Inorganica Chimica Acta, 62 (1982) 237–240

Crystal and Molecular Structure of Uranyl Nitrate Trimethylphosphate

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Received January 18, 1982

The crystal and molecular structure of uranyl nitrate trimethylphosphate has been determined by three dimensional X-ray analysis, U---U intermolecular distances are correlated to solid state photochemical behavior in this class of compounds.

The mode of bonding of the nitrate ion to uranyl is compared with other known uranyl nitrate compounds, and it is confirmed that upon coordination the two $N-O_{coordinate}$ bonds are lengthened by 0.05 Å, with a simultaneous reduction of the O–N–O coordinate angle from 120° to 112–115°.

Extended Hückel calculations and VSEPR theory interpret this feature as being due to a donation of electron density from the $N-O_{coordinate}$ bonds to uranyl bonding orbitals.

Introduction

The photochemical production of a localized charge transfer triplet state recently observed in crystalline $UO_2(NO_3)_2(TEP)_2$ (TEP = triethylphosphate) [1] does not occur for the simpler compound $UO_2(NO_3)_2(TMP)_2$ (TMP = trimethylphosphate).

In an attempt to relate this behaviour to the crystal (and molecular) structure, and since the structure of the TEP derivative is already known [2], we have undertaken the crystallographic study of the title compound.

Large differences in crystal packing have clearly emerged between the two compounds, as expected. Differences in molecular structure are also manifest, especially for the NO_3^- ion; however since the structure determination of the TEP derivative was two-dimensional the distances are not reliable. Furthermore the accuracy of our structure determination allows a discussion of the deformation of NO_3^- upon coordination which, in this class of compounds, occurs most commonly with two bidentate nitrate and two unidentate phosphate groups around the uranyl axis [3].

Experimental

Preparation of the Complex

To a benzene solution of TMP was added a solution of $UO_2(NO_3)_2 \cdot 6H_2O$ in HNO_3 6 *M*. The organic phase containing the reaction product was extracted and dried over Na_2SO_4. By evaporation of the solvent a yellow crystalline material was separated. This product was recrystallized from chloroform as well-formed yellow, monoclinic crystals. Their purity was stated from elemental analysis, which is in accordance with the formula $UO_2(NO_3)_2(TMP)_2$. It melts at 130–132° without decomposition.

Crystal Data and Single Crystal Diffractometry

$UO_2(NO_3)_2(TMP)_2$, M = 674.2; Monoclinic, a = 10.535(4), b = 12.758(4), c = 7.658(3) Å, β = 96.76(5)°, U = 1022.1 Å^3, $Z = 2, D_{calc} = 2.19$ g/cm^3, μ(Mo-Kα) = 77.9 cm^{-1}; space group $P2_1/n$ (from systematic absences).

Data were collected on a Philips four-circle diffractometer (Mo-Kα radiation, λ = 0.7107 Å) at the Istituto di Chimica e Tecnologia dei Radioelementi of Padua (C.N.R.), using a single crystal cut in a nearly cubic shape with dimensions 0.13 mm. A total of 3303 unique reflections were measured up to a $2\theta_{max}$ = 50° using the $\omega-2\sigma$ step scan technique. After the usual Lorentz, polarization and absorption corrections, the systematically absent

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TABLE I. Fractional Atom Co-ordinates ($\times 10^4$) with Estimated Standard Deviations in Parentheses.

Atom	*x/a*	*y/b*	*z/c*
U	0000	0000	0000
O(1)	416(11)	1153(8)	−1044(15)
N(1)	1390(16)	−1308(11)	−2379(20)
O(2)	223(12)	−1061(11)	−2731(15)
O(3)	1943(11)	−933(11)	−970(18)
O(4)	1965(14)	−1833(11)	−3340(18)
P	3111(4)	298(4)	2868(7)
O(5)	1855(10)	147(13)	2011(15)
O(6)	3183(19)	1014(16)	4520(27)
C(1)	2393(21)	1028(18)	5859(29)
O(7)	3945(22)	−717(20)	3208(31)
C(2)	3609(22)	−1764(20)	3146(31)
O(8)	3932(26)	1000(22)	1595(34)
C(3)	4904(31)	1519(25)	1531(40)

TABLE II. Selected Bond Distances (Å) and Angles (°) with Estimated Standard Deviations in Parentheses.

