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Research Paper

Determination of Sub Microgram Amounts of Copper (II) by its Catalytic Effect on Hexacyanoferrate (III)-Citric Acid Redox Reaction

Chemistry

KEYWORDS : Kinetics, Catalytic effect, Redox process, Spectrophotometer, Hexacyanoferrate(III), Citric acid, Copper(II)

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ABSTRACT

A catalytic kinetic-spectrophotometric method for the determination of copper (ll) concentration as low as 250 ng/ml, based on its catalytic effect on oxidation of citric acid by alkaline hexacyanoferrate (lll) is developed. The reaction has been followed by measuring the decrease in absorbance at 420nm (max of Fe (CN)6)3- =1020 dm3 mol-1 cm-1).

A "Fixed-time-procedure" is used to obtain a linear calibration curve between the initial rate and the log of catalyst concentration (log [Cu 2+]) in the range 4x 10-3M–4x10-6M. The Maximum percentage error is 5% for the lowest concentration limit. The effect of presence of some cations commonly associated with Cu2+ and some anions has also been discussed. The method is sensitive, accurate, rapid and inexpensive compared to other techniques available for such low concentrations.

Introduction

Instrumental methods for trace determination have undergone spectacular developments in the recent past. The range analysis has been extended in many cases from ppm to ppb level using the sophisticated neutron-activation, differential pulse poloarography, ionometry, emission and absorption spectrometric techniques[1] etc. However, due to financial constraints, the much less expensive colorimetric and molecular absorption spectrophotometric methods still remain the most popular methods for estimation of a large majority of analytes[2-4]. The catalytic spectrophotometric methods for trace determination offer many advantages and analytical potential of such reactions is now being recognized[5-13]especially for environmental and industrial traces analysis.

The oxidation of citric acid by alkaline hexacyanoferrate (lll) is copper (ll) catalyzed and a detailed kinetic study of this reaction has been reported by Kumar and Mathur[14]. This paper describes the analytical application of this indicator reaction for determination of copper (ll) in a range of concentration including sub microgram levels ($4x10^{-3}$ to $4x10^{-6}$M).

Material and Methods

Reagents

Triple Distilled deionized water was used to prepare all the solutions throughout the study. Citric acid (GR, Thomas Baker) used in this study recrystallised twice and a 0.16 M solution was prepared by accurate weighing. $4x10^{-2}$M solution of potassium hexacyanoferrate (lll) (AR, S.D.S.) was prepared and its strength was checked iodometrically[15]. All other chemicals used were of AR Grade. Sodium hydroxide solution of 2M strength was prepared and was standardized before use. $4x10^{-3}$M solutionof copper sulphatepenta hydrate was prepared and was standardized with benzoin - α- oxime[16]. Except the catalyst concentration which was varied, a set of concentration of the other reagents was judiciously chosen for analytical procedure (vide supra) from the detailed kinetic data reported earlier[17].

Apparatus

The measurement of decrease in absorbance was made on a shimadzu recording spectrophotometer mode UV 1800 using optically matched rectangular quartz cuvettes of 1 cm path length. An ultra cryostate model -2 NBE (VEB Kombination Medizin and Labortechnik Kombinatsbetrieb, GDR) thermostatic bath was used to maintain temperature of the reactants and also to circulate water around thethermo stated cell compartment. Certified 'A' grade corning brand volumetric glassware was used throughout. Scrupulous cleaning is very necessary for obtaining consistent results. Therefore, all glassware was washed by synthetic liquid soap followed by distilled water, steamed and finally rinsed with triple distilled water. The apparatus was dried with AR grade acetone.

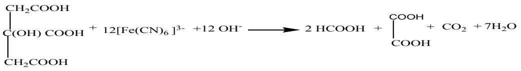
Procedure

In a 50 ml glass Stoppard Earlenmeyer flask, 5 ml each of potassium ferricyanide and NaOH and in another similar 50 ml flask, 5 ml each of citric acid and $CuSO_4$, all at specified concentrations, were taken. Both flasks were thermo stated at 60±0.1 °C for half an hour. After thermal equilibrium was established, the contents of the first flask were quickly poured in to that of the second flask with stirring and a stop watch was started simultaneously. One minute after mixing, 1 ml of reaction mixture was withdrawn by a 1ml transfer pipette (dropping time-3 sec.) and added immediately to a 50 ml flask containing 50 ml ice – cold triple distilled water in order (a) to arrest the reaction rate and (b) to bring absorbance with in measurable range. After through mixing a portion of this solution was transferred to a cuvette of 1cm path length and the absorbance was measured against distilled water.

