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Study on Oximino-3-Methyl-1-(2′,4′-dinitrophenyl)-2-Pyrazolin-5-One as a Gravimetric Reagent for Co(II), Ni(II) and Cu(II)

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4-Oximino-3-methyl-1-(2′,4′-dinitrophenyl)-2-pyrazolin-5-one can be used as a gravimetric reagent for Co(II), Ni(II) and Cu(II). An attempt has been made to determine (a) Cu(II) and Ni(II) (b) Cu(II) and Co(II) from their binary mixture at selective pH value. The estimation of Co(II), Ni(II) and Cu(II) metal ions in the presence of different metal ions such as Sr(II), Ca(II), Cd(II), Al(III), Pb(II) and Mg(II) has also been carried out. Such interfering metal ions failed to respond.

Key Words: Oximino-3-methyl-1-(2′,4′-dinitrophenyl)-2-pyrazolin-5-one, Gravimetric, Co(II), Ni(II), Cu(II).

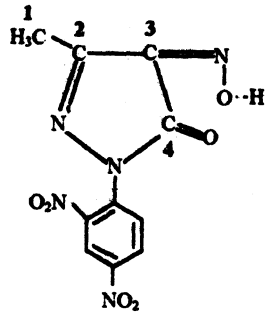
INTRODUCTION

The use of oximes in the gravimetric determination of certain metal ions is well known[1–3]. In an earlier communication from our laboratory, we have reported the synthesis and characterization of some divalent and trivalent metal ion complexes with 4-substituted-2-pyrazolin-5-ones[4–9]. In continuation of studies on 2-pyrazolin-5-one chemistry, here we report the study on 4-oximino-3-methyl-1-(2′,4′-dinitrophenyl)-2- pyrazolin-5-one (OMNPPZ) as a gravimetric reagent.

EXPERIMENTAL

All chemicals used were of reagent grade (BDH). 3-Methyl-1-(2′,4′-dinitrophenyl)-2-pyrazolin-5-one was synthesized (m.p. found 92°C; reported 92°C) by the reported method[10]. 4-Oximino-3-methyl-1-(2′,4′-dinitrophenyl)-2-pyrazolin-5-one was prepared as reported earlier[4]. All pH measurements were done on a Equiptronics digital pH meter. The complexes were analyzed for metal content using literature methods[11,12]. The reagent and metal complexes were analyzed for carbon, hydrogen and nitrogen on a Carlo-Eraba-1108 micro analyzer. The FT-IR spectra were recorded on a shimadzu-8201 PC FT-IR spectrophotometer in KBr pellets. The ^{13}C-NMR spectra were recorded on a Bruker DRX-300 FT-NMR spectrophotometer.

Structure of the reagent (OMNPPZ) used in the present study:



m.p. 245°C, yield 71% (% Found : C, 41.48; H, 2.47; N, 22.99% Calc. For $C_{10}H_7N_5O_6$ C, 40.95; H, 2.38; N, 23.89%); FT-IR[4] (KBr) (cm^{-1}) : 3382 [ν(O—H) of oximino group], 1736 [ν(O=H) of pyrazolin ring], 1618 [ν(C=N) of oxime], 1590 [ν(C=N) of pyrazolin ring], 1336 (νNO_2), 1024 [ν(N—O) of oxime], ^{13}C-NMR[13,14] (δ) ppm : 14.3 (C_1), 135.1 (C_2), 148.2 (C_3) and 1770.0(C_4).

RESULTS AND DISCUSSION

Stock solution of 0.05 M $CoCl_2 \cdot 6H_2O$, 0.05 M $NiCl_2 \cdot 6H_2O$ and 0.05 M $CuCl_2 \cdot 2H_2O$ was prepared in double distilled water. This solution was used after standardization with EDTA[11,12]. The 5% ethanolic solution of OMNPPZ was prepared.

The solution containing known amount of metal(II) ions was diluted to about 50 mL with distilled water and pH was adjusted using suitable buffer. To the warm solution of metal(II) ion, the 5% ethanolic solution of OMNPPZ was added with constant stirring till precipitation was complete. For complete precipitation little excess of OMNPPZ solution was added. The coloured precipitate of metal complex was digested on a water bath for 30–45 min. and then it was filtered, washed with hot water and then rectified spirit to remove any excess reagent. The metal complex was dried at 90–95°C till constant weight was obtained.

To determine the applicability of OMNPPZ as gravimetric reagent for estimation of Co(II), Ni(II) and Cu(II) the metal ion was precipitated from the solutions having pH values in the range as shown in Table-1. The composition of metal complex has been established from this laboratory by known procedures[4].

Estimation of Co(II), Ni(II) and Cu(II) metal ion using 5% ethanolic solution of OMNPPZ in the presence of various metal ions such as Sr(II), Ca(II), Cd(II), Al(III), Ba(II) and Mg(II) has been carried out. For Co(II) complex the pH range is 7.5–7.6 for Ni(II) complex the pH range is 5.5–5.6 and for Cu(II) complex the pH range is 3.9–4.0.

The resulting solution of metal complexes (for all sets) as well as the filtrate were tested separately for the interfering metal ions. The results (Table-2) show that the metal ions like Sr(II), Ca(II), Cd(II), Al(III), Ba(II) and Mg(II) etc. failed to respond.

