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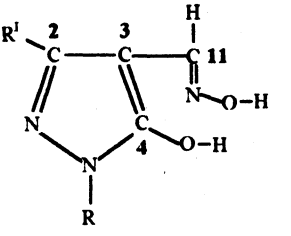
4-Formyloxime-3-methyl-1-(2′,4′-dinitrophenyl)-5-one can be used as a gravimetric reagent for Co(II), Ni(II) and Cu(II). An attempt has been made to determine (a) Cu(II) and Ni(II) (b) Cu(II) and Co(II) from their binary mixture at selective pH value. The estimation of Co(II), Ni(II) and Cu(II) metal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

Key Words: Formyloxime, Metal complexes, Gravimetric reagent.

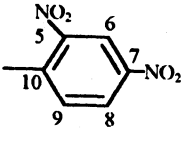
INTRODUCTION

The use of oximes in the gravimetric determination of certain metal ions is well known[1–7]. From our laboratory, we have reported the synthesis and characterization of some bivalent and trivalent transition metal complexes with 4-substituted-2-pyrazolin-5-ones[6–13]. In continuation of our studies on 2-pyrazolin-5-one chemistry, here we report the study on 4-formyloxime-3-methyl-1-(2′,4′-dinitrophenyl)-2-pyrazolin-5-one (FMNPPZ) as a gravimetric reagent.



(FMNPPZ)

where

R =  R^I = -- $^1CH_3$

EXPERIMENTAL

All chemicals used were of reagent grade (BDH). The reagent 4-formyloxime-3-methyl-1-(2′,4′-dinitrophenyl)-2-pyrazolin-5-one was prepared as reported earlier[13].

All pH measurements were done on an Equiptronics digital pH-meter. The complexes were analyzed for metal content using literature methods[15, 16]. The reagent and metal complexes were analyzed for carbon, hydrogen and nitrogen on a Carlo-Erba-1108 micro-analyzer. The FT-IR spectrum of the reagent was recorded on a Shimadzu-8201 PC FT-IR spectrophotometer in KBr pellets. The ^{13}C-NMR spectrum of the reagent was recorded on a Bruker DRX-300 FT-NMR spectrophotometer.

m.p. 87°C, yield 67% (% found: C, 43.06; H, 3.05; N, 23.06; % calcd. for $C_{11}H_9N_5O_6$, C, 43.00; H, 2.93; N, 22.80); FT-IR[13] (KBr) (cm^{-1}): 3400–3100 (ν(O—H) of oxime + 5-OH group); 1675 (ν(C=N) oxime), 1620 (ν(C=N) pyrazolin ring), 1410 (ν(C—O) enol), 1124 (ν(N—O) oxime); ^{13}C-NMR[17, 18] (δ) ppm: 12.3 (C_1), 148.2 (C_2), 99.3 (C_3), 153.7 (C_4), 129.6 (C_5) 128.6 (C_6), 140.8 (C_7), 117.3 (C_8), 123.2 (C_9), 139.5 (C_{10}), 164.8 (C_{11}).

RESULTS AND DISCUSSION

Stock solutions of 0.05 M $CoCl_2 \cdot 6H_2O$, 0.05 M $NiCl_2 \cdot 6H_2O$ and 0.05 M $CuCl_2 \cdot 2H_2O$ were prepared in double distilled water. This solutions were used after standardization with EDTA[15, 16]. A 5% ethanolic solution of reagent FMNPPZ was prepared.

The solution containing known amount of metal(II) ion 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 FMNPPZ was added with constant stirring till precipitation was complete. For complete precipitation little excess FMNPPZ 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 of the excess reagent. The metal complex was dried at 90–95°C till constant weight was obtained.

To determine the applicability of FMNPPZ 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 minimum error was found, at pH = 7.0 for Co(II), at pH = 5.5 for Ni(II) and pH = 4.0 for Cu(II). The composition of metal complex was established elsewhere from this laboratory[13].

Estimation of Co(II), Ni(II) and Cu(II) metal ions using 5% ethanolic solution of FMNPPZ in the presence of various metal ions such as Ba(II), Sr(II), Ca(II), Cd(II), Al(III) and Mg(II) has been carried out. For Co(II) complex the pH range is 6.9–7.1, for Ni(II) complex the pH range is 5.4–5.6 and for Cu(II) complex the pH range is 3.9–4.1.

The resulting solutions of metal complexes (for all sets) as well as the filtrate were tested separately for interfering metal ions. The results (Table-2) show that the metal ions like Ba(II), Sr(II), Ca(II), Cd(II), Al(III) and Mg(II), etc. do not interfere.

