution.

$C_{Co(II)}=3.38\times10^{-5}$ M; $C_{HDBT} = 5.0\times10^{-4}$ M; КФК-2, $\lambda$=490 nm *l* = 1 cm

The complex of cobalt with HDBT is stable in aqueous and organic solvent and does not decompose for two days. Maximum light absorption is achieved within 5 minutes. The complex is stable when heated to 80° C. The maximum analytical signal in the complexation of cobalt with HDBT is observed at 517 nm. HDBT maximally absorbs at 336 nm. Bathochromic shift is 181 nm. The molar absorption coefficient is 2.10 × $10^4$.

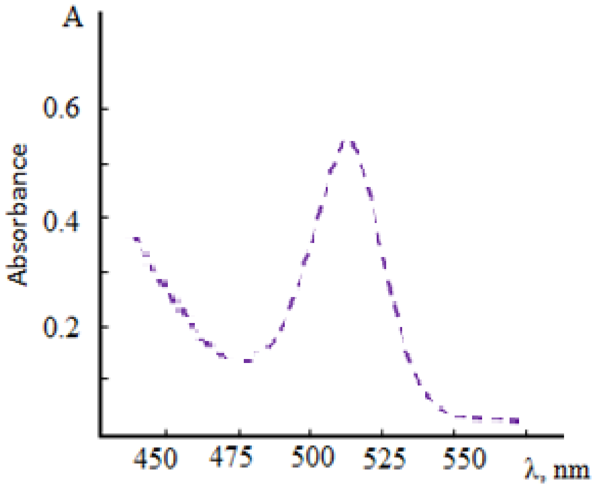


Fig.2. Absorption spectra

$C_{Co(II)}$=3.38×$10^{-5}$M; $C_{HDBT}$ = 5.0×$10^{-4}$ M; CФ-26, *l*=1 cm

The chemical structure of Co(II)-HDBT complex was determined equilibrium shift, the relative output of Starik Barbanel and the straight line methods [14]. All methods showed that the ratio of components in the complex is Co: HDBT = 1: 2. The data of these were utilized to calculate stability constant of complex.

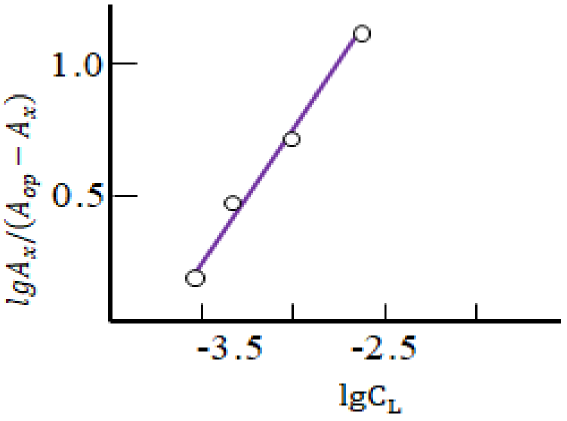


Fig. 3. Determination of the ratio of components by equilibrium shift method

$C_{Co(II)}$=3.38×$10^{-5}$M; CФ-26, *l*=1cm.

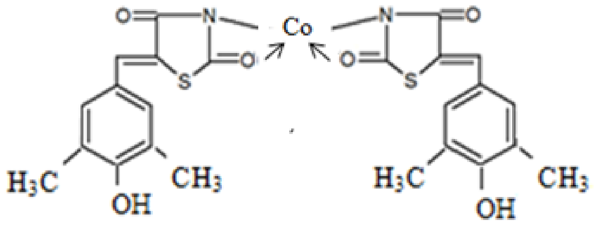
The complex of Co(II) with HDBT was synthesized and investigated by IR spectroscopy. The IR spectrum of the complex is compared with the spectrum of the reagent. The observed band in the region of 1593-1448 cm$^{-1}$ corresponds to the aromatic ring (C = C). In the IR spectra of the complex in the region of 3050-3020 cm$^{-1}$ there are strong absorption bands associated with $\nu_{CH}$ in the aromatic core. In the IR spectra of the complex in the region of 3050-3020 cm$^{-1}$ there are strong absorption bands associated with $\nu_{CH}$ in the aromatic core. The IR spectra of the BMBT shows ν(C=S) band at 1320 cm$^{-1}$, ν(C=N) band at 1590 cm$^{-1}$.

