

## Preparation, Properties and Structure of Crystalline Silver Ketenide ( $\mu$ -Oxoethenylidene Disilver) and its Pyridine Complex

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Silver ketenide of empirical formula  $\text{Ag}_2\text{C}=\text{C}=\text{O}$  is obtained by direct reaction of ketene or an *in situ* source of ketene such as acetic anhydride, isopropenyl acetate, vinyl acetate or phenyl acetate with certain silver salts, normally in the presence of a base.

X-ray powder diffraction studies have shown that silver ketenide, prepared from silver acetate and ketene or acetic anhydride in pyridine, followed by removal of complexed pyridine, has a tetragonal unit cell,  $a = b = 4.03 \text{ \AA}$ ,  $c = 5.84 \text{ \AA}$ . The simplicity and symmetry of the cell allows deduction of much of the crystal structure: the ketenide groups are aligned along the four-fold axis of the cell with the silver atoms in the positions  $[\frac{1}{2}00]$  and  $[0\frac{1}{2}0]$ . The structure thus consists of flat sheets of square packed silver atoms with an Ag–Ag distance of  $2.84 \text{ \AA}$ , slightly less than the Ag–Ag distance of  $2.89 \text{ \AA}$  in silver metal, separated by perpendicular rod-like  $\text{C}=\text{C}=\text{O}$  groups. The terminal carbon atom of the ketenide group is apparently bonded to four equidistant silver atoms in a square array: this provides a rare example of six-coordinate carbon. Complexes of silver ketenide with pyridine and 3- and 4-methylpyridine of stoichiometry  $\text{Ag}_2\text{C}_2\text{O}\cdot\text{L}$  have similar layered structures but with greater separation between the monolayers of silver atoms. Electron diffraction and micrography studies support the proposed structures as does an IR study of oriented crystallites using plane-polarised light. Reaction of ketene with silver salts at  $20^\circ\text{C}$  in the absence of pyridine or in the presence of 2-methylpyridine gives amorphous silver ketenide, although crystalline material can be obtained at lower temperatures. Both tetragonal and amorphous silver ketenides are yellow solids, insoluble in all common solvents including  $0.880$  ammonia. They explode when strongly heated or struck, giving carbon suboxide as the major gaseous product. Silver ketenide reacts very slowly with methyl iodide to give dimethylketene dimer. With gaseous hydrogen chloride it gives ketene and thence acetyl chloride. With aqueous hydrochloric acid it gives acetic acid. Acetylene gives ketene and silver acetylide, and bromine gives tribromoacetyl bromide. Treatment with dinitrogen tetroxide gives silver nitrate and silver cyanide. In concentrated aqueous silver nitrate solution silver ketenide forms a red, crystalline, explosive double salt of composition  $(\text{Ag}_2\text{C}_2\text{O})_2\text{AgNO}_3$  which is more shock sensitive than silver ketenide itself. Decomposition of this double salt by treatment with aqueous ammonia gives a yellow crystalline dimorph of silver ketenide. Reaction of silver nitrate with acetic anhydride in acetonitrile gives a stable, non-explosive, yellow double salt of composition  $\text{Ag}_2\text{C}_2\text{O}\cdot\text{AgCN}$ .

It is remarkable that, despite the ease of preparation, there were no references to silver ketenide or related species in the literature prior to the preliminary report of this work.<sup>1</sup> Although substituted ketenes having Si–C or Ge–C bonds are known,<sup>2</sup> these are not simple metal ketenides of the type  $\text{M}_2\text{C}_2\text{O}$ , and cannot be prepared by direct metallation of ketene. Silver ketenide is readily prepared by reaction of ketene or acetic anhydride with silver salts. Späth referred in 1912 to a

'yellow cheesy precipitate' formed from silver nitrate and acetic anhydride, but this observation was apparently not followed up.<sup>3</sup> Certain simple inorganic silver compounds provide the closest known analogues to silver ketenide. Silver cyanamide,  $\text{Ag}_2\text{NCN}$ , is isoelectronic with silver ketenide, but appears to be a distinctly ionic compound involving the symmetrical  $\text{N}=\text{C}=\text{N}^{2-}$  ion.<sup>4</sup> Silver ketenide however, as we show later, has an extensive and unusual form of covalent bonding. Other simple compounds having linear triatomic groups anionically isoelectronic with the ketenide group include silver fulminate,  $\text{AgCNO}$ , silver cyanate,  $\text{AgNCO}$ , silver azide,  $\text{AgN}_3$ , and disilver diazomethane,  $\text{Ag}_2\text{CN}_2$ .<sup>5</sup> We have also described copper<sup>6</sup> and gold ketenides.<sup>7,8</sup>

We now report that silver ketenide of empirical formula  $\text{Ag}_2\text{C}_2\text{O}$  is readily prepared in high yields by reaction of certain silver salts with ketene or preferably *in situ* sources of ketene, normally in the presence of a base. It is a yellow solid, insoluble in all common solvents, and shows in its IR spectrum characteristic intense absorption at *ca.*  $2000 \text{ cm}^{-1}$ . Although it is *explosive* when struck and on sudden heating, samples have been kept in the dark at room temperature for several years without substantial decomposition apart from an apparently superficial darkening. The double salt with silver nitrate is shock sensitive and *must be handled with great care*, but silver ketenide itself is much less sensitive, and can be handled safely in small quantities with the normal precautions applicable to any explosive substance. The complexes with pyridine and other heterocyclic bases appear to be insensitive to shock.

Few  $\sigma$ -bonded organosilver compounds are stable at room temperature, and none is known containing the group Ag–C–Ag. However the relative stability of silver ketenide is consistent with known organo-silver chemistry. The thermal stability of silver-carbon  $\sigma$ -bonds is enhanced by three factors. Firstly, by a lack of stability in the organic free radical formed by homolytic fission of the silver-carbon bond;<sup>9</sup> secondly, by an adjacent  $\pi$ -bond, as in silver acetylides; and thirdly by inductive withdrawal of electron density from the silver-carbon bonds as in perfluoro-organosilver compounds.<sup>10</sup> The latter two effects are certainly operative in  $\text{Ag}_2\text{C}=\text{C}=\text{O}$ . The crystal structure (see later) suggests that lattice energy and a degree of Ag–Ag bonding also make significant contributions to the thermal stability.

Silver ketenide has been obtained in an amorphous form and in at least two distinct crystal modifications; but the structure of only one of these, the tetragonal form described in this paper, has so far been established. Apart from its unique structure, silver ketenide is of interest in that its formation directly from ketene appears to demonstrate experimentally for the first time the potential carbon acidity of the hydrogen atoms of ketene: this is normally obscured by the tendency of nucleophiles to



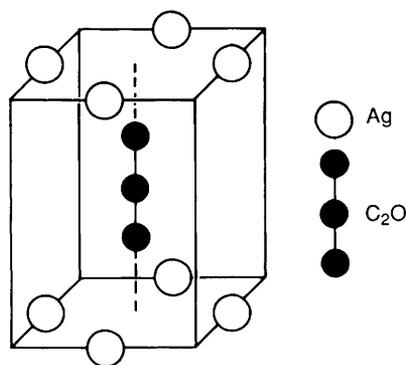


Fig. 1 Unit cell of silver ketenide

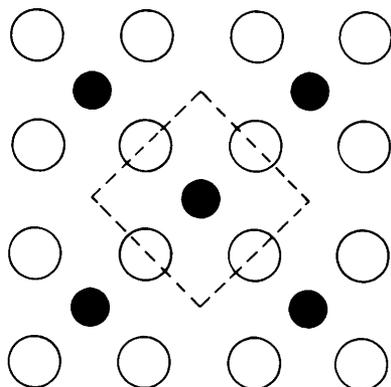
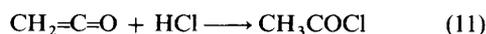
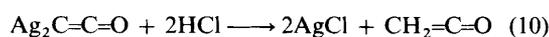


Fig. 2 Proposed structure of silver ketenide projected onto  $ab$  plane; (○), silver atoms in plane of page, Ag–Ag = 2.84 Å, interplanar distance = 5.84 Å; (●), rod-like ketenide groups viewed end-on and placed between and perpendicular to the planes of silver atoms; (---), projection of the tetragonal unit cell

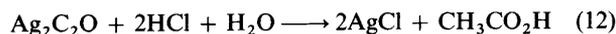
were 65, 64, 43 and 31% respectively. With phenyl acetate the yield was 51%. These admittedly crude results support a mechanism in which ketene is formed by dissociation of the enolate anion derived from the ester into phenoxide ion and ketene, analogous to that proposed in eqns. (7) and (8).