An attempt has been been made to determine (a) Cu(II) and Ni(II) (b) Cu(II) and Co(II) from their binary mixtures at selective pH values using OMNPPZ. The result (Table-3) shows that with proper control of pH between 3.9–4.0, it is possible to determine Cu(II) metal ion (for binary mixture-a). From the filtrate of binary mixture-a, precipitation of Ni(II) ion has been made at pH 5.5–5.6. Similarly from the binary mixture-b, (*i.e.*, Cu(II)) and Co(II), precipitation of Co(II) ion as $Co(OMNPPZ)_2(H_2O)_2$ has been made at pH 7.5–7.6.

TABLE-1
ESTIMATION OF METAL(II) ION

Complex	$Co(OMNPPZ)_2(H_2O)_2$	$Ni(OMNPPZ)_2(H_2O)_2$	$Cu(OMNPPZ)_2(H_2O)_2$
pH range	5.5–8.5	5.0–8.0	2.5–5.5
Selected pH	7.5	5.5	4.0
Colour of complex	Dark brown	Green	Dark brown
Weight of metal complex found (in mg)	337.0	335.6	340.8
Weight of metal (II) ion found (in mg)	29.24	29.02	31,68
Weight of metal (II) ion taken (in mg)	29.28	29.10	31.64
% Error	–0.14	–0.27	+0.13
Conversion factor $M/ML_2(H_2O)_2$	0.0868	0.0865	0.0929
*Elemental analysis (%)			
M	8.74 (8.68)	8.23 (8.65)	9.76 (9.29)
C	35.54 (35.34)	35.40 (35.36)	35.01 (35.11)
H	2.54 (2.36)	2.16 (2.36)	2.01 (1.85)
N	20.70 (20.62)	20.43 (20.63)	20.92 (20.48)

*Values given in parenthesis are calculated ones.

The percentage error of measurement was found ranging from +0.13 to +0.35% for Cu(II) ion, from –0.14 to –0.21% for Ni(II) ion and from –0.17 to –0.20% for Co(II) ion.

The results suggest that solubilities of metal complexes are pH dependent and selective precipitation can be made for the use of OMNPPZ as analytical reagent.

OMNPPZ reagent can be used (Table-2) to determine Co(II), Ni(II) and Cu(II) in the presence of Sr(II), Ca(II), Cd(II), Al(III), Ba(II) and Mg(II) ion.

Table-2 shows that percentage errors range from –0.17 to –0.41% for Co(II), from–0.14 to –0.34% for Ni(II) and from +0.13% to +0.35 for Cu(II) in the presence of Sr(II), Ca(II), Cd(II), Al(III), Ba(II) and Mg(II) interfering metal ion.

TABLE-2
ESTIMATION OF METAL(II) ION IN PRESENCE OF VARIOUS INTERFERING METAL IONS

Metal ion added	Amount of added metal ion (in mg)	Weight of metal complex found (in mg)	Weight of metal (II) ion found (in mg)	Weight of metal (II) ion taken (in mg)	Error (%)
		Co(II)			
Sr(II)	13.30	336.0	29.16	29.28	–0.41
Ca(II)	8.60	336.4	29.20	29.28	–0.27
Cd(II)	17.60	336.8	29.23	29.28	–0.17
Al(III)	24.30	336.2	29.17	29.28	–0.38
Ba(II)	12.20	336.0	29.16	29.28	–0.41
Mg(II)	12.30	336.4	29.20	29.28	–0.27
		Ni(II)			
Sr(II)	13.30	335.4	29.00	29.10	–0.34
Ca(II)	8.60	335.8	29.04	29.10	–0.21
Cd(II)	17.60	335.6	29.02	29.10	–0.27
Al(III)	24.30	335.8	29.04	29.10	–0.21
Ba(II)	12.20	335.6	29.02	29.10	–0.27
Mg(II)	12.30	336.0	29.06	29.10	–0.14
		Cu(II)			
Sr(II)	13.30	341.0	31.70	31.64	+0.19
Ca(II)	8.60	341.0	31.70	31.64	+0.19
Cd(II)	17.60	341.0	31.70	31.64	+0.19
Al(III)	24.30	341.6	31.75	31.64	+0.35
Ba(II)	12.20	340.0	31.68	31.64	+0.13
Mg(II)	12.30	340.8	31.68	31.64	+0.13

The estimation of Co(II), Ni(II) and Cu(II) metal ions has been carried out from their binary mixture.

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TABLE-3
ESTIMATION OF Cu(II), Ni(II) AND Co(II) FROM THEIR BINARY MIXTURES

Composition of metal(II) ion taken (in mg)			Wt of Cu(II) complex found (in mg)	Wt of Cu(II) ion found (in mg)	Error (%)	Wt of Ni(II) ion found (in mg)	Wt of Ni(II) ion found (in mg)	Error (%)	Wt of Co(II) complex found (in mg)	Wt of Co(II) ion found (in mg)	Error (%)
Cu(II)	Ni(II)	Co(II)									
31.64	29.10	—	340.8	31.68	+0.13	336.0	29.06	–0.14	—	—	—
15.82	29.10	—	170.8	15.87	+0.34	335.8	29.04	–0.21	—	—	—
31.64	14.55	—	340.8	31.68	+0.13	167.9	14.52	–0.20	—	—	—
31.64	—	29.28	341.0	31.70	+0.19	—	- -	—	336.8	29.23	–0.17
15.82	—	29.28	170.9	15.88	+0.35	—	—	—	336.8	29.23	–0.17
31.64	—	14.64	341.0	31.70	+0.19	—	—	—	168.2	14.51	–0.20

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