The absorption bands at 830–720 cm$^{-1}$ can be attributed to C-H deformation vibrations, the absorption bands at 1630–1460 cm$^{-1}$ to the stretching vibrations of phenyl rings, and the absorption bands at 1370 cm$^{-1}$ to $\nu_{(CN)}$. $\nu_{CS}$ is observed at 685 cm$^{-1}$, and $\nu_{CO}$ is observed at 1291 cm$^{-1}$. The absorption bands at 450 cm$^{-1}$ and 575 cm$^{-1}$ correspond to ν (Co-O) and ν (Co – N), respectively [12,13]. The disappearance of the absorption band in the region of 3500–3250 cm$^{-1}$ with a maximum at 3364 cm$^{-1}$ indicates the absence of free NH groups in the synthesized complex. This indi-cates that metal is kovalently bonded with nitrogen and coordinate bonded with oxygen.

A thermogravimetric study of the Co-HDBT complex showed that its thermal decomposition occurs in two stages. The dehydration temperature (90° C - 110° C) on the DTA curve by the endothermic effect (weight loss 4.89%) indicates the dehydration of the complex. In the temperature range of 380-460 $^oC$, the maximum rate of mass loss is observed, which is associated with the removal of HDBT (weight loss 41.76%). The end product of thermolysis of the complex is CoO.

It was found that the complexing form of cobalt is $Co^{2+}$ [15, 16]. At the same time, the number of hydrogen atoms, which it displaces from one HDBT molecule, turned out to be equal to 1.

Based on the ratio of components in the resulting complexes, the number of protons being displaced, and the ionic form of cobalt, one can imagine the probable structure of the complexes on Co-HDBT



It was established that with 5-(4-hydroxy-3,5-dimethylbenzylidene) thiazoli-dine-2,4-dione the colored comp-lexes also form ions of Fe(III), Cu(II), Ni(II), Mo(VI), Pt(II), Mn(II), Cd(II), Zn(II) and Pd(II). The selectivity of the determination increases significantly in the presence of masking agents or when the pH of the me-dium changes. Large amounts of oxalate, thiosulfate, fluoride, chloride, bromide, sulfate, acetate, tartrate and citrate ions do not interfere with the determination. Thiocyanate, thiourea and phosphate ion interfere, even when present in small quantities. The in-terference of Zn(II), Pb(II) Se(IV), Ce(IV), Cu(II), Cd(II) and Pd(II) can be eliminated by using 1.0 ml of 0.5% thiosulphate solution.

The extract of the complex obeys the basic law of absorption at a concentration of 0.5-14 µg / mL. The data obtained for the construction of the calibration curve were processed by the method of least squares [16]. Based on the equation of the calibration graphs, the limit of photometric detection and the limit of quantitative determination of cobalt were calculated.

In tab. 1 shows the main spectrophotometric characteristics of the method for determining Co(II) with HDBT.

**Table 1.** Formation conditions and some chemical and analytical properties of Co(II) with HDBT

| Parameter | Value |
|---|---|
| Color | red |
| pH $_{op}$ | 5.7-6.9 |
| $\lambda_{max}$ (nm) | 517 |
| Bathochromic shift | 181 |
| Molar absorptivity (L· mol$^{-1}$ cm$^{-1}$) | $2.10 \cdot 10^{4}$ |
| Sandell's sensitivity (ng·cm$^{-2}$) | 2.80 |
| The equation of calibration curves | 0.045+0.0708x |
| Correlation coefficient | 0.9954 |
| Stability constant (lgβ) | 13.5 |
| Beer's law range (µg·mL$^{-1}$) | 0.5-14 |
| Limit of detection (LOD): ng·mL$^{-1}$ | 11 |
| Limit of quantification (LOQ): ng·mL$^{-1}$ | 36 |

Table 2 shows the data that allow us to compare the analytical characteristics of the photometric methods of cobalt(II) developed by us with some already known [3, 9, 17]. As can be seen from the table, the methods proposed by us are quite selective, sensitive, they are expressive and allow to determine even small amounts of these metals and to obtain reproducible results.

