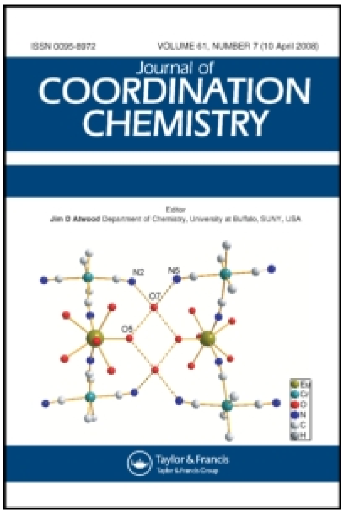

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Doretti, L. , Faleschini, S. , Sitran, S. and Faraglia, G.(1976) 'Adducts of bis(8-hydroxyquinolinato)dioxouranium(VI)', Journal of Coordination Chemistry, 6: 2, 115 — 117

To link to this Article: DOI: 10.1080/00958977608079894

URL: http://dx.doi.org/10.1080/00958977608079894

J. Coord. Chem.
1976, vol. 6, pp. 115–118

SHORT COMMUNICATION
Adducts of bis(8-hydroxyquinolinato)dioxouranium(VI)

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(Received March 24, 1976; in final form June 1, 1976)

Uranyl complexes with 8-hydroxyquinoline (Hox) have been reported in the literature many times. The red compound $UO_2ox_2 \cdot Hox$ was obtained under appropriate conditions from aqueous solutions of reagents$^{(1-3)}$. The crystal structure of the chloroform solvate $UO_2ox_2 \cdot Hox \cdot CHCl_3$ has been determined,[4] showing two chelated oxine molecules, the third acting as a monodentate ligand through the oxygen atom. The hydrogen is on the nitrogen and forms a bridge bond with the oxygen of one of the chelated oxines. The existence of the group N–H–O was confirmed by IR spectra.[5]

By thermal conversion the red $UO_2ox_2 \cdot Hox$ gives the green UO_2ox_2,[6] the structure of which is unknown, probably owing to the difficulty of obtaining pure crystalline samples.[7]

The uranyl group bonded to two oxine radicals appears to be coordinatively unsaturated and tends to make up donor molecules. The red compound is usually slightly deficient in oxine, and the reason was ascribed to coordination of water, which replace the neutral oxine.[6,8] Uranyl salts and 7, 7–5, 7–2 substituted 8-hydroxyquinolines form adducts with water, ammonia and acetone in aqueous (or aqueous-acetonic) solutions; the preferential coordination of small molecules was imputed to steric hindrance of the 7-substituent towards the neutral oxine.

This paper reports the preparation of some new UO_2ox_2 adducts with ligands of various basicity. Most of these compounds have been prepared from anhydrous UO_2ox_2 to prevent the competition of water and oxine. The reaction of uranyl nitrate with sodium oxinate in water and methanol provided a useful method to prepare dichelated compounds avoiding the coordination of the third oxine.

EXPERIMENTAL

The materials used were as follows: uranyl nitrate hexahydrate (Fluka) and 8-hydroxyquinoline were used without purification. Solvents and ligands have been purified with the usual methods.[9] The red $UO_2ox_2 \cdot Hox$ was prepared as in ref. 1, UO_2ox_2 according to ref. 6, sodium oxinate as reported in ref. 10.

The oxine content in the compounds I and II was determined by bromometric titration.

Solution spectra in anhydrous methanol, acetone, pyridine and spectra of solid samples finely grinded in nujol and adsorbed on Whatman No. 1 paper were measured on a Beckman DK-2A Spectrophotometer.

IR spectra in nujol in the 4000–400 cm^{-1} region (CsI discs) were recorded on a Perkin–Elmer 621 Spectrophotometer.

The adducts were prepared as follows:

i) $UO_2(C_9H_6NO)_2 \cdot CH_3OH$

A methanolic solution of sodium oxinate was added to methanolic uranyl nitrate (molar ratio 2:1). Immediately an orange solid was formed, which turns to dark red on boiling under stirring for a few minutes. The compound was washed with methanol and dried in vacuo over P_2O_5. Yield 80%. By heating the methanol adduct in vacuo at about 190°, UO_2ox_2 was obtained.

Anal. Calcd. for $UC_{19}H_{16}N_2O_5$: C, 38.65; H, 2.73; N, 4.74; O, 13.54; ox, 48.83. Found: C, 38.44; H, 2.73; N, 4.74; O, 13.26; ox, 48.65.

ii) $UO_2(C_9H_6NO)_2 \cdot H_2O$

Aqueous sodium oxinate was added to aqueous uranyl nitrate (molar ratio 2:1); the orange solid turns to brown on boiling. The compound was washed with water, acetone and ether, and was dried in vacuo over P_2O_5. Yield 90%. The same product was obtained by adding water to an acetonic solution of I or to a suspension of UO_2ox_2 in the same solvent. By heating in vacuo at about 180°C the brown solid releases water giving the green chelate.