A preferred method for obtaining pure, highly crystalline silver ketenide in *ca.* 90% yield, is to add a large excess of acetic anhydride to a filtered solution of silver acetate in pyridine at room temperature. This results in an almost immediate precipitation of silver ketenide pyridinate,  $\text{Ag}_2\text{C}_2\text{O}\cdot\text{Py}$  (described in detail later) from which pyridine may be completely removed by fractional distillation of the contents of the reaction flask. The silver ketenide prepared in this way is a bright yellow explosive solid analysing as  $\text{Ag}_2\text{C}_2\text{O}$  and showing strong characteristic absorption at *ca.*  $2000\text{ cm}^{-1}$ . The chemical reactions of this material are consistent with its formulation as a disilver(I) ketenide,  $\text{Ag}_2\text{C}=\text{C}=\text{O}$ , (referred to in *Chem. Abstr.* as  $\mu$ -oxoethenylidene disilver) in which both silver atoms are linked to the terminal carbon atom of the ketenide group. Thus, reaction of an excess of the ketenide, suspended on glass wool, with HCl gas (diluted with  $\text{N}_2$  to moderate the exothermic reaction and so prevent detonation of the ketenide) gives silver chloride, ketene, and acetyl chloride: with an excess of HCl, acetyl chloride is the only volatile product. The products obtained are those expected from the reaction sequence [eqns. (10) and (11)]. Reaction of silver ketenide with acetylene in

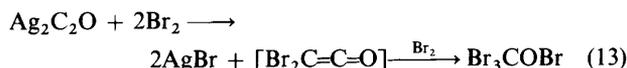


acetone gives ketene and silver acetylide. Reaction of the ketenide with  $1.0\text{ mol dm}^{-3}$  aqueous hydrochloric acid at  $25^\circ\text{C}$

gives silver chloride and acetic acid (95.5% yield, based on ketenide) together with traces of an unidentified, involatile, organic oil [eqn. (12)]. Reaction of the ketenide with  $\text{Br}_2$  in



$\text{CCl}_4$  gives silver bromide and tribromoacetyl bromide (98%), presumably *via* dibromoketene [eqn. (13)]. Reactions (10)–(13)



all occur readily at room temperature and support the proposed formulation of the ketenide as  $\text{Ag}_2\text{C}=\text{C}=\text{O}$ .

Silver ketenide is surprisingly inert towards organic halides and its seeming potential as a quick route to disubstituted ketenes has not so far been realised. Heating the ketenide with an excess of methyl iodide at reflux ( $43^\circ\text{C}$ ) for 12 days gave a low conversion ( $\sim 1\%$ ) to dimethylketene dimer (1,1,3,3-tetramethylbutan-2,4-dione): most of the ketenide was recovered unchanged. Acid halides such as benzoyl chloride react only very slowly even at  $120^\circ\text{C}$ , to give silver chloride and organic tars.

Although it has not proved possible to prepare single crystals suitable for X-ray diffraction analysis, the X-ray powder diffraction data show a tetragonal unit cell,  $a = b = 4.028 \pm 0.001$ ,  $c = 5.846 \pm 0.004$  Å. The density of silver ketenide, measured by carbon tetrachloride displacement, is  $4.45 \pm 0.03\text{ g cm}^{-3}$ . On the basis of one molecule per unit cell this gives a molecular weight of  $254.2 \pm 1.7$ , *cf.*  $\text{Ag}_2\text{C}_2\text{O}$ ,  $M = 255.8$ .

Although no space group can be unequivocally assigned, the data are consistent with the  $P4mm$  space group, with silver atoms in special positions  $2(c)$  and the  $\text{C}=\text{C}=\text{O}$  group in special position  $1(b)$ . Packing considerations lead to the same structure. The only way of arranging two silver atoms per tetragonal unit cell which is consistent with the X-ray data is to place them in a square-packed array, with the atoms at  $[\frac{1}{2}00]$  and  $[0\frac{1}{2}0]$  in the unit cell (Fig. 1). The rod-like ketenide groups must now be accommodated in this structure. Whether covalently or ionically, the groups must interact strongly with the silver atoms. It therefore seems highly probable that the ketenide group is aligned along the four-fold axis of the unit cell, since any arrangement of lower symmetry would result in an interaction between the ketenide groups and silver atoms which would tend to distort the tetragonal arrangement of silver atoms. Therefore a lamellar structure based on the unit cell shown in Fig. 1 is proposed.

The data do not provide information about the regularity or otherwise with which ketenide groups are bonded to a particular layer network of silver atoms, *i.e.* whether C(1) of the groups is always located on one face of a silver layer, or whether some other arrangement obtains. These questions are considered later in connection with the structure of the pyridinate.

In the structure shown in Fig. 1, the silver atoms form a network of square-packed planes with a silver–silver distance of 2.84 Å; the planes being separated by the  $c$  dimension of 5.84 Å. The silver–silver distance in silver metal is 2.89 Å: this suggests a degree of metal–metal bonding in silver ketenide. Between and perpendicular to the planes, and lying along the four-fold axis of the unit cell, are the rod-like ketenide groups. A plan view of the structure is shown in Fig. 2. The layer nature of the structure is consistent with the observed diffuseness of reflection from planes having an  $l$  component, indicative of thinness or irregular stacking of planes in the  $c$  direction, and with the observed

Table 1

	CH <sub>2</sub> CO	CD <sub>2</sub> CO	Me <sub>2</sub> CCO
C=O stretch	2151	2119	2134
C=C stretch	1120	870	1392
C=C=O bend, in-plane	588	530	676
C=C=O bend, out-of-plane	529	450	500

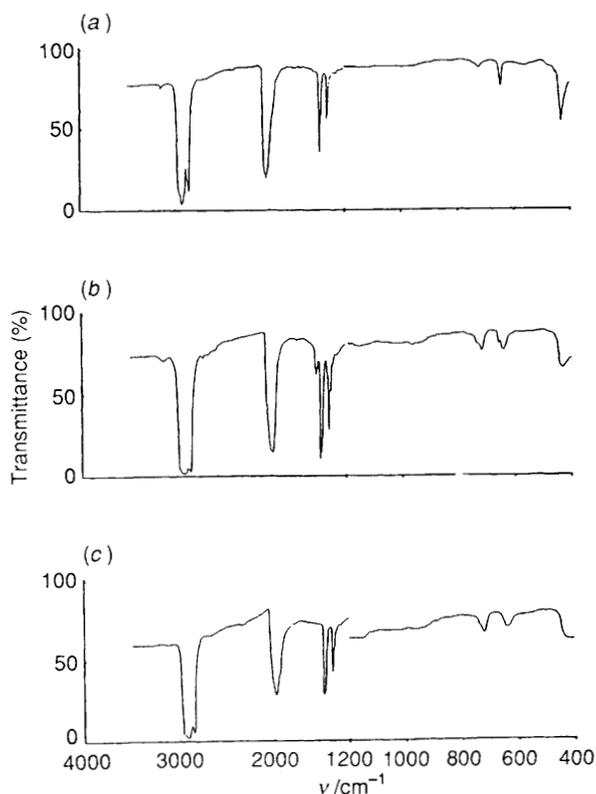


Fig. 3 IR spectra of silver ketenide species as mulls in Nujol: (a) tetragonal silver ketenide; (b) silver ketenide-silver acetate complex; (c) amorphous silver ketenide

lamellar nature of the crystals. Electron micrographs of silver ketenide also show the crystals to be flat plates, with 90° angles prominent. Single-crystal electron diffraction patterns with the plane of the crystal perpendicular to the beam show only *hko* spots, showing that the long axis of the tetragonal unit cell is normal to the crystal plane.