**Table 2.** Comparative characteristics of cobalt determination methods

| Reagent | pH | Solvent | $\lambda$ , nm | $\varepsilon \times 10^{-4}$ | Beer's law range (µg·mL$^{-1}$) |
|---|---|---|---|---|---|
| 1-nitrosonaphthol-2 [3] | pH≥3 | Chloroform | 415 | 2.9 | |
| Nitroso R-salt [3] | Weak acid | | 500 | 1.5 | |
| Bromopirogall red [17] | 2.0 | | 575 | 1.08 | 0.25-110 |
| 4-(2-pyridylazo)-resorcinol+ chloride 2-(4-iodophenyl)-3-(4-nitrophenyl)-5-phenyl-2H-tetrazolium [9] | 4.7 | | 515 | 1.4 | |
| HDBT | 5.7-6.9 | Methanol | 517 | 2.10 | 0.5-10 |

Based on the results of spectrophotometric studies of Co(II) with HDBT, were developed methods for the quantitative determination of cobalt in plants, wastewater and bottom sediments (Tables 3 and 4).

**Table 3.** The results of the determination of cobalt (**II**) in plants (n = 6, P = 0.95)

| Analysis object | Reagent | $S_r$ | Found, mg/kg |
|---|---|---|---|
| Beans | 1-nitrosonaphthol-2 | 0.024 | 0.21±0.0055 |
| | 8-mercaptoquinoline | 0.023 | 0.19±0.0050 |
| | HDBT | 0.019 | 0.18±0.0039 |
| Peas | 1-nitrosonaphthol-2 | 0.035 | 0.11±0.0042 |
| | 8-mercaptoquinoline | 0.049 | 0.13±0.0058 |
| | HDBT | 0.038 | 0.12±0.0048 |
| Wheat | 1-nitrosonaphthol-2 | 0.038 | 0.12±0.0048 |
| | 8-mercaptoquinoline | 0.026 | 0.12±0.0036 |
| | HDBT | 0.019 | 0.14±0.0042 |

**Table 4.** Results of determination of cobalt(II) in wastewater and bottom sediments (n = 6, P = 0.95).

| Analysis object | | Added, mg/kg | $\bar{X}$ | $S_r$ | Found mg / kg (with addition ) |
|---|---|---|---|---|---|
| Sewage water | Sample 1 | 2.0 | 0.073 | 0.035 | 2.48±0.086 |
| | Sample 2 | 5.0 | 0.084 | 0.037 | 6.16±0.092 |
| Bottom sediments | Sample 1 | 5.0 | 0.066 | 0.042 | 6.26±0.105 |
| | Sample 2 | 5.0 | 0.071 | 0.038 | 6.95±0.158 |

## Conclusions

The results obtained show that the newly developed method in which the reagent 5-(4-hydroxy-3,5-dimethylbenzylidene) thiazolidine-2,4-dione (HDBT) was used, can be effectively applied for quantitative detemination of Co(II) in aqueous media. Complex of cobalt(II) with HDBT have been investigated by spectrophotometric method.

Complex is maximal formed at pH 5.7-6.9. The proposed method is quick and requires less volume of organic solvent.The optimal conditions for the complexformation and the ratios of components in the complexes have been determined.The Beer's law was applicable in the range of 0.5-10 µg/ml.

A simple, rapid and sensitive methods proposed for the determination of trace amounts of cobalt. The developed techniques are used to determine cobalt in sewage water, bottom sediments and in steel.

