

Analytical Studies of Cu(II), Ni(II) and Pd(II) Complexes with 3-Phenyl-Quinazolin-4(3H)-one-2-Carboxaldehydoxime

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3-Phenyl quinazolin-4-(3H)-one-2-carboxaldehydoxime forms water insoluble chelates with Cu(II), Ni(II) and Pd(II). It has been found to be a selective reagent for the gravimetric estimation of these metal ions in presence of many interfering ions. All the chelates have 1 : 2 (metal : ligand) stoichiometry as shown by Job's method of continuous variation and elemental analysis. Structures of the metal chelates have been established on the basis of magnetic measurements, visible and IR spectra.

INTRODUCTION

In this work, we report here the use of 3-phenyl quinazolin-4-(3H)-one-2-carboxaldehydoxime (PQCO) as a gravimetric reagent for the estimation of these transition metal ions. This reagent (PQCO) is found to have the following distinct advantages over the other common reagents like dimethyl glyoxime, acetophenone oxime, etc. used previously: (i) The reagent is colourless and crystalline solid having high molecular weight. (ii) 40% aqueous ethanolic solution of this reagent is quite stable and can be stored for months without any decomposition. (iii) Complexes formed with the reagent are insoluble in ethanol and so any excess reagent which precipitates on dilution can be easily removed by washing the metal chelate (complex) with 40% aqueous ethanol in which the reagent is soluble.

EXPERIMENTAL

The solution of the reagent (PQCO) in 40% aqueous ethanol precipitates quantitatively Cu(II) between pH 3.0 and 6.0, Ni(II) between pH 5.5 and 8.0 and Pd(II) between pH 1.0 and 4.0. The three coloured metal chelates were found to be insoluble in water, ethanol and acetone but soluble in chloroform, carbon tetrachloride and benzene.

3-Phenyl-quinazolin-4-(3H)-one-2-carboxaldehyde (1 g) dissolved in freshly distilled pyridine (10 mL) was treated with hydroxylamine hydrochloride (0.32 g) and the reaction mixture kept overnight. It was poured into crushed ice, the white solid filtered, washed with water and crystallised from ethylacetate to afford 3-phenyl-quinazolin-4-(3H)-one-2-carboxaldehydoxime^{1,2} as colourless needles (0.8 g; 75.4%), m.pt. 200°C. It was soluble in aqueous alkali and reprecipitated

on acidification having no change in m.p. Analytical data of C, N and H of reagent (PQCO) having molecular formula $M(C_{15}H_{11}N_3O_3)$ are given as follows:

% Analyses Found (Calcd.) for $C_{15}H_{11}N_3O_3$, C = 67.92 (67.98), N = 15.85 (15.90), H = 4.15 (4.19).

The infrared spectra of reagent (PQCO) are given in Table-1.

TABLE-1

$C_{15}H_{11}N_3O_3$	Assignments
1660 cm^{-1}	C=O Stretching
1690 cm^{-1}	C=N Stretching
1600 cm^{-1}	N—O Stretching
1450 cm^{-1}	O—H Stretching

The 1% solution of the reagent (PQCO) in 40% aqueous ethanol was used in all gravimetric estimations.

The solutions of Cu(II) and Ni(II) were prepared by dissolving copper chloride and nickel chloride (BDH, AR) in doubly distilled water. A little free acid was added to prevent hydrolysis of the salts.

The solution of Pd(II) was prepared by dissolving 1 g palladium chloride (Johnson-Mathey) in minimum quantity of hydrochloric acid and the solution was made to 500 cm^3 with doubly distilled water. All these solutions were standardised by standard method³. All other chemicals and solvents used were BDH reagents of AR grade.

The Gouy method was used for measuring magnetic susceptibilities and $Hg[Co(NCS)_4]$ was used as the standard. Visible spectra of metal chelates in their chloroform solutions were recorded on a Perkin-Elmer UV-visible double beam spectrophotometer model 137 IR spectra of the reagent and metal chelates were recorded on a Perkin-Elmer IR spectrophotometer model 237.