U–O(1)	1.75(1)	O(2)–U–O(3)	49.7(4)
U–O(2)	2.53(1)	O(2)–U–O(5)	115.8(4)
U–O(3)	2.55(1)	O(3)–U–O(5)	66.1(4)
U–O(5)	2.35(1)	U–O(5)–P	166.5(9)
Nitrate group			
N–O(2)	1.27(2)	O(2)–N–O(3)	115.3(1.4)
N–O(3)	1.26(2)	O(2)–N–O(4)	123.5(1.6)
N–O(4)	1.21(2)	O(3)–N–O(4)	121.2(1.7)
Trimethylphosphate group			
P–O(5)	1.42(2)	$(\mathrm{O(5)–P–O})_{\mathrm{mean}}$	113.1(1.2)
P–O(6)	1.56(2)	$(\mathrm{C–O–P})_{\mathrm{mean}}$	135.0(2.2)
P–O(7)	1.57(3)		
P–O(8)	1.64(3)		
O(6)–C(1)	1.39(3)		
O(7)–C(2)	1.38(3)		
O(8)–C(3)	1.23(4)		

reflections were rejected and the equivalent reflections were merged (internal consistency index was 0.062), a total of 1807 reflections being obtained. Only the 1196 reflections having $I > 3\sigma(I)$ were used in the subsequent structure determination.

Structure Solution

The structure was solved by the heavy atom method, Fourier synthesis and full matrix least-squares refinement using the crystallographic program set SHELX [4].

Scattering factors for neutral atoms were those of Cromer and Mann [5], while for uranium atoms the scattering factor of Doyle and Turner [6] was used.

Towards the end of the refinement it appears evident that the trimethylphosphate group is disordered: this is reflected by the high thermal factors of oxygen atoms of TMP group. Similar disorder has already been found for this group coordinated to uranyl ion [7].

With all non-hydrogen anisotropic atoms the final R factor ($R = \Sigma\|F_o|-|F_c\|/\Sigma|F_o|$) was 0.042; nevertheless the anisotropic thermal parameters of the TMP atoms were unrealistic, especially for the oxygen atoms and then it was decided to treat these atoms as isotropic, in this way the R factor increased to 0.050.

TABLE III. Equations of Least Squares Planes.[a,b]

Plane A. Equatorial Plane.

Fitting: U, O(2), O(3), O(5) and centrosymmetrically related atoms.
Equation: $3.239x + 10.594y - 3.811z = 0.000$
Distance: U 0.000; O(2) −0.011; O(3) 0.011; O(5) −0.010.

Plane B. Nitrate plane.

Fitting: N(1), O(2), O(3), O(4).
Equation: $3.259x + 10.459y - 3.944z = 0.0359$
Distance: N(1) −0.013; O(2) 0.004; O(3) 0.004; O(4) 0.005.
Inter-plane angle A–B: 1.16°.

[a] The equations of the plane are expressed in direct space where *x*, *y* and *z* are fractional coordinates. [b] Distances in Å and angles in deg.

TABLE IV. Intermolecular Distances (Å) less than 3.5 Å. Roman numerals specify one of the symmetry operations:

I) $1 - x; -y; 1 - z$
II) $x; y; 1 + z$
III) $\frac{1}{2} - x; \frac{1}{2} + y; \frac{1}{2} - z$
IV) $\frac{1}{2} + x; -\frac{1}{2} - y; \frac{1}{2} + z$
V) $1 - x; -y; -z$

$UO_2(NO_3)_2(TMP)_2$	
O(6)- - -O(7)^{I}	3.33
C(1)- - -O(1)^{II}	3.34
C(1)- - -O(4)^{III}	3.35
C(2)- - -O(2)^{IV}	3.36
C(2)- - -O(4)^{II}	3.37
C(3)- - -O(4)^{V}	3.45
C(3)- - -O(3)^{V}	3.48
C(1)- - -N(1)^{II}	3.49

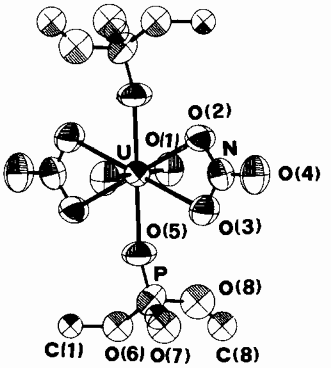

Fig. 1. Molecular structure of $UO_2(NO_3)_2(TMP)_2$ (TMP = trimethylphosphate). The numbering system used is shown. The drawings were obtained with ORTEP and the thermal vibration ellipsoids are scaled to enclose 50% probability. For clarity the disordered atoms of TMP group are shown as half of the true isotropic thermal parameters.