The position of the ketenide groups is fixed according to the projection onto the *ab* plane shown in Fig. 2. This is confirmed by IR studies discussed later. Their positioning along the *c* axis is not determined, however. The ketenide group is presumed to bond to the silver atoms through its terminal carbon atom since the oxygen orbitals will tend to be filled at the expense of the carbon atoms, by virtue of oxygen's greater electronegativity. Consideration of the known bond lengths of ketene<sup>12</sup> and the known Ag-C and Ag-O distances in silver fulminate<sup>13</sup> suggests that a reasonable estimate for the Ag-C bond length would be about 2.3 Å, which would make the Ag-O distance about 3.0 Å. These are however only estimates and may vary by a few tenths of an Ångstrom either way.

The closest structural analogue to silver ketenide is orthorhombic silver fulminate, the crystal structure of which has been established by Britton and Dunitz.<sup>13</sup> Despite the difference in stoichiometry (Ag<sub>2</sub>C<sub>2</sub>O against AgCNO) there are marked similarities between the two structures: planes of silver atoms are separated by perpendicular rod-like groups and the silver atoms are close enough together to suggest some degree of

silver-silver bonding, linear in the fulminate and two-dimensional in the ketenide.

A further interesting and unusual feature of the proposed structure of silver ketenide is the bonding of the ketenide group to the silver atoms. The bonding clearly cannot be predominantly ionic, since electrostatic forces would then force the silver atoms apart. Covalent bonding implies that the terminal carbon atom of the ketenide group is bonded equally to its four neighbouring silver atoms, since any other arrangement would distort the tetragonal arrangement of the silver atoms. This requires the bonding to be described in delocalised or multi-centre terms, since the carbon atom can only accommodate four bonding electron pairs. It is interesting that orthorhombic silver fulminate appears to involve three-centre Ag-C-Ag bonds.<sup>13</sup>

*Spectroscopic Properties.*—A study of the IR spectrum of oriented crystallites of silver ketenide provides strong confirmatory evidence that linear ketenide groups are aligned along the *c* axis of the unit cell, perpendicular to the planes of silver atoms: these coincide with the major flat planes of the crystal as a whole, as shown by electron microscopy and electron diffraction studies.

Consideration of the structure (Fig. 2) deduced from the X-ray data suggested that if the crystals could be mounted in known orientations in a beam of polarised infrared radiation it should be possible to observe marked variations in the relative intensities of the IR absorption bands of the ketenide groups as the orientation of the crystals with respect to the beam was changed. In particular, absorption bands due to stretching modes of the C=C=O group should be least intense when the ketenide groups lie parallel to the beam, when the transition moment of the vibration is perpendicular to the electric vector of the radiation. As the crystal is rotated to bring the ketenide groups towards a position perpendicular to the beam, so the transition moment becomes more and more aligned with the electric vector and the intensity of absorption should increase.

Several workers have studied the IR spectra of ketene and substituted ketenes, and have assigned their absorption bands (Table 1).<sup>14,15</sup>

Silver ketenide shows only three absorption bands in the region 400–4000 cm<sup>-1</sup>, the positions of which vary slightly in different polymorphs. In tetragonal silver ketenide the bands occur at 430 m, 640 w and 2060 vs cm<sup>-1</sup> [Fig. 3(a)]. The position and intensity of the 2060 cm<sup>-1</sup> band makes obvious its assignment to the C=O stretch: the small reduction in frequency from the corresponding band in ketene is presumably due to a withdrawal of electron density from the C=C=O group by its bonding to silver, as in many metal carbonyls. No band corresponding to the C=C stretching band observed in the IR spectrum of ketene is found in the IR spectrum of silver ketenide; 640 cm<sup>-1</sup> is too low a frequency. The C=C stretching absorption band would be expected to show the same orientation dependence as that of the C=O stretching band at 2060 cm<sup>-1</sup>, whereas the 640 cm<sup>-1</sup> band shows no such dependence (Fig. 6).

Unambiguous assignment of the absorption bands at 430 and 640 cm<sup>-1</sup> is not possible at this stage. Both bands could be ascribed to bending modes of the CCO group, as these frequencies are of the right order (Table 1) and neither band exhibits orientation dependence (Fig. 4). Alternatively, the 640 cm<sup>-1</sup> band could arise from an in-plane bending mode of the ketenide group, and the 430 cm<sup>-1</sup> band from an asymmetric Ag-C vibration of the Ag<sub>4</sub>-C ensemble.

For comparison, the IR absorption bands and assignments for silver cyanamide, Ag<sub>2</sub>NCN, which is isoelectronic with silver ketenide, are 1977 (asymmetric str.), 1281 (symmetric str.), and 631 cm<sup>-1</sup> (bend).<sup>16</sup>

For the IR study, silver ketenide of larger than usual crystal

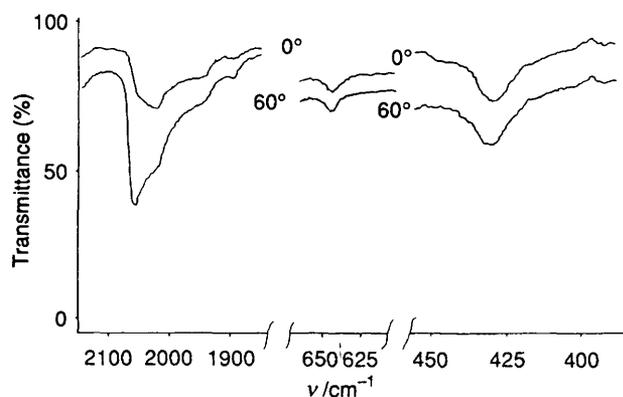


Fig. 4 The three principal IR absorption bands of tetragonal silver ketenide, oriented on a polyethylene support with the normal to the plane at angles of 0° and 60° to the IR beam

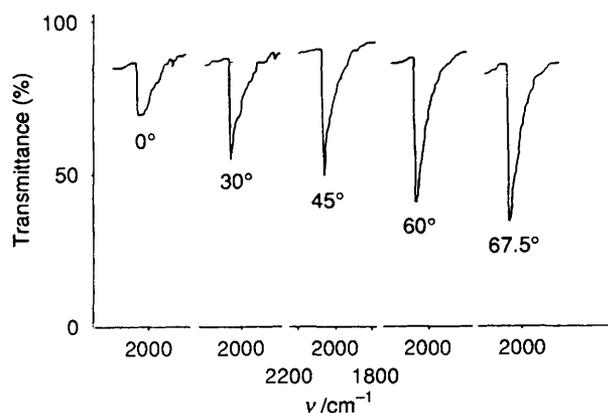


Fig. 5 Increase in intensity of the 2060  $\text{cm}^{-1}$  absorption band of silver ketenide oriented on a polyethylene support as the angle of the normal to the plane to the IR beam is increased from 0° to 67.5°

Table 2

Absorption band/ $\text{cm}^{-1}$	Orientation of substrate	Optical density of band	Ratio $\text{OD}_{60^\circ}/\text{OD}_{0^\circ}$
Oriented crystallites			
430	0°	0.096	1.16
	60°	0.112	
640	0°	0.027	1.46
	60°	0.039	
2060	0°	0.075	4.95
	60°	0.374	
Randomly-oriented crystallites			
430	0°	0.184	1.23
	60°	0.227	
640	0°	0.065	1.21
	60°	0.078	
2060	0°	0.392	1.34
	60°	0.526	

size was prepared by slow addition of acetic anhydride to a solution of silver acetate in refluxing pyridine, followed by removal of the pyridine by fractional distillation. This material, which had a graphite-like sheen and texture was rubbed onto a thin film of polyethylene and surplus material shaken off. Scanning electron micrographs of such films clearly showed a closely-packed layer of platelets lying parallel to the surface of the film, as required, with only a minor degree of mis-orientation. Polyethylene was chosen as the substrate because of its transparency in the appropriate regions of the IR spectrum

and because the silver ketenide samples stuck well to it. The thin, regular nature of the film, however, resulted in optical interference effects, particularly at longer wavelengths, which obscured the spectrum being observed. Film sufficiently thick to eliminate interference effects was too opaque. This problem was overcome by supporting the silver ketenide on an outside face of a 'sandwich' of petroleum jelly ('Vaseline') between two thin polyethylene films. Petroleum jelly is optically similar to polyethylene so the 'sandwich' behaved optically as a thin polyethylene film of slightly uneven thickness. The prepared sample was mounted under slight tension in a rotatable frame in the sample area of the spectrophotometer and was oriented to give the desired angle ( $\theta$ ) between the normal to the plane of the ketenide-coated film and the IR beam.