RESULTS AND DISCUSSION

Gravimetric determination of Cu(II), Ni(II) and Pd(II) using (PQCO): An aliquot containing a known amount of metal ion was diluted to about 250 cm^3 and pH was adjusted using acetate buffer for Cu(II). In case of Ni(II), pH was adjusted using NH_3 and CH_3COOH buffer. In case of Pd(II), pH was adjusted using hydrochloric acid-acetate buffer. The solution was warmed to 60–70°C and 1% solution of PQCO in 40% aqueous ethanol was added with constant stirring, followed by about 10% excess to ensure complete precipitation. The coloured precipitate of metal chelate was digested on a water bath (50–80°C) for 50 min. It was filtered while hot through a sintered glass crucible (G-4) and washed with hot water. The precipitate was finally washed with 40% ethanol to remove any excess reagent. The precipitate was dried at 100°C to constant weight and weighed as $M(C_{15}H_{11}N_3O_3)_2$ where M = Cu(II), Ni(II) and Pd(II).

It was found that the precipitation is quantitative in the pH range 3.0 to 5.5 for Cu(II), 6.0 to 8.0 for Ni(II) and 1.0 to 3.5 for Pd(II). Estimations with different

aliquots of metal ions were done at pH 3.5 for Cu(II), at pH 6.0 for Ni(II) and at pH 2.0 for Pd(II). Results are given in Table-2.

TABLE-2
DETERMINATION OF Cu(II), Ni(II) and Pd(II) using PQCO

Metal ion taken (mg)	Metal chelate (mg)	Metal ion found (mg)	Error (%)
Copper; pH = 3.5 Conversion factor (M/ML ₂) 0.1325			
6.85	58.40	6.86	+0.12
14.70	117.70	14.70	0.00
38.27	295.20	38.21	-0.15
46.13	355.40	46.18	+0.10
61.84	475.00	62.02	+0.29
Nickel; pH = 6.0 Conversion factor 0.1237			
8.22	59.20	8.20	-0.270
15.44	117.80	15.44	0.000
44.33	352.20	44.33	0.000
37.11	293.00	37.12	+0.027
58.78	468.20	58.79	+0.017
Palladium; pH = 2.0 Conversion factor 0.2036			
4.10	28.1	4.12	+0.32
16.32	88.2	16.36	+0.21
22.42	118.0	22.43	+0.04
28.52	147.8	28.49	-0.10

Interference from other ions

It was observed that in the determination of Cu(II) (50 ppm) at pH 3.5, 5000 ppm of tartrate, acetate, sulphate, chloride, bromide, iodide, nitrate, citrate; 5000 ppm of Na(I), K(I); 1000 ppm of Zn(II), Cd(II), Sr(II), Mg(II), Ca(II), Be(II); 500 ppm of Mn(II), Al(III), Cr(III); 200 ppm of Ni(II), Co(II) could be tolerated. Maximum error in any case did not exceed $\pm 1.0\%$ in metal ion.

In the case of Ni(II) (60 ppm) at pH 6.0 acetate, tartrate, sulphate, chloride, bromide, iodide, nitrate citrate of Na(I), K(I), Zn(II), Cd(II), Sr(II), Mg(II), Ca(II), Be(II), Mn(II), Al(III) could be tolerated. Maximum error in any case did not exceed $\pm 0.85\%$ in metal ion.