The same withdrawal procedure was reported after 3 and 5 minutes of mixing for obtaining the initial rates by the so called "Fixed Time Procedure". The absorbance after 1,3 and 5 minutes i.e., A_1,A_3 and A_5 were plotted against log [Cu^{2+}] as shown in figure 4. The "initial rate method" was followed to avoid the complications which may arise due to interference by the products or other reagents present in the system[18-20].

Stoichiometry:

To determine the number of moles of hexacyanoferrate (lll) reacted per mole of citric acid was mixed with 20 times the molar concentration of alkaline hexacyanoferrate (lll) along with Cu (ll) ions as catalyst and the mixture was maintained at 60^0C. It was noted that 12 moles of hexacyanoferrate consumed per mole of citric acid to giveproducts which are not further oxidized. The stoichiometry may be represented by equation.



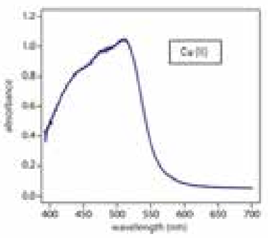
$$\begin{array}{l} CH_2COOH \\ | \\ C(OH)\ COOH \\ | \\ CH_2COOH \end{array} + 12[Fe(CN)_6]^{3-} + 12\ OH^- \longrightarrow 2\ HCOOH + \begin{array}{l} COOH \\ | \\ COOH \end{array} + CO_2 + 7H_2O$$

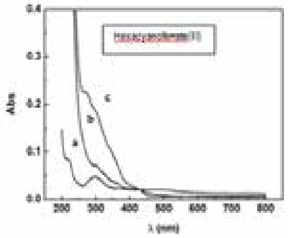
Formic acid was identified as a volatile product by the chromo tropic acid reaction test in the distillate of the reaction mixture. It was also estimated in the distillate by titrating against standard alkali. It was found that 2 moles are formed per mole of citric acid which is accordance with the above equation. Oxalic acid was detected by a test through conversion in to oxanilide derivative (mp 247^0C) in the residue left after the evaporation of the acidified reaction mixture.

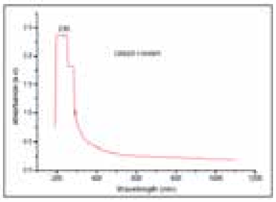
INSTRUMENTAL ANALYSIS

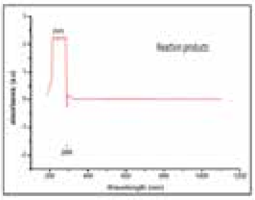
UV- Spectral measurements showed that the sharp absorption band was observed that 520 nm for Cu (II) (catalyst) and 320 nm for hexacyanoferrate (oxidant) and a mixture of oxidant with catalyst showed the absorption band at 235 nm. While in the set of reaction mixture such as citric acid, catalyst & excess of oxidant were taken in the reaction vessel and kept for 48 h at room temp. Showed absorption band at 243nm and 288 nm it shows 2 complexes are form in reaction mixture. The identity of the product was further confirmed from FT-IR Spectrum.

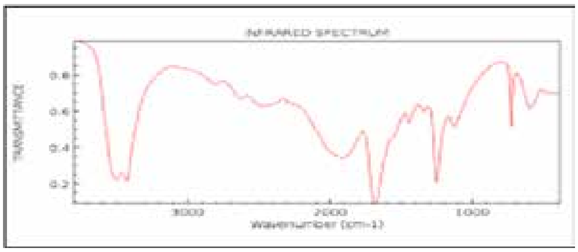
In the proposed work we have also interpreted the FT-IR spectroscopy which is a powerful tool for determination of molecular structure and fundamental importance of modern chemistry. It has been applied for structure problem and identifies end products. An FT–IR spectrum consist of a plot of stretching frequency (in cm^{-1}) vs intensity (as measured by %transmittance). The studied compound contains 2 carbon atoms. The symmetric stretching vibration of v-OH observes at 3600cm^{-1} in the experiment. The C=O vibration observes at 1700 cm^{-1} ascribed to the C=0 stretching vibration. The C-O-H in plane bending appears at 1150cm^{-1} confirms the presence of – OH group to the carbon frame .The C-C stretching vibration appears at 1010 cm^{-1}.