The three principal IR absorption bands of silver ketenide, oriented on a polyethylene support with the normal to the plane at angles of 0° and 60° to the IR beam are shown in Fig. 4. As expected, there is a large increase in the  $\nu\text{C}=\text{O}$  absorption at 2060  $\text{cm}^{-1}$  as the group is swung into interaction with the beam, but little change in the 640 and 430  $\text{cm}^{-1}$  absorption bands. Fig. 5 shows the progressive increase in absorption of the 2060  $\text{cm}^{-1}$  band as the angle between the ketenide crystallites and the beam is progressively increased. Quantitative treatment of these results would be exceedingly complex for several reasons. Firstly, precise calculation of the effects of the degree of mis-orientation of the crystallites particularly on the 0° value would be difficult. Secondly, uncertainty as to path-length through the solid: this depends on the orientation of the crystallites to the beam, their geometry, and their refractive index in the region of the absorption band, which can vary considerably in the region of the band (Christiansen effect). Also, the amount of 'scatter' in the layer may vary with orientation. Nevertheless, a reasonable estimate of the magnitude of variation of intensity of absorption bands with orientation can be obtained. The absorption peak heights (peak minus base-line) for 0° and 60° orientation, and their ratios, for all three bands shown by a well-orientated sample, and by a sample of silver ketenide of particularly small crystal size, applied so as to give minimum orientation of crystallites on the substrate, are shown in Table 2.

The values obtained for randomly-oriented silver ketenide (Table 2) show that increasing the angle between the beam and substrate from 0° to 60° gave an increase in intensity of absorption by about a factor of  $\sim 1.25$ , which may be taken as due to the increase in path-length of the beam through the sample. For oriented crystallites, the absorption band at 2060  $\text{cm}^{-1}$  increased in intensity by a factor of 4.95, four times the 0° value corrected for extra path-length.

If the proposed structure of tetragonal silver ketenide is correct, then when the ketenide groups are aligned as described at an angle (such as 60°) to the beam, the  $\text{C}=\text{C}=\text{O}$  stretch will only interact with radiation whose electric vector has a horizontal component.

Thus, an oriented sample should show strong absorption of light plane-polarised in the one direction, and negligible absorption of light plane-polarised in the perpendicular direction. Just such behaviour is observed (Fig. 6). The polariser was adjusted to give maximum absorption at 2060  $\text{cm}^{-1}$ , then rotated through 90°. The ratio of peak heights (in terms of optical density) for the 2060  $\text{cm}^{-1}$  absorption band was 14:1. The 430 and 640  $\text{cm}^{-1}$  absorption bands showed no detectable change in intensity through a 360° rotation of the polariser.

The value of 14 for the dichroic ratio is consistent with the proposed structure. Again, rigorous quantitative treatment is not possible owing to factors such as the birefringence of the small crystals and the general differences in optical properties of the array of thin flat crystals to light, polarised in the two directions, which is incidental at an oblique angle. The dichroic

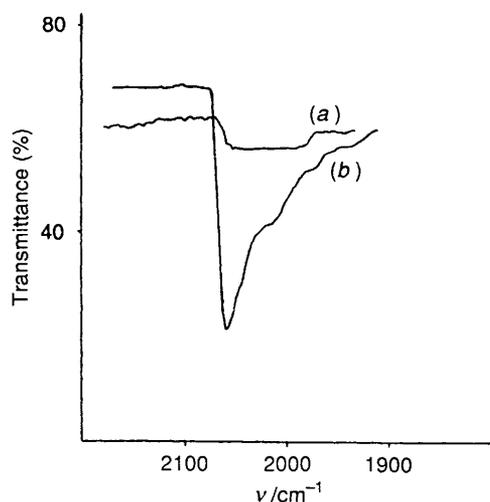


Fig. 6 C=O stretch band of silver ketenide, ketenide groups at  $60^\circ$  to the beam. Beam plane polarised, polariser setting for curve *a* was  $80^\circ$ , for *b*,  $170^\circ$

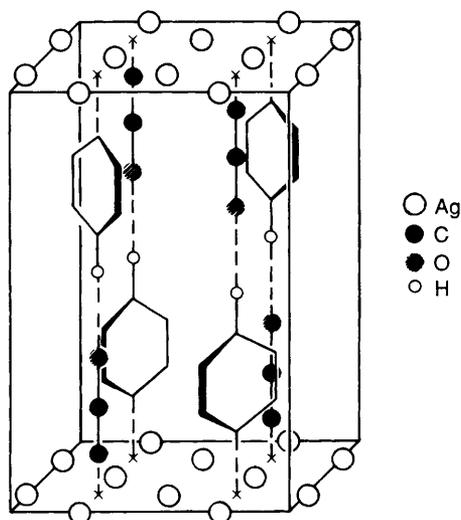


Fig. 7 Proposed structure of the unit cell of  $\text{Ag}_2\text{C}_2\text{O}\cdot\text{Py}$  with adjacent pyridine molecules parallel to each other

ratio,  $R_D$ , for light polarised parallel and perpendicular to the mean of a set of transition moments which diverge from that mean direction by an average angle  $\alpha$  is given by the equation  $R_D = 2 \cot^2 \alpha$ , and for the present oriented case,  $R_D = 2 \cos^2 30^\circ \cot^2 \alpha$ .<sup>17</sup> From the latter equation, when  $R_D = 14$ ,  $\alpha = 18^\circ$ . If the crystallites were perfectly aligned parallel to the polyethylene substrate this result would mean that the orientation of the ketenide groups in the crystals is within  $10^\circ$  of the normal to the silver atom plane. However, the crystals are not perfectly aligned, as is apparent from scanning electron micrographs. Study of these suggests that the average deviation of the crystals from the plane of the polyethylene substrate is of the order of  $12\text{--}16^\circ$ . Thus the mean deviation can be largely accounted for by the imperfect orientation of the crystals so that the orientation of the ketenide groups is within  $2^\circ$  of the normal to the silver atom plane, and the ketenide groups lie essentially parallel (or anti-parallel) to each other, as required by the proposed structure.

Silver ketenide in the above pure tetragonal form is obtained from reactions conducted in pyridine or certain substituted pyridines *via* the intermediacy of weak complexes of stoichiometry  $\text{Ag}_2\text{C}_2\text{O}\cdot\text{Py}$ . The pyridine complex may readily be isolated from reactions of silver acetate with acetic anhydride in an excess of pyridine at temperatures between  $20$  and  $100^\circ\text{C}$ .