Anal. Calcd. for $UC_{18}H_{14}N_2O_5$: C, 37.51; H, 2.45; N, 4.86; O, 13.87; ox, 50.02. Found: C, 37.40; H, 2.53; N, 4.71; O, 13.58; ox, 49.97.

iii) $UO_2(C_9H_6NO)_2 \cdot CO(NH_2)_2$

An acetonic suspension of urea and UO_2ox_2 (molar ratio 1:1) was boiled for a few minutes; an orange solid was obtained. The compound was also prepared by adding an excess of urea to compound I in methanol, and, in another way, by the reaction of uranyl nitrate with sodium oxinate (molar ratio 1:2) in methanol containing urea (molar ratio U:urea = 1:4). The solid, washed with methanol, was dried as usual.

Anal. Calcd. for $UC_{19}H_{16}N_4O_5$: C, 36.90; H, 2.61; N, 9.06. Found: C, 37.09; H, 2.56; N, 9.04.

iv) $UO_2(C_9H_6NO)_2 \cdot C_5H_5N$

The green uranyl oxinate was dissolved into warm pyridine; the dark red complex was obtained with quantitative yield by adding hexane. The solid was carefully washed with hexane and the small excess of pyridine was removed under vacuum. It decomposes at about 190°C into a grey green unidentified product.

Anal. Calcd. for $UC_{23}H_{17}N_3O_4$: C, 43.33; H, 2.69; N, 6.59. Found: C, 43.22; H, 2.72; N, 6.60.

v) $UO_2(C_9H_6NO)_2 \cdot C_{12}H_8N_2$

The orange compound was obtained by adding an excess of 1,10-phenanthroline to acetonic UO_2ox_2 or acetonic $UO_2ox_2 \cdot CH_3OH$. It does not decompose up to 280°C.

Anal. Calcd. for $UC_{30}H_{20}N_4O_4$: C, 48.78; H, 2.73; N, 7.59. Found: C, 48.46; H, 2.73; N, 7.41.

vi) $UO_2(C_9H_6NO)_2 \cdot C_9H_7N$

The brown complex containing quinoline was prepared as the pyridine adduct; it decomposes at about 130°C.

Anal. Calcd. for $UC_{27}H_{19}N_3O_4$: C, 47.17; H, 2.88; N, 6.17. Found: C, 47.37; H, 2.90; N, 6.20.

vii) $UO_2(C_9H_6NO)_2 \cdot C_6H_7N$

Uranyl dioxinate was dissolved in warm aniline and the excess of ligand was extracted with many volumes of pentane. The pale brown complex obtained following this method contains often some impurity.

Anal. Calcd. for $UC_{24}H_{19}N_3O_4$: C, 44.24; H, 2.94; N, 6.45. Found: C, 44.60; H, 3.02; N, 6.52.

Attempts to prepare thiourea and 2,2′-bipyridyl adducts following a similar method failed.

DISCUSSION

The compounds prepared dissolve in polar solvents, generally in small quantities, giving orange-red solutions. The absorption spectra of the compounds I, II, III, IV, VI and UO_2ox_2 in methanol present the same maxima at 331, 369, 475(sh) nm; in acetone the maxima lie at 375, 475(sh) nm; in pyridine at 333, 380, 475(sh) nm.

This behaviour would suggest either an identical decomposition of all the compounds in each solvent, or, more likely, a displacement of the secondary ligand by the solvent. In such a way the neutral oxine in $UO_2ox_2 \cdot Hox$ was released in DMSO to give free oxine and solvated UO_2ox_2.[8]

The spectra of solids in nujol present, in spite of rather different colours of powders, the same bands, with the maxima at about 365 nm; only a shifting of the broad shoulder in the range 450–600 nm was observed.

IR spectra of all the compounds prepared were recorded. The uranyl dioxinate obtained by heating under vacuum the compounds I and II, presents the spectrum of the usual compound.[11] The adducts do not present the broad band at 2650 cm^{-1}, assigned to N–H–O hydrogen bond in compounds containing free oxine.[5]

The spectra of the adducts are very close to the spectrum of UO_2ox_2, except for peaks due to the secondary ligand. The sharp peak around 1005 cm^{-1} in the compound I, falling in a zone where primary alcohols absorb, is absent in the spectra of uranyl oxinate and of the other adducts, and is probably due to methanol.

The intense peak at 917 and 906 cm^{-1} in UO_2ox_2 and $UO_2ox_2 \cdot Hox$ respectively has been assigned to the asymmetric stretching vibration of the UO_2 group.[11,12] The corresponding band in the adducts is present at the frequencies (in cm^{-1}): I, 907, II, 894; III, 896; IV, 890; V, 892; VI, 902. A shifting of the stretching band of uranyl to lower frequencies was ascribed to an increase in coordination number on the uranium atom.[12,13] The adducts follow this trend, but it is difficult to correlate the shift of this band with the basicity of the secondary ligands, owing to the small range of displacement.

ACKNOWLEDGEMENTS

The authors are grateful to Mr. F. Madalosso and Mr. A. Berton for technical assistance.

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