

Synthesis and Investigation Extraction Properties of 4-Methylacetophenone, 4-Chloroacetophenone and Isonitrosoacetophenone 4-Aminobenzoylhydrazones

Ramazan GÜP¹, Ziya Erdem Koç²

Abstract: 4-Methylacetophenone p-aminobenzoylhydrazone (L₁), 4-chloroacetophenone p-aminobenzoylhydrazone (L₂) and isonitrosoacetophenone p-aminobenzoylhydrazone (L₃) were prepared by reaction of 4-aminobenzoic acid hyrazide with p-methylacetophenone, p-chloroacetophenone and isonitrosoacetophenone, respectively. The structures of these new compounds were proposed on the basis of elemental analysis, ¹H-NMR and IR data. The extraction abilities of these new compounds were also examined by the solid-liquid extraction of selected transition metal [Ni(II), Cu(II), Co(II), Zn(II), Mn(II) and Cd(II)] ions.

Key Words: p-Aminobenzoic acid, hydrazide, hydrazone, extraction

4-Metilasetofenon 4-Aminobenzoil Hidrazon, 4-Kloroasetofenon 4-Aminobenzoil Hidrazon ve Isonitrosoasetofenon 4-Aminobenzoil Hidrazon'un sentezi ve Ekstraksiyon Özelliklerinin İncelenmesi

Özet: Bu çalışmada, 4-aminobenzoik asit hidrazinin 4-metilasetofenon, 4-kloroasetofenon ve isonitrosoasetofenon ile reaksiyonundan sırasıyla 4-metilasetofenon 4-aminobenzoil hidrazon (L₁), 4-kloroasetofenon 4-aminobenzoil hidrazon (L₂) ve isonitrosoasetofenon 4-aminobenzoil hidrazon (L₃) bileşikleri sentezlenmiştir. Bu yeni bileşiklerin yapıları ¹H-NMR, IR ve elementel analiz teknikleri kullanılarak aydınlatılmıştır. Ayrıca bu bileşiklerin Ni(II), Cu(II), Co(II), Zn(II), Mn(II) ve Cd(II) iyonları ile katı-sıvı ekstraksiyon özellikleri incelenmiştir.

Anahtar Kelimeler: p-Aminobenzoik asit, hidrazin, hidrazon, ekstraksiyon

Introduction

The hydrazones of 4-aminobenzoic acid hydrazide are known to possess antibacterial, antifungal and antimicrobial activities. Not only do transition metals complexes of these kinds of compounds show antitumor activity but they are found to be useful in polymer coating inks and pigments [1-3].

4-Aminobenzoic acid hydrazide and their hydrazones form a variety of complexes with metal ions. When the -NH₂ group (CONHNH₂) of 4-aminobenzoic acid hydrazide is condensed with aldehydes and ketones, the resulting schiff bases have carbonyl oxygens and azometine nitrogens as donor sites. Therefore, these kinds of compounds have been found to be flexidentate and form complexes of structural and biochemical interest [4,5].

The process of solvent extraction is one of the most versatile procedures used for the removal, separation and concentration of the metallic species, broadening its application in the

¹ Muğla Üniversitesi, Fen-Edebiyat Fakültesi, Kimya Bölümü, Muğla, E-mail: Ramazangup@hotmail.com

² Selçuk Üniversitesi, Fen Edebiyat Fakültesi, Kimya Bölümü, Konya

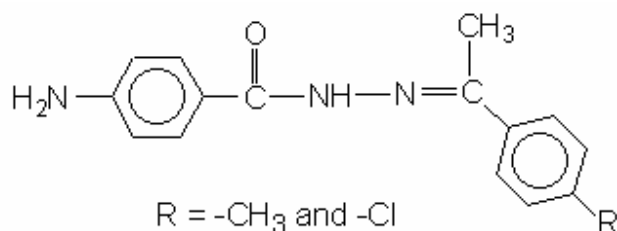
recycling of the resources in the field of metallurgy and waste water treatment as demand increases for the development of new approaches to resolve the various problems presented. For this purpose many oxime derivatives have been synthesized and their properties investigated by solvent extraction [6,7].

4-Methylacetophenone p-aminobenzoylhydrazone, 4-chloroacetophenone p-aminobenzoylhydrazone and isonitrosoacetophenone p-aminobenzoylhydrazone posses a number of potential bonding sites such as the carbonyl oxygen, azomethine and imine nitrogens. Furthermore, isonitrosoacetophenone p-aminobenzoylhydrazone has the oxime (-CH=N-OH) group as an additional bonding site. In this paper we reported the synthesis and extraction properties of three new 4-aminobenzoic acid hydrazide hydrazones (Figure 1).