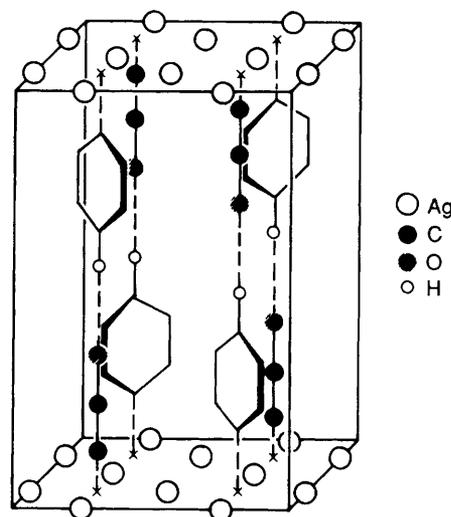


Fig. 8 Proposed structure of the unit cell of  $\text{Ag}_2\text{C}_2\text{O}\cdot\text{Py}$  with adjacent pyridine molecules normal to each other

The unusual stoichiometry of the pyridine complex  $\text{Ag}_2\text{C}_2\text{O}\cdot\text{Py}$  initially suggested that not all the silver atoms in the complex are equivalent, as no other instance of a complex of a silver compound in which all the silver atoms are equivalent, containing less than one molecule of pyridine or other monodentate ligand per silver atom, has yet been reported. However, an X-ray powder diffraction study of the highly crystalline pyridine complex indicates that all the silver atoms are equivalent and form extensive sheet-like arrays, as in the derived tetragonal silver ketenide. The pyridine complex appears to be a semi-clathrate or interstitial compound in which the nitrogen of each pyridine is very weakly associated with four silver atoms in the sheet-like array.

The  $\text{Ag}_2\text{C}_2\text{O}\cdot\text{Py}$  complex has an orthorhombic unit cell. The  $a$  and  $b$  values of  $8.086$  and  $8.058 \text{ \AA}$  are very close to twice the  $a$  and  $b$  values of  $4.028 \text{ \AA}$  for tetragonal silver ketenide, which is readily obtained from the pyridine complex by loss of pyridine. Thus, it seems probable that the unit cell of the pyridine complex, which contains four molecules, consists essentially of four silver ketenide unit cells in which the Ag–Ag spacings within layers are essentially maintained, with pyridine molecules inserted so as to lengthen interlayer separation along the  $c$  axis. This interpretation is strongly supported by the observed reflection intensities: the strongly-scattering silver atom nets are maintained, resulting in strong reflections only for both  $h$  and  $k$  even, and the degeneracy of the cell is removed by the comparatively weakly scattering light atoms, which account for the other reflections.

Fitting four pyridine molecules into a unit cell, of the dimensions described, derived from four silver ketenide unit cells, poses a problem. The maintenance of reasonable distances between non-bonded atoms imposes stringent constraints on the positioning of the molecules. The van der Waals dimensions of the pyridine molecules are such that it is impossible to pack more than one molecule with its 'flat' plane parallel to the  $ab$  plane in the projection of the unit cell onto the  $ab$  plane. Packing of all four pyridine molecules with their 'flat' planes parallel to the main silver atom planes would give a stack some  $10 \text{ \AA}$  thick, allowing for the maximum permissible staggering. This is too near the  $c$  dimension of  $12.09 \text{ \AA}$  to leave room for the silver atoms, still less the ketenide groups. Similar arguments forbid any canted arrangement of the pyridine molecules. The only possible arrangement involves the pyridine molecules interleaved between, and thus substantially parallel to, the ketenide groups. This arrangement is only feasible if the ketenide groups are staggered, two up and two down, in the four-molecule unit

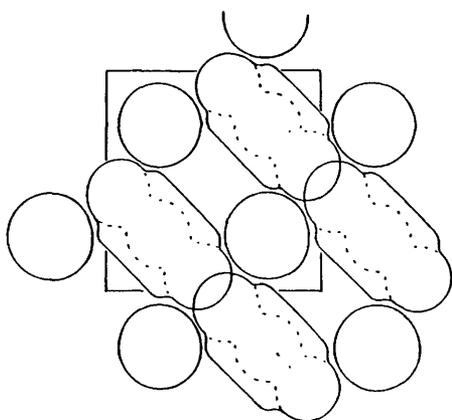


Fig. 9 Projection of the structure shown in Fig. 7 onto the *ab* plane

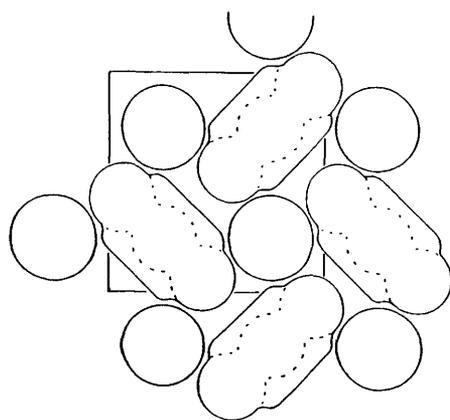


Fig. 10 Projection of the structure shown in Fig. 8 onto the *ab* plane

cell. The nitrogen atom of each pyridine molecule is then symmetrically placed adjacent to four silver atoms which are bonded to an underlying ketenide group. Two possible structures are illustrated in Figs. 7 and 8: these differ in that adjacent pyridine molecules in the same 'layer' are either parallel (Fig. 7) or perpendicular (Fig. 8).

The projections of these structures onto the *ab* plane are shown in Figs. 9 and 10 respectively, only the lower half of the unit cell being shown. Contact between adjacent pyridine molecules is rather too close in the 'pyridine parallel' case, the distance between adjacent  $\alpha$  (and  $\beta$ ) carbon atoms being only 3.1 Å. Therefore the arrangement of pyridine molecules indicated in Figs. 8 and 10 is preferred. Interatomic distances along the *c*-axis are also acceptable.

We take the Ag–C bond as 2.3 Å, as estimated earlier, the C–C–O distance as about 2.45 Å as in ketene,<sup>12</sup> the van der Waals radii of H and O as 1.2 and 1.4 Å respectively as given by Pauling,<sup>18</sup> and the effective van der Waals radius of the silver atoms as about 1.6 Å. These data indicate that van der Waals contact between the terminal O of the ketenide group and the  $\gamma$ H of the underlying pyridine would lead to a distance of about 2.7 Å between the  $\alpha$ -H atoms and the nearest silver atoms in the plane to which the pyridine molecule is coordinated. This is close to the estimated van der Waals separation of 2.8 Å. Thus the *c*-dimension of the unit cell (the interlayer spacing) is satisfactorily accounted for by an Ag–C bond of 2.3 Å and van der Waals contacts between the ketenide group, the underlying pyridine molecule, and the lower plane of silver atoms. The  $\beta$ -H atoms of pyridine molecules in the upper and lower halves of the cell nearly eclipse each other when viewed along the *c*-axis. On the basis described, their separation is about 2.8 Å, rather above the sum of van der Waals radii.

The Ag–Ag distance in this proposed structure is 2.85 Å, slightly greater than in tetragonal silver ketenide.

Close approach of the N to the Ag atoms is prevented by the van der Waals contact of the  $\alpha$ -H atoms with the Ag planes: the N–Ag distance is about 2.9 Å. This is a large N–Ag separation, compared with Ag–N distances of 2.15 Å in a silver-8-hydroxyquinoline compound,<sup>19</sup> and 2.21 Å in a silver nitrate-pyridine complex.<sup>20</sup> The separation is close to the sum of van der Waals radii, which is 3.0 Å. However, although the large N–Ag distance suggests that the stoichiometry of the complex is more due to steric factors than to chemical bonding, there is spectroscopic evidence for weak bonding interaction between the silver atoms and the nitrogen atoms of the pyridine molecules. A characteristic of the IR spectrum of coordinated pyridine is that the in-plane and out-of-plane ring deformation absorption bands of the free base at 604 and 405  $\text{cm}^{-1}$  respectively are shifted to higher frequencies:<sup>22</sup> usually the shifts are of the order of 30–50  $\text{cm}^{-1}$ .<sup>21</sup> In the spectrum of the silver ketenide-pyridine complex, corresponding bands occur at 609, 413 and 417  $\text{cm}^{-1}$  (the latter two being a split band), consistent with a weak bonding interaction. Also, the intense C=O stretching absorption band of the ketenide group which has  $\nu_{\text{max}}$  at 2060  $\text{cm}^{-1}$  in silver ketenide is shifted in the pyridine complex to 2020  $\text{cm}^{-1}$ .