In case of Pd(II) (pH 2.0) maximum error did not exceed $\pm 0.85\%$ in metal ion. Co(II) gives orange yellow coloured complex with PQCO at pH 6.0 and it can, therefore, interfere in the determination of Cu(II) and Ni(II) at this pH, but the cobalt complex is soluble in ethanol and so any cobalt complexes co-

precipitated at this pH can be washed in final washing of metal chelate with ethanol. As Cu(II) starts precipitating at pH 3.0, Ni(II) at pH 5.5 and Pd(II) at 1.0 it was possible to determine Cu(II) and Ni(II) as well as Pd(II) and Ni(II) in their binary mixtures by working at controlled pH. In case of a mixture of Cu(II) and Ni(II), Cu(II) was first precipitated and separated at pH 3.5 when Ni(II) remained in solution 1; Ni(II) was determined in the filtrate after raising the pH of the solution to 6.0. The same technique was used for determination of Pd(II) and Ni(II) in a mixture. Pd(II) was first separated and estimated at pH 1.5. The error in any estimation did not exceed $\pm 1.0\%$.

Structure of Cu(II), Ni(II) and Pd(II) Complexes

Compositions of the metal chelates were established on the basis of Job's method of continuous variation, analytical data and various physico-chemical techniques. The analytical data of the complexes (Table-3) corresponded to the formulae $M(C_{15}H_{11}N_3O_3)_2$ for all the chelates, indicating metal : ligand ratio of 1:2. The 1:2 stoichiometry was confirmed by Job's method of continuous variation. For this the chelates formed were extracted into chloroform and the absorbances were measured at λ_{\max} of the chelates. The absorbance maxima corresponded to metal : ligand ratio of 1:2.

TABLE-3
ANALYTICAL DATA OF METAL COMPLEXES

Chelate	Found (Calcd.)%			
	M	C	H	N
Cu(C ₁₅ H ₁₁ N ₃ O ₂) ₂	10.18 (10.15)	57.70 (57.55)	5.50 (3.51)	13.48 (13.42)
Ni(C ₁₅ H ₁₁ N ₃ O ₂) ₂	9.49 (9.45)	57.81 (57.99)	3.50 (3.54)	13.59 (13.53)
Pd(C ₁₅ H ₁₁ N ₃ O ₂) ₂	15.90 (15.93)	53.81 (53.85)	3.19 (3.29)	12.50 (12.56)

The copper complex with PQCO was found to be paramagnetic with a magnetic moment of 1.74 B.M. This is quite near to spin only value of 1.73 B.M., expected for one unpaired electron. The complexes of nickel and palladium were found to be diamagnetic and hence these have most probably square-planar structures.

In the IR spectrum of PQCO, four bands observed are shown in Table-1. The coordination of metal ion through nitrogen of (C=N) (oxime) is indicated by lowering of (C=N) band from 1690 cm^{-1} in the ligand to 1625–1620 cm^{-1} in the complexes. The position of other bands are not affected on complexation. This indicates that the oximino hydroxyl does not take part in coordination.

In the visible spectrum, the copper(II) complex shows a band^{4,5} at 650 nm which could be assigned to the transition⁶, $A_{1g} \leftarrow {}^2B_{1g}$. A strong band observed at 365 nm could be assigned to charge transfer. A weak band at 600 nm in the spectrum of nickel(II) complex could be assigned to ${}^1B_{1g} \leftarrow {}^1A_{1g}$ transition

and a strong band at 380 nm could be assigned to charge transfer. In the spectrum of palladium(II) complex a strong band observed at 360 nm can be treated as a combination of all the three spin allowed transitions (${}^1A_{1g} \rightarrow {}^1A_{2g} \rightarrow {}^1B_{1g} \rightarrow {}^1B_{1g}$)

ACKNOWLEDGEMENTS

The authors are thankful to Prof. (Dr.) U.S. Pandey (Retd. Head Chem. V.K.S.U., Ara), Prof. (Dr.) L.A.K. Saran (V.K.S.U., Ara) and Prof. (Dr.) K.N. Singh (Head, H.D. Jain College, Ara) for their keen interest. They are very grateful to Prof. (Dr.) K.M. Prasad of V.K.S. University, Ara for his suggestions.

The authors are also thankful to microanalyser of Patna University and Central Fuel Research Institute (CFRI), Dhanbad.

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(Received: 21 December 1998; Accepted: 25 March 1999)

AJC-1706