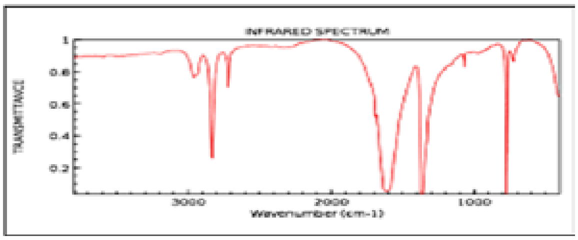












Kinetics:

Preliminary experiments were performed to determine suitable conditions of temperature and concentration of the reactants. Fig 1a and Fig 1b show the results of those at 0.01 M oxidant and 0.04M citric acid concentration with 0.5M alkali and 5x10-4M copper sulphate, between 300c and 600c. Disappearance of hexacyanoferrate (ll) Follow below Table 1 shows the values of first order rate constants at different temperatures.

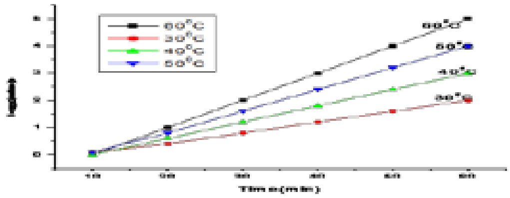


Figure 1a

Table1.[Citric acid]= 4.0x10^{-2}mole L^{-1}, [Fe (CN) 6]$^{3-}$ = 1x10^{-2}moleL^{-1}, [NaOH]=5x10^{-1} Mole L^{-1}, [CuSO$_4$]=5x10^{-4} moleL^{-1}

Temp(°C)	K_1x10^3 sec^{-1}
30	1.150
40	1.535
45	2.110
50	2.686
60	4.686

Initial rate dependence on the concentration of the reactants (fig 2 & 3).These graphs represent dependence of the initial reaction rate on the concentration of reactants. It id interred from these observations that the reaction is first order with respect to the oxidant and Cu(II). The order with respect to citric acid is unity at lower concentration. The reaction rate increase linearly with citric acid concentration up to a maximum value beyond which it falls.

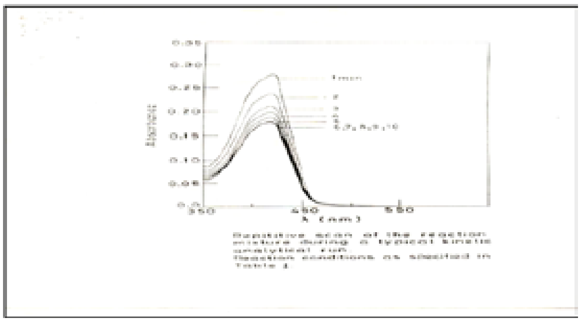


Figure 1b

The alkali dependence of the reaction rate is best expressed by the equation:

$$\text{Rate} = \frac{A[OH^-]^2}{1 + B[OH^-]^2}$$

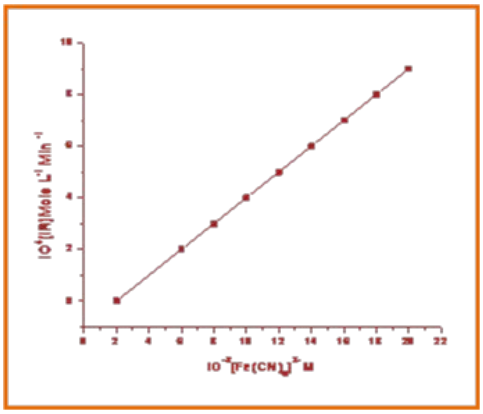


Figure 2

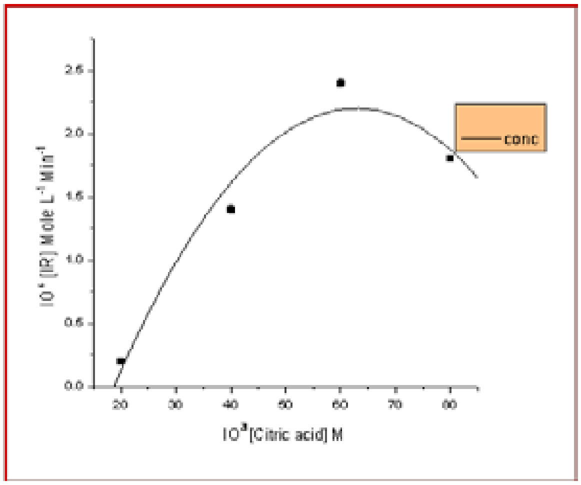


Figure 3

Since a plot of 1/rate vs 1/ [OH^{-2}] is Linear. From this it is concluded that the reaction is second order with respect to alkali at low concentrations but it deviates from two at higher concentrations. The value of constants A and B have been evaluated as 1.33×10^{-3} and 1.33 respectively, from the slope and intercept of the plot for 60^0C.

Theory and Calculation:

The spectral changes occurring in the reaction mixture at different times are shown fig. 7. There is a decrease in absorbance peak at 420nm due to disappearance of K_3 [Fe (CN) $_6$] as the reaction proceeds. There are no other notable features in the spectrum because the spectra of the other reactants and products are featureless in this region. The plots of A_1, A_3, and A_5 versus log [Cu^{2+}] are linear (fig 4) and can serve as calibration curves for the determination of copper (ll). Semi-log plots were preferred to cover the whole range of [Cu^{2+}] (4×10^{-6}M) in a single plot. The expression relating A_t, s to log [Cu^{2+}] follows an empirical general expression (eqn.1)

$$A_t \quad = \quad S \; \mathrm{Log}[Cu^{2+}] \; + \; I \quad \text{———————} \quad (1)$$

Where S = Slope (which includes equilibrium constants and some concentration terms),

I= intercept. The intercept is related to the rate of uncatalyzed reaction which is negligible.

The chosen time interval of 1,3 and 5 minutes give sufficient and convenient absorbance changes for measuring the initial reaction rates. After a detailed kinetic study a rate expression (eqn.2) has been derived for catalyzed reaction by applying steady state treatment to the various intermediates and resorting to some necessary approximations for initial states of the reaction.

$$\frac{-d}{dt}[Fe(CN)_6]^{3-} \; = \; \frac{K[Cit^{3-}][Fe(CN)_6]^{3-}[Cu]^{2+}[OH^-]^2}{1+K[OH^-]^2} \quad \text{——————} \quad (2)$$

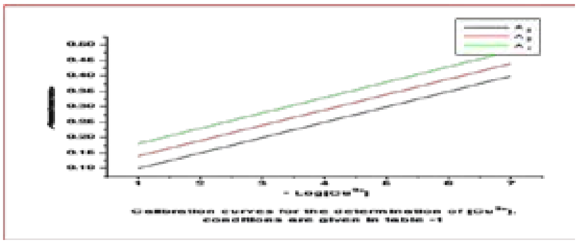
Thus other concentrations remaining fixed, the rate of disappearance of hexacyanoferrate (lll) is linearly related to the concentrations of Cu (ll).

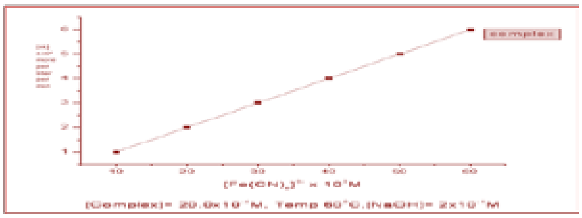
Table 2 shows the results for determination of Cu (ll) using all the three calibration curves covering the concentration range 4×10^{-3} M – 4×10^{-6}M of Cu (II). Standard deviations and percentage errors have also been included in the same table. The standard deviation is 0.95% at 4×10^{-3}M and 1.05% at 4×10^{-6}M of Cu(ll) concentration and the maximum error is 5%. The calibration curve for A_3 gives the minimum errors (1- to 2.75%) and is recommended for analytical procedure.