## REFERENCES

1. Nieboer E., Sanford W.E. Essential, toxic and therapeutic functions of metals (including deter-minant of reactivity) // Rev. Biochem. Toxicol. New York, 1985.P. 205–245.
2. Marchenko Z., Bal'tsezhak M.K. Metody spektrofotometrii v UF i vidimoy oblastyakh v neor-ganicheskom analize [Spectrophotometry methods in the UV and visible regions in inorganic analysis]. Moscow, Binom. Laboratoriya znaniy Publ., 2007. 711 p. (in Russian).
3. Umland F., Yansen A., Tirig D., Vyunsh G. Kompleksnyye soyedineniya v analiticheskoy khimii. M.: Mir, 1975, S.286
4. Peshkova V. M., Sovostina V.M. Analiticheskaya khimiya nikelya. M. Nauka. 1966. 200 s.
5. Ciftci H. Solid phase extraction method for the determination of cobalt in water samples on duolite XAD-761 resin using 4-(2-Pyridylazo) resorcinol by FAAS // Current Analytical Chemistry, 2010. V. 6, №. 2, pp. 154–160
6. Makhijani R.M., Barhate V.D. Development of extractive spectrophotometric determination of cobalt(II) with [N-(O-hydroxy benzylidene) pyridine-2-amine] // International Journal of Scientific and Research Publica-tions, 2016, V. 6, № 4, pp. 108-111
7. Kuliev K.A., Verdizadeh N.A, Suleymanova G.S. Spectrophotometric determination of cobalt(II) with 2,6-dithiolphenol and its derivatives in the presence of hydrophobic amines. American Journal of Chemistry, 2016, V.6, № 4, pp.95-103
8. Kuliev K.A., Verdizade N.A, Suleymanova G.S., Efendiyeva N.N. Solvent extraction of cobalt(II) with 2,6-dithiolphenol and its derivatives in the presence of hydrophobic amines. Journal of the Chemical Society of Pakistan, 2020. V.42, No. 02, pp. 253-262
9. Racheva P.V., Gavazov K.B., Lekova V.D., Dimitrov A.N. Complex formation in a liquid-liquid extraction system containing cobalt(II), 4-(2-pyridylazo) resorcinol, and nitron // Journal of Materials, V. 2013, 7 pages.
10. Divarova V.V, Gavazov K.B., Lekova V.D., Dimitrov A.N. Spectrophotometric investigations on liquid-liquid extraction systems containing cobalt, 4-(2-pyridylazo)-resorcinol and tetrazolium salts // Chemija, 2013, V.24, №2, pp. 81–87.
11. Pinheiro D.S., Junior E.N.S., Consolini G., et al. Optimized synthesis and characterization of thiazolidine-2, 4-dione for pharmaceutical application. MOJ Biorg Org Chem. 2017;1(4):122–126. DOI: 10.15406/mojboc. 2017. 01.00022
12. Ioffe B.V., Kostikov R.R., Razin V.V. Fizicheskiye metody opredeleniya stroyeniya organicheskikh soye-dineniy [Physical methods for determining the structure of organic compounds.] M.: Vysshaya shkola. 1984. 336 s. (in Russian).
13. Anisimova N.A. Identifikatsiya organicheskikh soyedineniy [Identification of organic compounds. Gorno-Altaysk.RIO Gorno-Altayskogo gosuniversiteta, 2009, 118 s. (in Russian).
14. Bulatov M. I., Kalinkin I.P. Prakticheskoye rukovodstvo po fotokolorimetricheskim i spektrofotometricheskim metodam analiza a [A practical guide to photocolorimetric and spectrophotometric methods of analysis]. Leningrad, Khimiya Publ., 1986. 432 p. (in Russian).
15. Nazarenko V.A., Biryuk Ye.A. Issledovaniye khimizma reaktsiy ionov mnogovalentnykh elementov s organicheskimi reagentami [Study of the chemistry of the reactions of ions of multivalent elements with organic reagents] // Journal of Analytical Chemistry.1967. T. 22. №1. S. 57-64. (in Russian).
16. Nazarenko V.A. Vzaimodeystviye ionov mnogovalentnykh elementov s organicheskimi reagentami i [Interaction of ions of multivalent elements with organic reagents]. // Transactions of the Commission for Analytical Chemistry of the USSR Academy of Sciences]. Moscow, Nauka Publ., 1969, 1969. T. 17. S.22-29. (in Russian).
17. Dorokhova Ye.N., Prokhorova G.V. Analiticheskaya khimiya (fiziko-khimicheskiye metody analiza) [Analytical chemistry (physicochemical methods of analysis)]. Moscow, Vysshaya shkola Publ., 1991. 250 p. (in Russian).
18. Sharp G.A., Soomro G.A. Spectrophotometric determination of cobalt(II) as complexes with brompirogallol red in micellar media // Journal of The Chemical Society Of Pakistan, 2006, V. 22, № 5, pp. 444-447