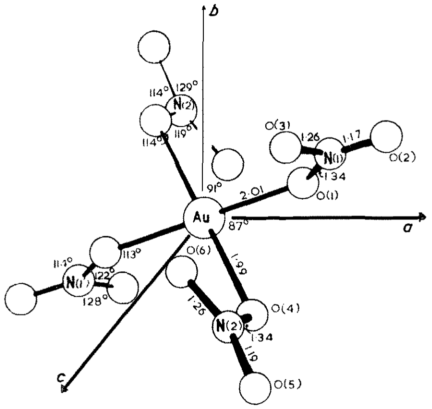
The Crystal Structure of Potassium Tetranitratoaurate(III)

By C. D. GARNER*† and S. C. WALLWORK
(*Department of Chemistry, University of Nottingham, Nottingham,* NG7 2RD)

THE crystal structure of potassium tetranitratoaurate(III) has been determined and found to contain discrete $[Au(NO_3)_4]^-$ ions in which the metal atom is co-ordinated in a square-planar manner by four unidentate nitrato-groups.

The compound has been prepared by a novel method[1] and the vibrational spectra of this and other tetranitrato-aurate(III) salts indicate the presence of co-ordinated nitrate groups. The expected square-planar geometry of Au^{III} suggested that the nitrate groups were co-ordinated in a unidentate manner whereas all previous tetranitrato-complexes have contained bidentate nitrato-groups. Little structural information is so far available concerning unidentate nitrato-groups and so a crystal structure of this compound was undertaken.



FIGURE

The crystals are monoclinic, space group $P2_1/c$, $Z = 2$, the unit cell volume 515·5 Å^3. The structure was solved by normal Patterson and Fourier methods and has been refined by a full-matrix least-squares programme to $R = 0{\cdot}072$ for 829 independent reflections. It consists of discrete K^+ and $[Au(NO_3)_4]^-$ ions and the arrangement of the nitrato-groups about Au^{III} in the latter is shown in the Figure (mean e.s.d's in the bond lengths are Au–O 0·02 Å and N–O 0·04 Å and in the bond angles 1·5°). Thus Au^{III} is co-ordinated in an essentially square-planar manner by four equivalent nitrato-groups with Au–O bonds of average length 2·00 Å.

However, one of the two terminal oxygen atoms in each nitrato-group makes a relatively close approach of 2·87 Å to the gold atom. In view of the lack of metal orbitals suitable for forming a bond in this direction, this close approach probably results mainly from the geometry of the nitrato-group and the M–O–N system, in which the two covalent bonds are expected to make an angle of *ca.* 110° at the oxygen atom. The observed angle of 114° supports the view that there is no strong interaction between Au and oxygen atoms of the type O(3) and O(6) as such bonding would be expected to cause a significant reduction in this angle, *e.g.* the value of about 94° observed for nitrato-groups bonded in a bidentate manner to similar sized metal atoms.[2]

Although the dimensions of the nitrato-groups have relatively large e.s.d.'s the very good agreement between the non-equivalent groups permits some discussion of the observed values. As expected the N–O bond involving the co-ordinated oxygen atom is significantly longer than the two terminal N–O bonds. Also, the inequality in the lengths of the latter is consistent with some weak interaction between Au and O(3) and O(6) at the distance of 2·87 Å. The geometrical considerations outlined above will probably result in some weak interaction of this type for all unidentate nitrato-groups and a corresponding effect on the terminal N–O bond lengths is therefore to be expected. The evidence available, for instance, in $Cu(NO_3)_2$-2MeCN,[3] $Ni(NO_3)_2,4H_2O$[4] and in the dimensions of pentra-erythritol tetranitrate[5] and nitric acid[6] supports this view.

(*Received, November* 21*st*, 1968; *Com.* 1781.)

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† Present address: Department of Chemistry, University of Manchester, Manchester 13.

[1] C. C. Addison, D. W. Amos, G. S. Brownlee, and N. Logan, to be published.
[2] C. D. Garner, D. Sutton, and S. C. Wallwork, *J. Chem. Soc.* (*A*), 1967, 1949.
[3] B. Duffin, *Acta Cryst.*, **1968**, **B24**, **396**.
[4] P. Gallezot, D. Weigel, and M. Prettre. *Acta Cryst.*, **1967**, **22**, **699**.
[5] J. Trotter, *Acta Cryst.*, **1963**, **16**, **698**.
[6] A. P. Cox and J. M. Riveros, *J. Chem. Phys.*, **1965**, **42**, **3106**.