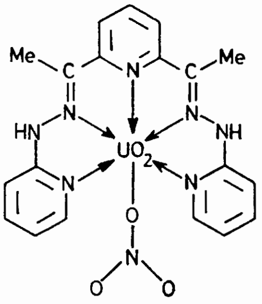
Unusual Reaction of Uranyl Nitrate with 2,6-Diacetylpyridine Bis(2-pyridylhydrazone): *X*-Ray Structure of Nitrato[2,6-diacetylpyridine-bis(2-pyridylhydrazone)-*NNNNN*]uranyl Tetranitratodioxouranium

By Giuliano Bandoli,* Dore A. Clemente, Giampaolo Marangoni, and Gino Paolucci
(*Laboratorio di Chimica e Tecnologia dei Radioelementi del C.N.R., C. so Stati Uniti,* 35100 *Padova, Italy*)

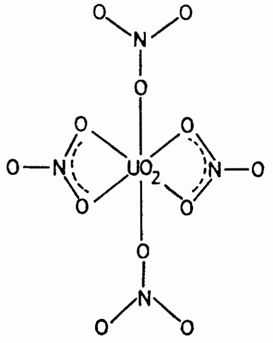
Summary Uranyl nitrate reacts with 2,6-diacetylpyridine-bis(2-pyridylhydrazone) (H_2dapp) to give $[UO_2(H_2dapp)NO_3]_2[UO_2(NO_3)_4]$, the unusual structure of which has been determined by *X*-ray diffraction.

Recently we reported[1] the preparation of the first penta-aza-neutral complex of the uranyl ion, containing diazinic =N–N= sequences, by deprotonation of the ionic polynuclear species obtained (I) by reaction of uranyl nitrate with 2,6-diacetylpyridine bis(2-pyridylhydrazone) (H_2dapp) in ethyl acetate under various conditions.

Analytical data for (I) (U:H_2dapp ratio of 3:2 for $C_{38}H_{38}N_{20}O_{24}U_3$) and complex spectroscopic features did not allow an unambiguous assignment of the bonding mode of the ligands and the geometry around the uranyl units. However, general chemical considerations suggested that the structure might be trinuclear. In view of the possible free rotation around the single bonds of H_2dapp, a trinuclear cationic structure containing two uranyl units penta-co-ordinated through four nitrogen atoms of H_2dapp and an oxygen atom of a monodentate nitrate group, bridging a uranyl dinitrate group through the fifth nitrogen atom, is one possibility.



(A)



(B)

An X-ray investigation in fact showed an unusual structure in which two highly distorted octaco-ordinated complex cations (A) are electronically balanced by the uranyl tetranitrate counteranion (B). Uranyl tetranitrate salts are known to be obtained from very concentrated (14—20 M) nitric acid solutions.[2]

The molecular structure of the compound, viewed along the c axis, is shown in the Figure. The unit cell contains two cations $[UO_2(H_2dapp)NO_3]^+$ related by a centre of symmetry and a $[UO_2(NO_3)_4]^{2-}$ anion, at the centre of symmetry.

The cation comprises four strained five-membered rings with a monodentate nitrate group co-ordinated to UO_2^{2+}. The anion contains two bidentate and two monodentate nitrate groups, leading to six-fold co-ordination of oxygen atoms in the equatorial plane perpendicular to the uranyl group.[3] The unique structure of the cation can be accounted for only by the high stabilizing effect of the 5,5,5,5-chelation mode of bonding.

The best least-squares plane formed by the U′ atom and its donors show high deviations [U′ −0·06; N(4) 0·53; N(6) −0·47; N(7) −0·06; N(8) 0·57; N(9) −0·45; O(10) −0·06 Å] so that an 'equatorial plane' normal to O(8)–U′–O(9) cannot be defined and the six donor atoms assume a twisted cyclohexane-like conformation. The four five-membered rings are not planar, their atoms showing deviations of up to 0·22 Å.

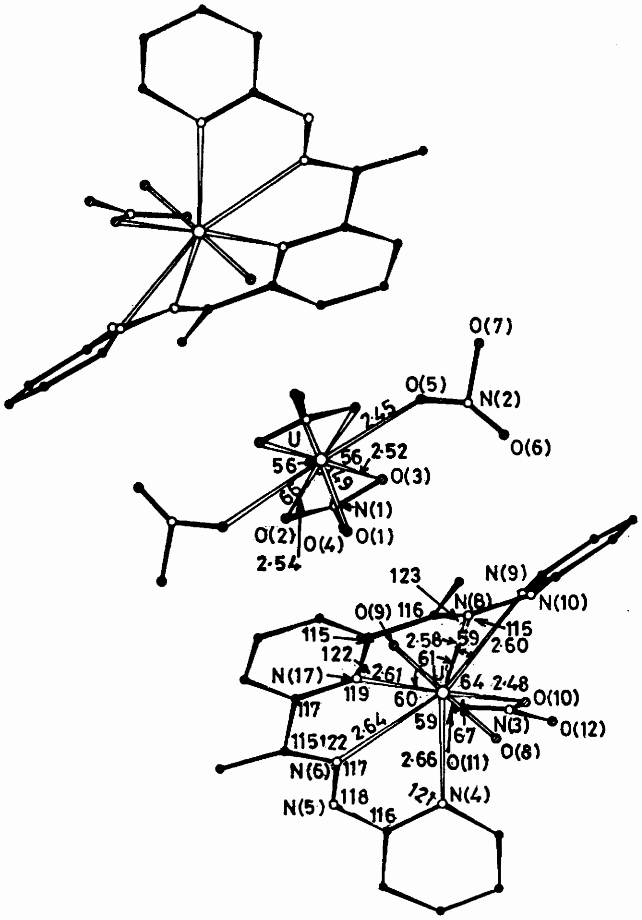


FIGURE. Molecular structure of $[UO_2(H_2dapp)NO_3]_2[UO_2(NO_3)_4]$, viewed along the c axis, with some bond distances (Å) (e.s.d.'s 0·02 Å) and angles (°) (e.s.d.'s 0·5°).

Crystal data: triclinic, space group $P\bar{1}$, M 1872·9, a = 14·071(9), b = 10·801(7), c = 10·122(6) Å, α = 63·86(7), β = 75·65(9), γ = 78·86(9)°, U = 1331·7 Å^3, D_c = 2·33 g cm^{-3}, Z = 1. Intensity data were recorded on a Philips PW 1100 diffractometer, employing the ω–2θ scan technique, with Mo-K_α radiation; for 3137 'observed' reflections the current conventional R value is 0·07 (anisotropic temperature factors only for heavy atoms; unit weights for each reflection).†

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

[1] G. Paolucci and G. Marangoni, *Inorg. Chim. Acta*, 1977, **24**, L5.
[2] L. Cattalini, U. Croatto, S. Degetto, and E. Tondello, *Inorg. Chim. Acta Rev.*, 1971, **5**, 19.
[3] I. I. Kapshukov, Yu. F. Volkov, E. P. Moskvichev, I. A. Lebedev, and G. N. Yakovlev, *Zhur. strukt. Khim.*, 1971, **12**, 94.