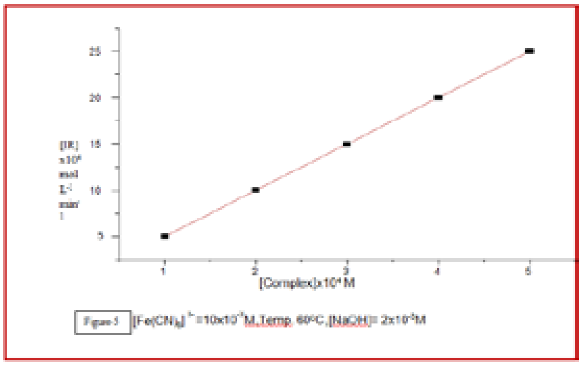
The effect of presence of some common ions associated with Cu (ll), taken in 10- fold excess to [Cu (ll)], using calibration curve of A3, has been investigated and given in table 3. The maximum error in the presence of these ions is 5% which is reasonable at such low concentration of the analyte. Any chelating agent which may complex with copper (II) strongly should, however, be absent.

An instantaneous but not insignificant change in absorbance is observed immediately after the reactants are mixed, followed by a slower absorbance change. The first change is attributed to the thermal and photochemical decomposition of $[Fe(CN)_6]^{3-}$ to $[Fe(CN)_5H_2O]^{2-}$ or $[Fe(CN)_5OH]^{3-}$ during storage which react faster with Citric Acid compared to $[Fe(CN)_6]^{3-}$. Thus it is always advisable to prepare a fresh solution of $K_3[Fe(CN)_6]^{3-}$ and store it in amber- colored bottles in dark and dilute the same to desired concentration immediately before use in order to minimize the side reaction. The lowest limit for Cu (ll) has been found to be 4×10^{-6}M. At lower concentration of Cu (ll), no conspicuous absorbance changes have been noticed in comparison to the uncatalyzed reaction. The temperature has been chosen 60^0C to obtain an enhanced rate (that is larger absorbance changes) a consequent decrease in the analysis time and increase in sensitivity.

Thus Cu(II) can be determined in the range of 4×10^{-3}M to 4×10^{-6}M by the proposed kinetic method in the presence of a number of cat ions and anions present in 10-fold excess compared to [Cu(ll)]. The method may be useful for trace determination of copper.







MECHANISM: The following mechanism is postulated. Thus the first step is the formation of a 1:1 Cu (ll) - Citrate complex. Such a complex has been reported earlier. This is slowly oxidized in to Cu (lll) -4 Citrate complexes in an intermediate which is then attacked by OH- to give intermediate products and Cu (l). Cu(l) is oxidized to Cu (ll) by [Fe(CN)6] 3- and also intermediate product acetone di-carboxylic acid which may formed in the presence of limited amounts of oxidant, is rapidly oxidized to give the end products oxalic and formic acids. The kinetics of oxidation of the synthesized Cu (ll) - citrate complex by alkaline hexacyano ferrate which reveals that the rate of oxidation of this complex has a linear dependence on the concentration of complex and oxidant (fig-5& 6). This supports the validity of the mechanism for low citrate concentrations. At higher citrate concentrations the rate falls, this may be due to formation of a bis-citrate complex which is resistant to oxidations.

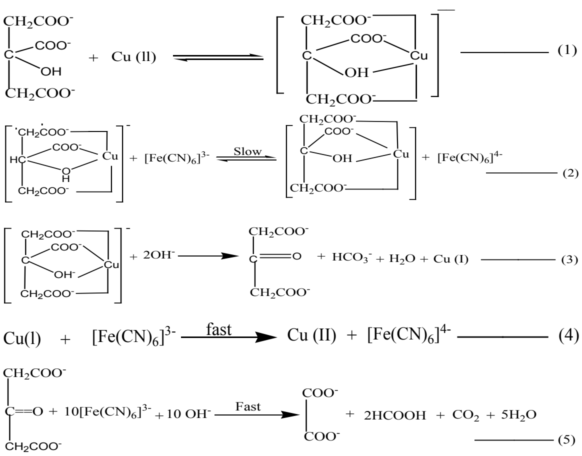
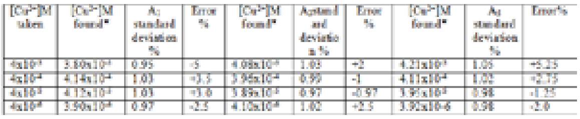


Table 2: Error in the proposed kinetic method for determination of Cu (ll):conditioned in the reaction mixture[K3Fe (CN) 6]= 1 x10-2m, [NaOH]= 0.5 M, [Citric Acid]= 4x10-2M, Temp. = 60 ± 0.10C.