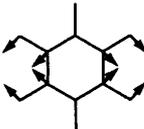
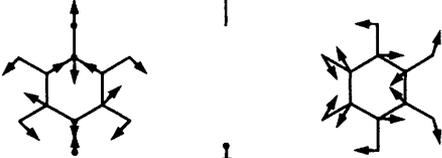
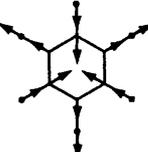
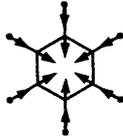
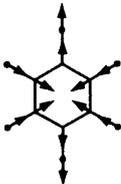
As in the case of tetragonal silver ketenide, the planes of silver atom sheets in the silver ketenide-pyridine complex coincide with the major flat planes of the crystal as a whole, as is shown by electron microscopy and electron diffraction studies. Thus, electron micrographs of the flake-like crystals show them to be flat plates with 90° angles prominent. Single-crystal electron diffraction patterns with the plane of the crystal perpendicular to the beam show only *hko* spots, indicating that the long axis of the orthorhombic unit cell is normal to the crystal plane.

In the structure of the silver ketenide-pyridine complex, the linear ketenide groups, and the twofold rotation axes of symmetry of the pyridine molecules through N and C-4, lie perpendicular to the major plane of the crystal. As in the case of tetragonal silver ketenide, it proved possible to mount the flat crystals of its pyridine complex at a known orientation and to observe marked variations in the intensities of certain IR absorption bands according to the orientation of the crystals to the IR radiation beam. In agreement with the proposed structure, the absorption bands whose intensities show marked orientation dependence are the C=O stretch of the ketenide group at 2020  $\text{cm}^{-1}$  and those vibration modes of pyridine having a transition moment parallel to the N–C(4) axis (Tables 3 and 4). As in the simple ketenide case (see Figs. 4, 5, 6 and Table 2), the absorption in the 2000  $\text{cm}^{-1}$  region increased greatly at the 60° orientation, showing orientation of the ketenide groups perpendicular to the crystal plane. Some of the pyridine absorptions increase on increasing the angle to 60° while others do not. Those peaks marked as increasing showed at least a threefold increase in peak height (in terms of optical density) on going from the 0° to the 60° orientation.

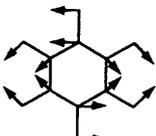
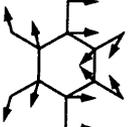
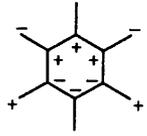
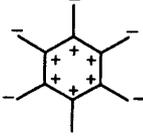
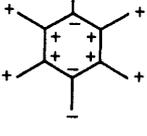
The two sets of absorption bands are listed in Tables 3, 4 with the vibrational assignments for pyridine<sup>23,24</sup> derived from the set of normal modes of benzene (less three) proposed by Langseth and Lord<sup>25</sup> indicated against the assignments: symmetry requires that when these are applied to pyridine the nitrogen atom must occupy the top or bottom position in the ring. It is apparent that the vibrations which do not give rise to increased absorption on inclining the normal to the substrate from 0° to 60° to the beam all have a component of the dipole change perpendicular to the twofold axis through the N and C(4) atoms, while those which do increase have dipole changes parallel to that axis: the increase noted in the 1062  $\text{cm}^{-1}$  band is attributed to mode 18a, which is coincident with 18b.

In view of the 'two-up two-down' structure deduced for the

**Table 3** Absorption bands of pyridine in  $\text{Ag}_2\text{C}_2\text{O}\cdot\text{Py}$  which increase when the crystal plane is inclined to the IR beam

Absorption	Assignment <sup>2,3</sup>	
1608mw	1599, 1 + 6a	
1588s	1583, 8a	
1062m	1068, 18b 18a	
1029m	1029, 12	
995m	992, 1	
609m	605, 6a	

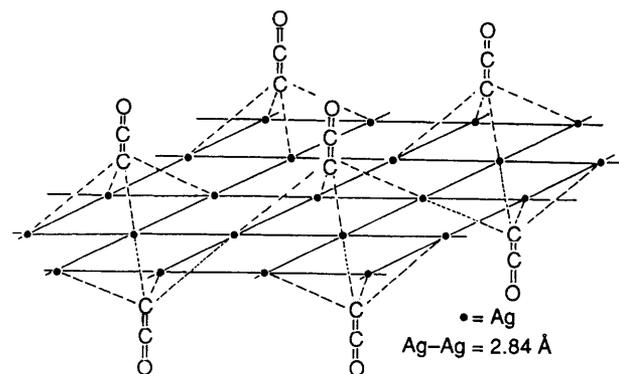
**Table 4** Absorption bands of pyridine in  $\text{Ag}_2\text{C}_2\text{O}\cdot\text{Py}$  which do not increase when the crystal plane is included to the IR beam

Frequency	Assignment <sup>2,3</sup>	
1570mw	1572, 8b	
1440vs	1439, 19b	
743 } s <sup>a</sup> 746 }	749, 10b	
702 } vs <sup>a</sup> 705 }	703, 11	
413 } m <sup>a</sup> 417 }	405, 16b	

<sup>a</sup> Absorptions due to these out-of-plane modes are split. Since  $a \neq b$  in the unit cell, the two mutually perpendicular sets of pyridine molecules in the proposed structure (Figs. 8 and 10) are probably crowded to differing degrees, giving rise to the splitting.

ketenide groups in the pyridinate unit cell, and the readily reversible loss of pyridine under very mild conditions, we conclude that tetragonal silver ketenide has the structure shown in Fig. 11. This conclusion implies that the unit cell may be twice or four times that proposed in Fig. 1, but the powder diffraction data do not provide sufficient information to verify this.

*Complexes with Methylpyridines.*—Complexes of silver ketenide with 2-, 3-, and 4-methylpyridine are obtained by

**Fig. 11** Tetragonal silver ketenide: showing alternating disposition of  $\text{C}_2\text{O}$  groups about a silver atom layer

reactions of silver acetate with acetic anhydride at 25 °C in the presence of an excess of the appropriate ligand. The methylpyridine complexes dissociate to silver ketenide and free base very readily, especially that from 2-methylpyridine, and have to be handled in the presence of an excess of the methylpyridine or else given only limited washing. Nevertheless it has been possible to index the X-ray diffraction pattern of the complex of silver ketenide with 3-methylpyridine, analysing as  $\text{Ag}_2\text{C}_2\text{O}\cdot\text{C}_6\text{H}_7\text{N}$ .

The unit cell dimensions are  $a = b = 8.10$ ,  $c = 13.58$  Å; *cf.*  $a = 8.086$ ,  $b = 8.058$ ,  $c = 12.09$  Å for the pyridinate. The unit cell contains four molecules, as for the pyridinate, and the pattern of absent reflections is similar to that for the pyridinate. This evidence suggests that the structures are closely similar, the interlayer separation being slightly greater for the 3-methylpyridinate.

The corresponding 4-methylpyridinate was crystalline, but the lines in the diffraction pattern were too few and too weak for satisfactory indexation. The 3- and 4-methylpyridinates readily lost the base to give tetragonal silver ketenide. The 2-methylpyridinate was of low crystallinity, and loss of the base

gave amorphous silver ketenide. Models and calculations for a 2-methylpyridinate suggest that in structures similar to those for the 3- and 4-isomers, the N...Ag separation would be too great to permit any significant degree of bonding.