Structure amplitudes and anisotropic thermal parameters are listed in the Supplementary Publication. Final positional parameters are given in Table I.

Results and Discussion

The crystal structure is a packing of well-separated units of $UO_2(NO_3)_2(TMP)_2$ (see Table IV), with the uranium atoms situated on the inversion centers at (0, 0, 0) and (½, ½, ½). The molecular structure reported in Fig. 1 shows that the uranyl group is equatorially surrounded by two bidentate nitrate and two monodentate phosphate groups. The six equatorial oxygen atoms form a nearly planar slightly puckered hexagon (±0.01 Å) around the uranium atom (see Table III).

The main differences from the TEP compound are the U- - -U distances which, owing to the lower steric requirements of the aliphatic moieties, are clearly more compact in the methyl derivative.

Near neighbour U- - -U distances are 7.658(*c*), 8.852 ((*a* + *b* + *c*)/2), 10.535 Å (*a*) in the methyl case and become 8.655(*b*), 9.066(*c*), and 9.125 Å (*a*) for the ethyl compound where only one molecule per unit cell is present. It is possible that these structural features alone are sufficient to explain the impossibility of trapping the metastable charge transfer triplet state in the methyl compound. Two properties in this respect may be crucially affected, namely the vibrational frequencies of NO_3^- with respect to UO_2^{++}, and the rates of energy transfer between the molecular units within the crystal.

As for other molecular structural features of interest, the nitrate group is slightly tilted with respect to the equatorial plane (1.16°), the N–O bonds of the nitrate group involved in the coordination are equal but slightly longer by about 0.05 Å (see Table II) than the nitrogen uncoordinated oxygen bond. Many works report this interesting feature for other coordinated nitrate ions [3, 8a, 8b] and also a reduction of the O(2)–N–O(3) angle from 120° to 112–115°, but these two findings have not been related.

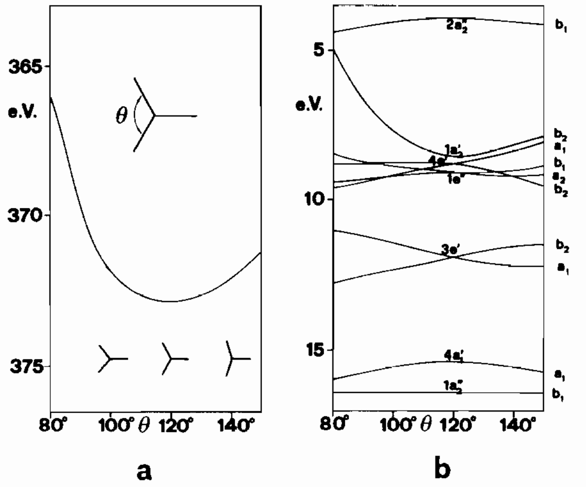

Fig. 2. (a) Variation in total orbital energy of NO_3^- ion on distorting the trigonal planar D_{3h} ion from θ = 80° to θ = 150°. (b) Energy changes of the frontier molecular orbitals of a NO_3^- ion on distortion.

We propose to interpret both of these events as being due to the donation of electron density from the bidentate nitrate group to uranyl bonding orbitals, which requires a reduction of bond order of the $N{-}O_{coordinate}$ bonds and a closure of the O–N–O angle. This is correctly explained by rule 4 of VSEPR theory [9] which states that angles containing multiple bonds are usually larger than those involving single bonds. The molecular orbital approach also matches with this idea: in fact we have built up a Walsh diagram by distorting the symmetrical D_{3h} NO_3^- group to C_{2v} symmetry, keeping constant the N–O bonds at 1.218 Å [10]. This diagram is reported in Fig. 2. The most interesting feature is that the HOMO orbital ($1a_2' \rightarrow b_2$) is greatly elevated by this distortion, in fact it may explain nearly 50% of the total energy variation. Consequently a distortion $D_{3h} \rightarrow C_{2v}$ of the NO_3^- ion must be accompanied by a depopulation of the highest lying a_2' orbital, which is symmetry-adapted to interact with the $\delta_g(6d_{xy})$ and $\phi_u(5f_{yx^2})$ molecular orbitals of uranyl ion, localized in the equatorial plane. The overlap population of the N–O bonds is consistent with this feature: the two equal N–O bonds decrease from 0.93 (θ = 120°) to 0.74 (θ = 80°), while the other N–O bond is practically constant.

