The Crystal Structure of α-Ag_3NSeO_3

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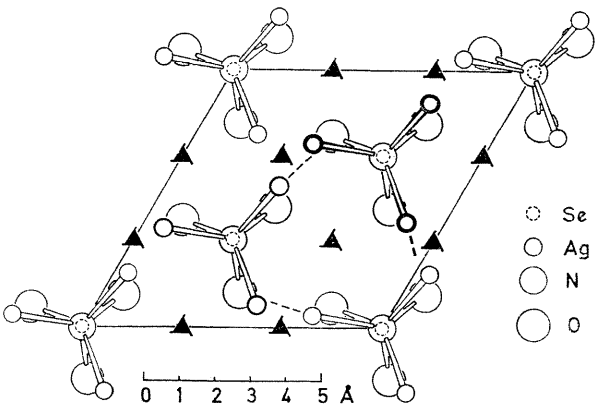
Summary The crystal structure of the α-form of Ag_3NSeO_3 shows it to be not a salt but to have discrete molecules with a 3-fold axis of symmetry.

THE structure of Ag_3NSeO_3 has been in doubt ever since it was prepared in two crystal modifications (α, β) by Dostál and Růžička.[1] I.r. studies[2] lent some support to the view that it might be formulated $Ag_3^{3+}NSeO_3^{3-}$.



FIGURE

We have carried out a full three-dimensional *X*-ray structure analysis on the α-form and find the molecule has Ag–N covalent bonds. Crystals belong to the rhombohedral system $a_r = 6{\cdot}184(3)$ Å, $\alpha = 86{\cdot}35(1)°$, space group $R3c$; D_m 6·63 g.cm.$^{-3}$, calculated for two formula units, 6·56 g.cm.$^{-3}$. Cu-K_α data were collected on an automated four-circle diffractometer, corrected for absorption, and interpreted *via* the Patterson vector map. The structure has been refined by full anisotropic least-squares analysis to a conventional R factor of 0·036. It is most easily described by reference to hexagonal axes $a_h = 8{\cdot}462(4)$, $c_h = 11{\cdot}372(6)$ Å, $Z_h = 6$. The Se and N atoms lie on special positions 0,0,x (*i.e.* on three-fold axes). The Se was arbitrarily placed at the origin, whence N is at (0,0,0·8533). The Ag and O atoms lie on the general positions generated from (0·2059, 0·2602, 0·7800) and (0·1280, 0·2085, 0·0568) respectively.

The Figure shows part of the structure. The molecules, which have three-fold axes of symmetry, have almost nearly regular tetrahedral configurations at each end: N–Se–O, 112·7(6)°, Se–N–Ag, 112·5(1·1)°. The Se–O and N–Ag bonds are almost exactly eclipsed, there being 11·1° between these bonds in z-projection. The bond lengths are Se–N, 1·667(50), Se–O, 1·670(15), and N–Ag, 2·178(18) Å. The molecules are arranged on double helices and only those belonging to one strand of the helix are shown in the Figure to avoid confusion. The helical packing comes about from the close intermolecular approach, 2·217(15) Å, between adjacent Ag and O atoms with N–Ag–O, 173·8(1·5)°, as indicated by broken lines. The other strand of the helix, coaxial with 3_1, has molecules located on the same three-fold axes but at $z = \frac{1}{2}$ from those shown in the Figure and c-glide related to them. This helical structure presumably arises from electrostatic forces between the polar molecules. Full details and discussion will be published elsewhere.

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[1] K. Dostál and A. Růžička, *Z. anorg. Chem.*, 1965, **337**, 325.
[2] R. Paetzold, K. Dostál, and A. Růžička, *Z. anorg. Chem.*, 1966, **348**, 1.