Material and Method

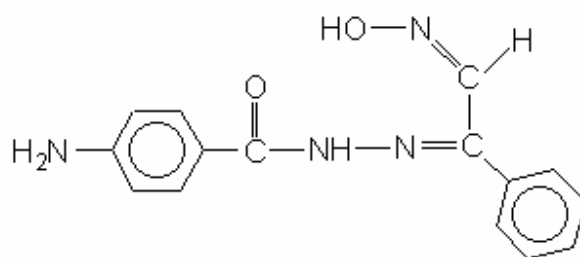
All reagents were purchased from Merck or Fluka Company and are chemically pure. IR spectra were obtained by using a Pye-Unicom SP-1025 spectrophotometer in KBr pellets. ¹H-NMR spectra were recorded on a Varion T 100-A model spectrometer with DMSO-d₆ as solvent. Elemental analysis (Carlo-Erba 1106 Model) and melting point (Buchi SPM-20) were used to elucidate the structure of the ligands.

4-Aminobenzoic acid hydrazide and isonitrosoacetophenone were prepared according to the published methods [8,9].



L₁ : 4-Methylacetophenone 4-Aminobenzoylhydrazone

L₂ : 4-Chloroacetophenone 4-Aminobenzoylhydrazone



L₃ : Isonitrosoacetophenone 4-Aminobenzoylhydrazone

Figure I. The Structures of Compounds

Experimental

Preparation of Ligands

4-Methylacetophenone, 4-chloroacetophenone and isonitrosoacetophenone 4-aminobenzoylhydrazones were prepared by refluxing the a solution of p-aminobenzoic acid hydrazide (10 mmol, 1.51 g) and glacial acetic acid (10 mmol,) in ethanol (25 mL) with p-methylacetophenone (L₁) (10 mmol, 1.34 g), p-chloroacetophenone (L₂) (10 mmol, 1.55 g) or isonitrosoacetophenone (L₃) (10 mmol, 1.49 g) in ethanol (15 mL) for 3 h. The compounds which precipitated during the reaction were filtered and washed with ethanol. They were recrystallized from hot ethanol. The hydrazones were characterized by elemental analyses, IR and ¹H NMR spectra.

Compound L₁; yield: 78 %, mp: 174 °C, IR (KBr, cm⁻¹); 3240 (N-H), 2975-2863 (C-H), 1660 (C=O), 1614 (C=N), 990 (N-N). ¹HNMR (DMSO-d₆): δ 2.17 s, 3 H, (-CH₃); 2.53 s, 3 H, (Ar-CH₃); 5.73 s, 2H (Ar-NH₂); 6.68-8.03 m, 8 H, (Ar-H); 10.70 s, 1 H, (-NH). For C₁₅H₁₅N₃O (253 g/mol) calculated: C, 71.15; H, 5.93; N, 16.60 . Found: C, 71.65; H, 5.79; N, 16.98.

Compound L₂; yield: 67 %, mp: 182-174 °C, IR (KBr, cm⁻¹); 3245 (N-H), 2977-2855 (C-H), 1664 (C=O), 1618 (C=N), 995 (N-N). ¹HNMR (DMSO-d₆): δ 2.20 s, 3 H, (-CH₃); 5.83 s, 2H (Ar-NH₂); 6.75-7.89 m, 8 H, (Ar-H); 10.73 s, 1 H, (-NH). For C₁₅H₁₅N₃O (253 g/mol) calculated: C, 62.61; H, 4.87; N, 14.61 . Found: C, 62.67; H, 4.84; N, 14.57.

Compound L₃; yield: 73 %, mp: 217 °C, IR (KBr, cm⁻¹); 3320 (O-H), 3265 (N-H), 1660 (C=O), 1610 (C=N), 985 (N-N), 968 (N-O). ¹HNMR (DMSO-d₆): δ 5.75 s, 2 H (Ar-NH₂); 6.95-7.89 m, 9 H (Ar-H); 8.60 s, 1 H, (-CH=N); 10.79 s, 1 H (NH); 11.40 s, 1 H (OH). For C₁₅H₁₄N₄O₂ (282 g/mol) calculated: C, 63.83; H, 4.96; N, 19.86. Found: C, 63.22; H, 4.54; N, 19.75.

Metal Cation Adsorption

A 10 mL metal nitrate solution (1 x 10⁻⁴ M) and powdered ligand L₁ (2.53 X 10⁻³ g) or L₂ (2.82 x 10⁻³ g) were place in a flask. The mixture was shaken for 1 h. at room temperature, and then filtered off. The concentration of metal ion remaining in the aqueous phase was then determined by AAS technique as follows:

$$\text{Ex \%} = \frac{[(\text{metal})_{\text{blank}} - (\text{metal})_{\text{water}}]}{(\text{metal})_{\text{blank}}} \times 100$$

Results and Discussion

In this study, 4-methylacetophenone p-aminobenzoylhydrazone (L₁), 4-chloroacetophenone p-aminobenzoylhydrazone (L₂) and isonitrosoacetophenone p-aminobenzoylhydrazone (L₃) were prepared by reaction of 4-aminobenzoic acid hydrazide with p-methylacetophenone, p-chloroacetophenone and isonitrosoacetophenone, respectively. The compounds are insoluble in common organic solvents such as dichloromethane, chloroform, benzene, ether, ethyl acetate and water, slightly soluble in ethanol. However, they are soluble in methanol, DMF and DMSO the structures of these new compounds were proposed on the basis of elemental analysis, ¹H NMR and IR data. The extraction abilities of these new compounds were also examined by the solid-liquid extraction of selected transition metal [Ni(II), Cu(II), Co(II), Zn(II) and Cd(II)] ions.

