X-Ray Crystal Structure of Ethylenebis(biguanide)silver(III) Perchlorate

By MARY L. SIMMS, J. L. ATWOOD,* and DAVID A. ZATKO*
(*Department of Chemistry, The University of Alabama, University, Alabama* 35486)

Summary The first crystal structure of a silver(III) complex, ethylenebis(biguanide)silver(III) perchlorate, has been determined by *X*-ray diffraction.

COMPOUNDS containing silver(III) ions fall into two groups: those with highly electronegative fluorine or oxygen donor atoms such as the periodate in $M_7Ag^{III}(IO_6)_2$, and those which contain biguanide frameworks.[1] In order to understand better the role of the biguanide group in the stabilization of high oxidation states of silver, we have determined the crystal structure of a silver(III) biguanide ion complex: $Ag(C_6N_{10}H_{16})(ClO_4)_3$.

Dark red polyhedral crystals of ethylenebis(biguanide)-silver(III) perchlorate were grown by slow evaporation from aqueous solution.[2] Contrary to a previous report,[3] the crystals exhibit no photolytic decomposition when coated with mineral oil. *Crystal data:* triclinic, space group $P\bar{1}$; $a = 11{\cdot}556(5)$, $b = 11{\cdot}452(5)$, $c = 8{\cdot}076(4)$ Å; $\alpha = 107{\cdot}96(4)°$, $\beta = 93{\cdot}65(3)°$, $\gamma = 103{\cdot}77(4)°$, $D_m = 2{\cdot}17$ g/cm^3, $D_c = 2{\cdot}16$ g/cm^3 for $Z = 2$. Cu-K_α data were collected up to $2\theta = 140°$ on an Enraf-Nonius CAD-4 automated diffractometer. A total of 2558 independent observed reflections were measured, corrected for absorption, and used in the structure determination.

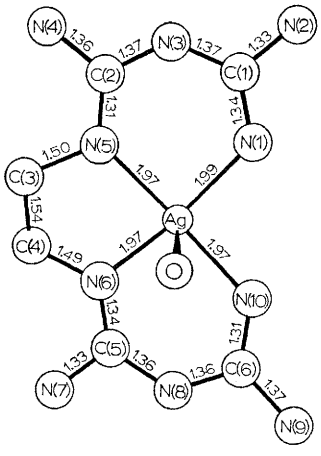

FIGURE. *Structure of the ethylenebis(biguanide)silver(III) ion. Standard deviations of all bond distances are less than* 0·01 Å.

The structure was solved by heavy-atom methods and refined by full-matrix least-squares techniques to a conventional *R* value of 8·1%. The silver ion lies in a plane of four strongly bonded nitrogen atoms (Figure); an oxygen atom from a perchlorate ion lies at 2·86(2) Å and the closest

atom from a neighbouring ethylenebis(biguanide)Ag^{III} fragment is N(8) at 3·54(2) Å. Each biguanide unit is essentially planar, but the ethylenebis(biguanide) framework is bowed away from the co-ordinated perchlorate ion.

The average Ag^{III}–N bond length is essentially the same as the Cu^{II}–N distance (1·96 Å) in the related compound, ethylenebis(biguanide)copper(II) chloride.[3] The C–N lengths found in the Ag^{III} complex show more uniform multiple bonding than that in the Cu^{II} and Ni^{II} [5] analogues indicating that the highly charged Ag^{III} ion is accommodated by extensive delocalization over the whole biguanide structure.

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[1] J. A. McMillan, *Chem. Rev.*, 1962, **62**, 65.
[2] P. Ray and N. C. Chakravarty, *J. Indian Chem. Soc.*, 1944, **21**, 47.
[3] B. Chatterjee and S. Syamal, *J. Indian Chem. Soc.*, 1970, **47**, 1021.
[4] N. R. Kunchur and M. Nathew, *Chem. Comm.*, 1966, 86.
[5] B. L. Holian and R. E. Marsh, *Acta Cryst.*, 1970, **B26**, 1049.