**Amorphous Silver Ketenide.**—Reaction of silver acetate with acetic anhydride at 20 °C in the presence of triethylamine or, as noted above, with 2-methylpyridine (rather than pyridine) gives an amorphous form of silver ketenide, readily distinguishable from the tetragonal form by the presence of a very strong broad band at 1975 cm<sup>-1</sup> in the IR spectrum and the absence of the very strong and sharp absorption at 2060 cm<sup>-1</sup> characteristic of the tetragonal form [Fig. 5(c)]. The IR difference suggests that the virtually featureless diffraction pattern for the amorphous form is not merely an effect of particle size. Unexpectedly, repetition of the above reactions at -20 °C gave mainly the tetragonal form. Further experiments using 2-, 3- and 4-methylpyridine, or sodium acetate in dimethyl sulfoxide, as the base, various sources of ketene *in situ*, and various reaction temperatures, tended to give mixtures of the amorphous and tetragonal forms in varying proportions; but no clear pattern of effects of these experimental variations has yet emerged. On the other hand, in the presence of pyridine, the tetragonal form was the only product formed under a variety of reaction conditions. Benzene, but not toluene, appears to resemble pyridine in favouring the formation of tetragonal silver ketenide although no benzene complex of silver ketenide has been isolated. Amorphous silver ketenide shows chemical reactions closely similar to those described earlier in this paper for the tetragonal form.

Treatment of either amorphous or tetragonal silver ketenide with 5 mol dm<sup>-3</sup> aqueous silver nitrate gives an insoluble red crystalline solid which analyses as (Ag<sub>2</sub>C<sub>2</sub>O)<sub>2</sub>·AgNO<sub>3</sub>. This detonates even under slight impact when dry, and should be handled with great care and only in small quantities.

The X-ray powder diffraction pattern and the IR spectrum showed that the compound has a structure distinct from that of its constituents. It may be analogous to the known 'double salts' of silver acetylde, e.g. Ag<sub>2</sub>C<sub>2</sub>·AgNO<sub>3</sub>.<sup>26</sup>

Treatment of (Ag<sub>2</sub>C<sub>2</sub>O)<sub>2</sub>·AgNO<sub>3</sub> with concentrated aqueous ammonium hydroxide removed the silver nitrate component, leaving a yellow-brown insoluble compound which analysed as silver ketenide, but gave a reasonably sharp X-ray powder diffraction pattern different from that of tetragonal silver ketenide. The IR spectrum differed from those of the tetragonal and amorphous forms, though all three were broadly similar. The explosive character of the precursor has discouraged further studies of this crystalline form.

A further crystalline modification of silver ketenide is formed by heating a suspension of silver acetate in acetic anhydride under reflux for 5 h in the absence of pyridine, and removing acetic acid by distillation as it is formed.<sup>27</sup> It is an insoluble yellow-brown solid and persistently retains ca. 10% by weight of silver acetate which cannot be removed by washing with aqueous ammonia (in which silver acetate is highly soluble). The microscopic appearance of the needle-like crystals is completely different from that of the lamellar crystals of tetragonal silver ketenide; the two compounds give markedly different X-ray powder diffraction patterns, but only slightly differing IR spectra [Fig. 3(a, b)]. However, treatment with aqueous silver nitrate gives a 'double salt' identical with that described above from tetragonal silver ketenide. It has not proved possible to obtain structural information from the X-ray data, but from the form of the crystals, a lamellar structure seems unlikely.

## Experimental

Ketene was generated by pyrolysis of acetone over a Nichrome filament. Silver acetate was prepared from 'Aristar' grade

sodium acetate and photographic grade silver nitrate. Pyridine was 'Aristar' grade. All other reagents were 'Analar' grade or equivalent except where otherwise stated. Silver ketenide is the tetragonal form except when otherwise stated.

**Tetragonal Silver Ketenide.**—A filtered solution of silver acetate (16.7 g, 0.1 mol) in pyridine (40 cm<sup>3</sup>) was added to a 500 cm<sup>3</sup> flask equipped with a fractional distillation column, followed by acetic anhydride (200 cm<sup>3</sup>). A bright-yellow gel-like solid formed immediately. The mixture was then heated to boiling and maintained at reflux for 80 min, the lowest boiling fraction (~135 °C) being continuously distilled off. The final volume of distillate was 90 cm<sup>3</sup>. The reaction mixture was allowed to cool to 25 °C, filtered, and the very finely divided yellow product in the filter washed with ethanol and then thoroughly with water and dried *in vacuo* over potassium hydroxide. Yield 11.3 g, 89% (Found: Ag, 84.2; C, 9.6; H, 0.08. Ag<sub>2</sub>C<sub>2</sub>O requires Ag, 84.4; C, 9.4%).

Tetragonal silver ketenide of larger crystal size required for the IR study of oriented crystals was obtained by a variation in the preparatory procedure. The filtered solution of silver acetate in pyridine was heated to reflux and the acetic anhydride then added dropwise over 30 min while maintaining the reaction mixture at reflux. Pyridine was then removed by fractional distillation and the product isolated as before.

**Silver Ketenide Pyridine Complex.**—Silver oxide (3.0 g, 0.013 mol), pyridine (20 cm<sup>3</sup>, 0.25 mol) and light petroleum b.p. 60–80 °C (70 cm<sup>3</sup>) were heated under reflux. Acetic anhydride (10 cm<sup>3</sup>, 0.1 mol) was added dropwise over 10 min and the mixture heated at reflux (60 °C) for 6 h. The reaction mixture was cooled to 25 °C and filtered. The dark-yellow solid in the filter was washed with light petroleum and dried in air. The product was in the form of platelets of average diameter about 1.5 μm (Found: Ag, 64.4; C, 25.0; H, 1.55; N, 4.20. Ag<sub>2</sub>C<sub>7</sub>H<sub>5</sub>NO requires Ag, 64.5; C, 25.1; H, 1.49; N, 4.18%).

**Silver Ketenide 3-Methylpyridine Complex.**—Acetic anhydride (50 cm<sup>3</sup>) was added over 5 min to a stirred solution of silver acetate (5 g) in 3-methylpyridine (30 cm<sup>3</sup>) at 25 °C. Stirring was continued for a further 25 min, then the light-yellow solid formed was filtered off, washed with 3-methylpyridine and light petroleum (b.p. 60–80 °C) and dried in air at 25 °C/760 mmHg. The IR absorption spectrum of the solid showed sharp ketenide peaks at 2027vs, 640m and 423s cm<sup>-1</sup> superimposed on the bands of 3-methylpyridine which showed the following differences from those of a thin film of the free base: 1580 (a broadened many-shouldered band), 1192 (relatively weakened), 1127, 1126 shifted to 1121, 1100, 788 shifted to 783 cm<sup>-1</sup> (Found: Ag, 62.5; C, 25.6; H, 1.9; N, 3.90. Ag<sub>2</sub>C<sub>8</sub>H<sub>7</sub>NO requires Ag, 61.7; C, 27.4; H, 2.3; N, 4.0%). These figures indicate a 2.5% deficit of 3-methylpyridine and indicate the material to be 97.5% Ag<sub>2</sub>O·C<sub>6</sub>H<sub>7</sub>N and 2.5% Ag<sub>2</sub>C<sub>2</sub>O. A single washing with ethanol removed all trace of 3-methylpyridine leaving tetragonal silver ketenide.

**Silver Ketenide–Silver Cyanide Double Salt.**—Silver nitrate (8.5 g, 0.05 mol) was dissolved in methyl cyanide (50 cm<sup>3</sup>, 0.95 mol) and acetic anhydride (150 cm<sup>3</sup>, 1.5 mol) added. The reagents were heated under reflux for 3 h, cooled to 25 °C and the yellow product filtered off and washed successively with ethanol, water, strong ammonia solution, water, ethanol and light petroleum (b.p. 60–80 °C), and dried in air. Yield 4.6 g (Found: Ag, 82.3; C, 9.0; N, 3.32; Ag<sub>2</sub>C<sub>2</sub>O·AgCN requires Ag, 83.1; C, 9.14; N, 3.59%). The IR spectrum of the complex showed absorption bands at 2160 m, 1980vs, 1320m, 640m and 428s cm<sup>-1</sup>. For comparison, silver cyanide also as a mull in paraffin shows absorption bands at 2165s and 1300 cm<sup>-1</sup>. This material

remained unchanged on treatment with 5 mol dm<sup>-3</sup> aqueous silver nitrate and was not decomposed by 0.880 ammonia.