$[Cu^{2+}]$M taken	$[Cu^{2+}]$M found*	A1 standard deviation %	Error %	$[Cu^{2+}]$M found*	A2standard deviation %	Error %	$[Cu^{2+}]$M found*	A3 standard deviation %	Error%
$4x10^{-3}$	$3.80x10^{-3}$	0.95	-5	$4.08x10^{-3}$	1.03	+2	$4.21x10^{-3}$	1.05	+5.25
$4x10^{-4}$	$4.14x10^{-4}$	1.03	+3.5	$3.96x10^{-4}$	0.99	-1	$4.11x10^{-4}$	1.02	+2.75
$4x10^{-5}$	$4.12x10^{-5}$	1.03	+3.0	$3.89x10^{-5}$	0.97	-0.97	$3.95x10^{-5}$	0.98	-1.25
$4x10^{-6}$	$3.90x10^{-6}$	0.97	-2.5	$4.10x10^{-6}$	1.02	+2.5	3.92x10-6	0.98	-2.0

*Average of at least three runs.

Table 3: effect of some interfering ions on the estimation of Cu (ll): [Fe (CN) 6]3- = 1x10-2M, [NaOH] = 0.5 M, [Citricacid] = 4x 10-2 M, [Cu (II)] = 8x10-6 M, Concentration of the interfering species = 8x10-6M, (added to the solution of [Cu (ll)]. Temp. = 60 ± 0.10C

Ions added	$[Cu^{2+}]$ found * $x10^{-6}$M	Error%	Standard deviation %
Pb^{2+}	8.12	+1.50	1.01
Cd^{2+}	8.23	+2.87	1.02
K^{+}	8.15	+1.87	1.01
Co^{2+}	7.76	-3.0	0.97
Fe^{2+}	8.41	+5.12	1.05
Cr^{3+}	8.40	+5.0	1.10
NO^{3-}	7.59	-5.12	0.90
SO_4^{2-}	7.60	-5.0	0.95
I^{-}	7.84	-3.25	0.98
Br^{-}	7.68	-4.0	0.96
Cl^{-}	8.52	+6.5	1.06

*Average of at least three runs.

REFERENCE

1. M. Pinta, Mordenmethods for trace analysis (An Arbor Science, michigan),1978. | 2. F. D. Snell, Photometric and Fluormetric methods of Analysis of Metals, John wiley, New york, 1978. | 3. Z. Marczenko, Spectrophotometric Determination of elements,John Wiley, New York,1976. | 4. Boltz,D.F. and Howell, J. A., Colorimetric Determination of Nonmetals, John Wiley,New York,1978. | 5. P. J. Ke, and R. J. Thibert, Microchim. Acta, (1972) 768. | 6. M. K. Gadia, and M. C. Mehra, Microchem.J. 23(1978) 278. | 7. M. Phull, H.C. Bajaj andP. C.Nigam, Talanta, 28(1981) 610. | 8. F. Lazaro, C. Luque de and M. Z. valcarcel, Anal. Chem., 320 (1985) 128. | 9. S. Prasad and P.C.Nigam, Int. sem. Anal. Techq. Monitoring the environment. | 10. C. Pedreno, Sanchez, M. I. Albero and M.S. Garcia, Talanta, 35(1988) 397. | 11. M. Phulland P.C. Nigam, Talanta, 28, (1981)591. | 12. S. Prasad and P. C. Nigam, Indian J. Envtl. Protection, 9, (1991) 113. | 13. Y. Baran and A. Ulgen, Int. J. Chem. Kinet., 30 (1998) 415. | 14. S. Kumar and P.C. Mathur, J.Inorg.Nucl.Chem., 40 (1978), 581. | 15. A. I. Vogel, Text Book of Quantitative Inorganis Analysis, 4th ed. (1978) 385. | 16. A.I. Vogel, Text Book of Quantitative Inorganis Analysis, 4th ed. (1978) 463. | 17. H. B. Mark Jr. and G. A. Rechnitz, kinetics of analytical chemistry, Int. Sci. Pub. New York, (1968)7. | 18. M. Kimura,N.Ieyama, M. Matsumoto, K. Shimada and K. Tsukahara, Bull. Chem. Soc. Japan, 74 (2001) 1871. | 19. S. Prasad, Transition Met. Chem., 28, 1 (2003). | 20. P. Yang, Y.L. Miao, H. Q. Zhou. andX. C. Yuan, Chinese J. Chem., 22 (2004) 841.