

α -Cyanobenzoylacetonilide as an Analytical Reagent for Uranium(VI)

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Reaction of α -cyanobenzoylacetonilide with uranium(VI) has been studied and the complex obtained has been characterised on the basis of analytical data, electrolytic conductance and IR spectra. The ligand has been found to be suitable for gravimetric determination of uranium(VI). The complex is precipitated quantitatively in the pH range 6.0-8.0; its separation from a large number of metal ions is described.

A critical examination¹ of the important gravimetric methods for the determination of uranium(VI) indicates that the reagents used are mostly oxygen-containing and the complexes formed are often of indefinite compositions or the procedures have poor selectivities. Among the reagents used for the gravimetric determination of UO_2^{2+} is benzoylacetonilide (BA). However, composition of the precipitate formed depends on experimental conditions^{2,3}. Benzoylacetonilide has been reported² to react with UO_2^{2+} as an enolate. It occurred to us that a derivative of (BA) with a substituent that enhances the formation of the enolate would improve the chelating potentiality. In the present investigation the UO_2^{2+} complex of α -cyanobenzoylacetonilide (I) has been synthesised and investigated by physicoanalytical techniques. The complex formation reaction has been utilized for the gravimetric determination of UO_2^{2+} . Previously, we have reported^{4,5} the use of (I) as an analytical reagent for iron(III).

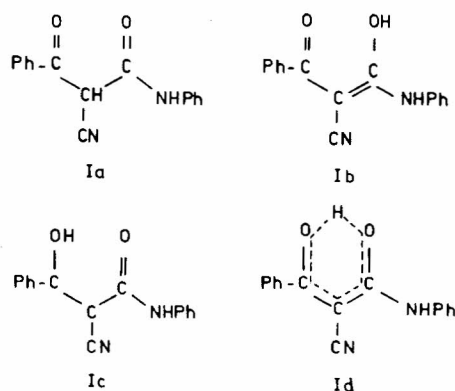
Solution of uranyl nitrate (AR grade) was prepared in triply distilled water and standardised by standard procedures⁶. Aqueous solutions of diverse ions were prepared from the nitrates or chlorides. α -Cyanobenzoylacetonilide (I) was prepared from benzoylacetonitrile and phenyl isocyanate using the procedure reported^{4,7} earlier (yield, 85%). Solution of the reagent was prepared in 1:1 ethanol-dioxane mixture.

pH measurements were carried out on a Pye Unicam pH-meter. The IR spectra (KBr) were recorded on NICOLET 7199-FTIR spectrophotometer. Electrolytic conductance was measured at $25 \pm 0.02^\circ\text{C}$ using a WTW LBR conductivity meter. Magnetic susceptibility measurements were carried out using a

"Galileo-Sartorius" air damped analytical balance.

Preliminary investigation showed that the optimum conditions for complete precipitation of the complex were: pH, 6.0-8.0 and reagent concentration 2-3 times the amount of metal ion taken in solution.

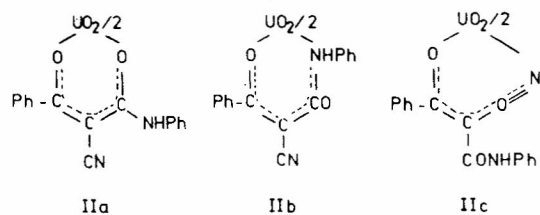
α -cyanobenzoylacetonilide can exist in any of the potentially tautomeric structures Ia-Id. Structure Ia seems to be the most likely in the solid state on the basis of its IR spectrum. In a previous publication⁴, the pK_a of the ligand was determined to be 3.40. This acidic pK_a indicates that in solution phase the enol forms Ib, Ic and/or the resonance hybrid Id are predominant.



Composition of the complex

Analytical data of the solid complex show the stoichiometry of the complex to be 1:2 (metal:ligand). The electrolytic conductance in DMF at 25° (Λ_M $8 \Omega^{-1} \text{cm}^2$, conc. = 0.001 M), indicates the nonelectrolytic nature of the complex and nonprotonated form of the ligand in the chelating species.

Regarding the mode of chelation, there are three possible structures (IIa-IIc).



IR spectrum of the ligand exhibits a broad band at 1635 cm^{-1} , characteristic of benzoyl and anilide carbonyl groups. On chelation with uranyl ion this band disappears which indicates that coordination occurs through the two oxygen atoms as in IIa and does not involve either the anilide nitrogen atom (IIb) or the cyano group (IIc). The presence of the uranium-oxygen covalent bond in the complex was established. The complex exhibits a very strong band at 930 cm^{-1}

characteristic of asymmetric stretching of uranyl ion in accordance with the earlier^{8,9} observation in many uranyl complexes (900-950 cm^{-1}). The magnetic susceptibility measurements showed the complex to be diamagnetic as expected for $5f^0$ configuration.

Procedure for gravimetric determination of UO_2^{2+}

An aliquot containing 10 to 60 mg of metal ion was heated to 70-80°. The reagent solution of concentration 2-3 times that of uranyl ion was then slowly added with constant stirring. The pH of the mixture was raised to 6.0-8.0 by the addition of ammonium hydroxide solution (1:4). The complex was precipitated and digested on a water bath for 30 min and then filtered through a sintered-glass crucible(G4), washed with water and finally with ethanol-water mixture (1:1). It was weighed as $\text{UO}_2(\text{C}_{16}\text{H}_{11}\text{N}_2\text{O}_2)_2$ after drying at 110-130°C. The complex was crystalline and yellow in colour [Found: C, 47.97; H, 3.13; N, 6.87; for $\text{UO}_2(\text{C}_{16}\text{H}_{11}\text{N}_2\text{O}_2)_2$ Reqd.; C, 48.24; H, 2.76; N, 7.03%].

Effect of diverse ions

Cu(II), Co(II), Ni(II), Zn(II), Mn(II), Sr(II), Ba(II), Pb(II), Hg(II), Al(III), Th(IV), Zr(IV) and Bi(III)

interfere in the estimation of UO_2^{2+} by the present reagent. However, these ions can be completely masked by adding magnesium-EDTA solution to the test solution, so that the total EDTA content is about five times the total concentration of the diverse ions present.

The present method has the advantage of being reproducible and precise as indicated by the low value of the standard deviation (0.11) for determination of solutions containing 30 mg uranium (10 determinations).

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