TABLE-1
ESTIMATION OF METAL(II) ION

Complex	$Co(FMNPPZ)_2 \cdot (H_2O)_2$	$Ni(FMNPPZ)_2 \cdot (H_2O)_2$	$Cu(FMNPPZ)_2 \cdot (H_2O)_2$
pH range	5.5–8.5	5.0–7.5	2.5–6.0
Selected pH	7.0	5.5	4.0
Colour of complex	Dark green	Reddish brown	Brownish green
Weight of metal complex found (in mg)	350.80	350.10	354.40
Weight of metal(II) ion found (in mg)	29.24	29.07	31.65
Weight of metal(II) ion taken (in mg)	29.28	29.10	31.64
% Error	–0.14	–0.10	+0.03
Conversion factor $M/ML_2 \cdot (H_2O)_2$	0.0833	0.0830	0.0893
**Elemental analysis* (%)			
M	8.15 (8.33)	8.87 (8.30)	8.86 (8.93)
C	37.53 (37.34)	37.03 (37.35)	37.78 (37.10)
H	3.22 (2.83)	3.81 (2.83)	2.92 (2.81)
N	19.71 (19.80)	19.74 (19.81)	19.77 (19.67)

*Values given in parentheses are calculated ones.

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 using the reagent FMNPPZ. The results (Table-3) show that with proper control of pH between 3.9–4.1, it is possible to determine Cu(II) metal ion (for binary mixtures a and b). From the filtrate of binary mixture-a, precipitation of Ni(II) ion has been made at pH 5.4–5.6. Similarly from the binary mixture-b, (*i.e.*, Cu(II) and Co(II)), precipitation of Co(II) ion as $Co(FMNPPZ)_2 \cdot (H_2O)_2$ has been made at pH 6.9–7.1.

The % error of measurement was found ranging from ±0.03 to ±0.19% for Cu(II) ion, from ±0.10 to ±0.20 for Ni(II) ion and from ±0.14 to ±0.27% 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 FMNPPZ as analytical reagent.

FMNPPZ 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 % error range from ±0.20 to ±0.34% for Co(II), from ±0.07 to ±0.14% for Ni(II) and from ±0.03 to ±0.09% for Cu(II) in the presence of Sr(II), Ca(II), Cd(II), Al(III), Ba(II) and Mg(II) interfering metal ions.

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

Metal ion added	Amount of metal ion added (mg)	Weight of metal complex found (mg)	Weight of metal(II) ion found (mg)	Weight of metal(II) ion taken (mg)	Error (%)
		Co(II)			
Sr(II)	13.30	350.60	29.22	29.28	–0.20
Ca(II)	8.60	350.00	29.18	29.28	–0.34
Cd(II)	17.60	350.20	29.20	29.28	–0.27
Al(III)	24.30	350.40	29.21	29.28	–0.24
Ba(II)	12.20	350.60	29.22	29.28	–0.20
Mg(II)	12.30	350.20	29.20	29.28	–0.27
		Ni(II)			
Sr(II)	13.30	350.20	29.08	29.10	–0.07
Ca(II)	8.60	350.10	29.07	29.10	–0.10
Cd(II)	17.60	350.10	29.07	29.10	–0.10
Al(III)	24.30	350.60	29.12	29.10	+0.07
Ba(II)	12.20	350.00	29.06	29.10	–0.14
Mg(II)	12.30	350.00	29.06	29.10	–0.14
		Cu(II)			
Sr(II)	13.30	354.00	31.61	31.64	–0.09
Ca(II)	8.60	354.70	31.67	31.64	+0.09
Cd(II)	17.60	354.00	31.61	31.64	–0.09
Al(III)	24.30	354.00	31.61	31.64	–0.09
Ba(II)	12.20	354.70	31.67	31.64	+0.09
Mg(II)	12.30	354.40	31.65	31.64	+0.03

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

Composition of metal(II) ion taken (in mg)			Weight of Cu(II) complex found (mg)	Weight of Cu(II) ion found (mg)	Error (%)	Weight of Ni(II) complex found (mg)	Weight of Ni(II) ion found (mg)	Error (%)	Weight of Co(II) complex found (mg)	Weight of Co(II) ion found (mg)	Error (%)
Cu(II)	Ni(II)	Co(II)									
31.64	29.10	–	354.0	31.61	–0.09	350.1	29.07	–0.10	–	–	–
15.82	29.10	–	176.9	15.79	–0.19	350.0	29.06	–0.14	–	–	–
31.64	14.55	–	354.4	31.65	+0.03	174.9	14.52	–0.20	–	–	–
31.64	–	29.28	354.0	31.61	–0.09	–	–	–	350.6	29.22	–0.20
15.82	–	29.28	176.8	15.79	–0.19	–	–	–	350.8	29.24	–0.14
31.64	–	14.64	353.8	31.59	–0.16	–	–	–	175.2	14.60	–0.27

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