The bond distances and angles of the trimethylphosphate are seriously affected by the disorder of this group, consequently the bond lengths derived from the final positional parameters are shorter than the true ones, especially for the bonds in the external part of the molecule. Probably only the two atoms of the P=O group have definite positions, in fact the distance 1.42 Å found here is only 0.02 Å shorter than that found in the $(Et_3O)_3PO$ molecule dipole–dipole bonded to benzotrifurazan [11]. Because of the disorder no attempt was made to locate hydrogen atoms.

The unusual distortion of the NO_3^- group in the TEP derivative is probably due to the two-dimensional nature of the refinement; moreover, since this unusual molecular structure could be related to the different photochemical behaviour of the two parent compounds, it is important to re-examine the TEP derivative.

Acknowledgements

This work was partially supported by Italian C.N.R. under grant N. 81.00581.03. We also wish to thank the quantum-chemical staff of Institute 'Le Bell', Strasbourg University, and in particular Dr. Marc Benard for making available the Hückel program.

Appendix

The Walsh diagrams of Fig. 2 were constructed from the results of an extended Hückel molecular orbital calculation performed with a version of Hoffmann's program. Burn's ζ exponents were used for 2s and 2p atomic orbitals on N and O atoms [12]. Coulomb integrals were obtained from a charge iterative calculation on D_{3h} NO_3^- ion with an assumed quadratic charge dependence of H_{ii} [13].

The H_{ij} exchange integrals were obtained using the weighted formula reported in [14]. The following parameters were used: N 2s: ζ = 1.875, H_{ii} = −28.3 eV; 2p: ζ = 1.650, H_{ii} = −15.4 eV; O 2s: ζ = 2.200, H_{ii} = −24.2 eV; 2p: ζ = 1.975, H_{ii} = −9.29 eV.

In order to make sure the observed trend is not depending on the Coulomb integrals used, another computation was performed using the more usual parameters: N 2s: H_{ii} = −26.0 eV; 2p: H_{ii} = −13.4 eV; O 2s: H_{ii} = −32.3 eV; 2p: H_{ii} = −14.8 eV.

With these parameters the $1a_2''$ is higher in energy than the $4a_1'$ orbital in accordance with the *ab initio* calculation [15] on D_{3h} NO_3^- ion, this gives also the 1e″ orbital higher than 4e′, which are indeed very near also in this Hückel computation. However we are more interested in the general trend of orbital energies than in their absolute values.

References

1 G. Giacometti, G. Agostini, G. Gennari and C. Corvaja, *Chem. Comm.*, 1019 (1981).

2 J. E. Fleming and H. Lynton, *Chemistry and Industry, London*, 1415 (1960).

3 J. H. Burns, *Inorg. Chem.*, *20*, 3868 (1981) and references therein.

4 G. M. Scheldrick, SHELX 76, Program for crystal structure determination, Univ. of Cambridge, England (1976).

5 D. T. Cromer and J. Mann, *Acta Cryst.*, *A24*, 321 (1968).

6 P. A. Doyle and P. S. Turner, *Acta Cryst.*, *A24*, 390 (1968).

7 J. C. Taylor and A. B. Waugh, *J. Chem. Soc. Dalton*, 1630 (1977).

8 a) N. K. Dalley, M. H. Mueller and S. H. Simonsen, *Inorg. Chem.*, *10*, 323 (1971) (Table VI page 327).
b) U. Casellato, M. Vidali and P. A. Vigato, *Coordination Chemistry Review*, *36*, 183 (1981) (Table 5 page 192).

9 J. K. Burdett, 'Molecular Shapes', Wiley, New York (1980) p. 45.

10 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry', Interscience, U.S.A. (1962) p. 263.

11 T. S. Cameron and C. K. Prout, *Acta Cryst.*, *B28*, 447 (1972).

12 G. Burns, *J. Chem. Phys.*, *41*, 1521 (1964).

13 H. Bash, A. Viste and H. B. Gray, *Theoret. Chim. Acta*, *3*, 458 (1965).

14 J. H. Ammeter, H. B. Burgi, J. Thibeault and R. Hoffmann, *J. Am. Chem. Soc.*, *99*, 3686 (1978).

15 R. A. Bowling, R. E. Sherrod, J. E. Bloor, J. D. Allen Jr. and G. K. Schweitzer, *Inorg. Chem.*, *17*, 3418 (1978) and references therein.