The ¹H NMR spectra of L₁ and L₂ display peaks at δ 2.17 (s) and 2.20 (s) for -CH₃ protons; 2.53 (s) for Ar-CH₃ protons; 5.73 (s) and 5.65 (s) for Ar-NH₂ protons; 6.68-8.03 (m) and 6.75-7.89 (m) for aromatic protons; 10.70 (s) and 10.73 (s) for hydrazone (-NH-) protons, respectively. L₃ exhibits signals at δ 5.75 (s), 6.95-7.89 (m), 8.60 and 10.79 (s). These peaks are attributed to Ar-NH₂ protons, aromatic protons, -CH=N proton and hydrazone (-NH-) proton, respectively. The characteristic oxime (OH) resonance of L₃ appears as a singlet at δ 11.40 ppm. These signals are in accordance with the values for other oximes and benzoylhydrazones. [3,5,7,8].

In the IR spectra of the ligands, the bands appearing at 3200 and 3265, 1660, 1614 and 1610, 990 and 985 cm⁻¹ are attributed to ν(NH and NH₂), ν(C=O), ν(C=N) and ν(N-N) modes, respectively. A broad band at 3320 cm⁻¹ is assigned to ν(OH) (oxime) in the spectra of L₃. [3,5,7,8,10]. The other characteristic band (NO) of oxime compound is seen at 968 cm⁻¹. Furthermore, the bands appearing at 2975-2863 cm⁻¹ are attributed to the aliphatic protons of ligands.

Both hydrazones and oximes have been widely employed in the formation of transition metal complexes and in the study of inclusion phenomena due to their relatively easy preparation, remarkable stability and high versatile. As yet, reports on the solvent extraction with these compounds are still scarce. Therefore, this work was focused on the extraction properties of these compounds which are insoluble in major solvent system and are immiscible with the aqueous phase by solid-liquid extraction. The cations studied were Ni(II), Co(II), Cu(II), Zn(II), Cd(II) and Mn(II). The results are summarized in Table I. These data were obtained by extracting metal nitrates from aqueous solution into organic phase. The metal cation remaining in the aqueous phase was then determined by AAS technique.

Table I. Solid-Liquid^a Extraction of Metal Cations with Ligands^b

Compounds	Ni ⁺²	Co ⁺²	Cu ⁺²	Zn ⁺²	Cd ⁺²	Mn ⁺²
L ₁	2.0	<1	40.3	<1	<1	<1
L ₂	10.	5.8	45.9	<1	<1	<1
L ₃	8.5	4.3	70.4	5.2	5.5	8.3

^asolid phase; [ligands = (2.53 X 10⁻³ g) and L₂ (2.82 x 10⁻³ g)]

^baqueous phase; [metal nitrate = 1 x 10⁻⁴ M].

From the extraction data shown in Table I. it can be seen that metal cations except Cu(II) were not significantly extracted by the ligands. The presence in the ligands of soft donor azomethine and imine nitrogens, which show high affinity to copper ion, causes the increase in the Cu(II) extraction ability of these ligands. Moreover, C=O group in the ligands may participate in the complexation.

When the copper (II) extraction efficiencies of ligands are compared, it can be seen that due to an additional oxime group (-CH=N-OH) the copper (II) extraction efficiency of L₃ is higher than that of L₁ and L₂. The oxime group probably join in complexation during solid-liquid extraction process.

In order to ascertain the stoichiometric composition of the copper complex formed with L₃, Job's method of continuous and the molar-ratio method were applied. A 1:1 (Cu :L₃) complex was indicated by both methods. The proposed structure of the complex of Cu⁺² formed with L₃ is shown in Figure 2.

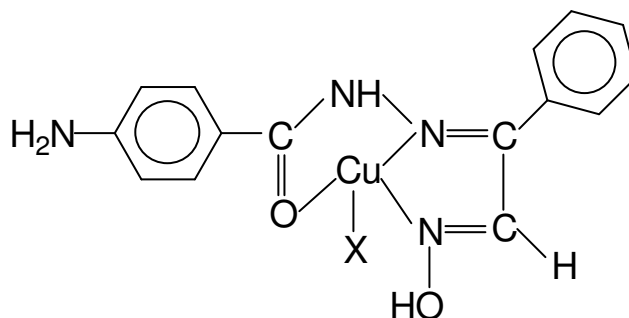


Figure 2. Proposed structure of copper (II) complex of L₃

Conclusion

In the present study, three new p-aminobenzoic acid hydrazide hydrazones have been synthesized. The solid-liquid extractions of transition metal ions with these compounds have been examined. Isonitrosoacetophenone 4-aminobenzoyl hydrazone is fairly selective for Cu(II) ion.

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