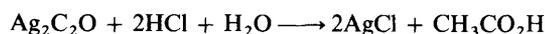
**Silver Ketenide–Silver Nitrate Adduct.**—Aqueous silver nitrate (5 cm<sup>3</sup>, 0.025 mol; 5 mol dm<sup>-3</sup>) was added to silver ketenide (0.5 g, 0.002 mol) at 20 °C. The colour of the solid changed from yellow to orange-red almost immediately. After standing for 30 h the red solid was filtered off, washed once with water, and dried *in vacuo* [Found: Ag, 78.8; C, 6.90; H, 0.20; N, 1.71. (Ag<sub>2</sub>C<sub>2</sub>O)<sub>2</sub>AgNO<sub>3</sub> requires Ag, 79.22; C, 7.05; H, 0.00; N, 2.05%]. The X-ray powder diffraction pattern of the highly explosive red solid showed it to be crystalline and to have a structure distinct from those of its constituents. The IR spectrum of the solid showed a multiple peak at 2000–1900 vs, a band attributable to nitrate at 1310s, and ketenide bands of diminished intensity at 640 and 430 cm<sup>-1</sup>.

**Amorphous Silver Ketenide.**—Silver trifluoroacetate (5.0 g, 0.0226 mol) was dissolved in toluene (100 cm<sup>3</sup>) at 20 °C. Ketene (and methane) from a ketene generator were passed through the reaction mixture for 20 min, corresponding to *ca.* 0.025 mol ketene. The yellow solid produced was filtered off, washed with benzene, and dried. Yield 3.0 g, 103% with respect to silver and between 47 and 94% with respect to ketene depending on the extent of reaction of ketene with liberated trifluoroacetic acid (Found: Ag, 78.8; C, 10.7; H, 0.32. Ag<sub>2</sub>C<sub>2</sub>O requires Ag, 84.4; C, 9.4; H, 0.0%). These poor analytical figures are typical for amorphous silver ketenide which has not so far been obtained in a high state of purity by this or other methods. The X-ray powder diffraction pattern of this material showed only one very diffuse line. The IR spectrum showed only three relatively broad absorption bands at 1965 vs, 635 m and 425 s cm<sup>-1</sup> corresponding to the absorption bands of tetragonal silver ketenide at 2060, 640 and 430 cm<sup>-1</sup>. Amorphous silver ketenide is **EXPLOSIVE** when dry. It forms the same crystalline **HIGHLY EXPLOSIVE** double salt (Ag<sub>2</sub>C<sub>2</sub>O)<sub>2</sub>AgNO<sub>3</sub> as does tetragonal silver ketenide on treatment with 5 mol dm<sup>-3</sup> aqueous silver nitrate (X-ray powder diffraction pattern). Amorphous silver ketenide is more reactive and less thermally stable than tetragonal silver ketenide.

**Reaction of Tetragonal Silver Ketenide with Hydrochloric Acid.**—Silver ketenide (2.00 g, 0.0078 mol) and 15.0 cm<sup>3</sup> of 1.0 mol dm<sup>-3</sup> aq. hydrochloric acid (0.015 mol) were shaken for 3 h, filtered, and the filtrate distilled. The distillation range was 101–104 °C. A very small amount of an oily residue, which did not distil at 120 °C/15 mmHg remained in the distillation flask. A 5 cm<sup>3</sup> portion of the distillate was neutralised to phenolphthalein with dil. NaOH and *S*-benzylthiuronium chloride (0.5 g) in 2 cm<sup>3</sup> water added, and the resulting derivative recrystallised from hot water and dried *in vacuo*, m.p. 129 °C. The *S*-benzylthiuronium derivative of an authentic sample of acetic acid prepared by a similar method melted at 129.5 °C, mixed m.p. 129 °C. Potentiometric titration of a further portion of the distillate against 0.100 mol dm<sup>-3</sup> NaOH at 25 ± 1 °C using a glass electrode, calomel reference electrode and an E.I.L. model 2320 pH meter gave a typical monobasic weak acid–strong base pH titration curve, with no inflexions indicating the presence of a single monobasic acid of p*K* 4.74 (*cf.* acetic acid has p*K* 4.75 at 25 °C).

The stoichiometry of the reaction was checked by a further experiment in which silver ketenide (1.00 g, 0.0039 mol) and 1.00 mol dm<sup>-3</sup> hydrochloric acid (10 cm<sup>3</sup>, 0.0100 mol) were shaken at 25 °C for 80 min. The suspension was diluted to *ca.* 80 cm<sup>3</sup> and filtered. The brown-grey solid in the filter was washed with water and the combined filtrate and washings made up to 100 cm<sup>3</sup>. Portions of the solution were potentiometrically titrated against silver nitrate using an Ag/AgCl indicating electrode and

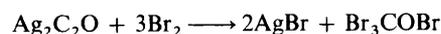
against sodium hydroxide using a glass indicating electrode to determine remaining chloride ion and the combined amounts of acetic acid produced and unreacted hydrochloric acid respectively. The results of these titrations indicated the consumption of chloride (0.00745 mol, 95.5%) and the production of acetic acid (0.00378 mol, 97%) in good agreement with the equation



The X-ray powder diffraction pattern of the brown solid obtained showed it to be silver chloride containing a trace of silver metal.

**Reaction of Tetragonal Silver Ketenide with Hydrogen Chloride.**—**CAUTION.** This reaction is strongly exothermic and unless the ketenide is thinly spread on an inert support and the hydrogen chloride diluted with an inert gas **the ketenide may explode**. Nitrogen (White Spot) was bubbled slowly through conc. hydrochloric acid in a Dreschel bottle and then dried by bubbling through conc. sulfuric acid. The dried gas, which contained *ca.* 10 mol% HCl was passed through a U-tube, 22 cm long and 0.7 cm internal diameter packed with glass wool coated with silver ketenide (*ca.* 0.3 g), immersed in a water-bath at 83 °C. The exit gases were passed through a 10 cm gas cell fitted with potassium bromide windows and vented through a Bunsen valve. The progress of the reaction was followed by observing the progressive change in colour of the contents of the U-tube from yellow to grey along the tube. When the reaction was nearing completion, the gas-cell was sealed. The IR spectrum of the gases in the cell showed intense ketene absorption bands at 2140, 2170 cm<sup>-1</sup> and weaker absorption bands of acetyl chloride at 1825 and 1370 cm<sup>-1</sup>. Since carbon monoxide has a double absorption at 2110, 2170 cm<sup>-1</sup>, the spectrum was run at high resolution in this region and compared with the spectra of authentic samples of ketene and carbon monoxide. This showed the bands to be identical with those of ketene and totally different from those of carbon monoxide which has a different band structure with well-developed rotational levels.

**Reaction of Tetragonal Silver Ketenide with Bromine.**—Silver ketenide (0.51 g, 0.002 mol) was shaken with carbon tetrachloride (30 cm<sup>3</sup>) containing bromine (3 ml, 0.96 g, 0.006 mol) for 30 h at 20 °C. A slight brown colour persisted which was discharged by the addition of a further 0.1 g of silver ketenide and shaking the mixture for a further 30 min. The IR spectrum of the clear colourless supernatant solution was superimposable on that of a 2% w/v solution of an authentic sample of tribromoacetyl bromide in carbon tetrachloride. To determine the stoichiometry of the reaction the experiment was repeated but at the 30 h stage a 15 cm<sup>3</sup> portion of the clear, brown supernatant liquor was removed, shaken with aqueous KI, and the liberated iodine, equivalent to the unreacted bromine, titrated against 0.025 mol dm<sup>-3</sup> sodium thiosulfate using a starch indicator: titre, 1.95 cm<sup>3</sup> ≡ 0.00005 mol I<sub>2</sub>. Thus, 0.002 mol silver ketenide reacts with 0.0059 mol Br<sub>2</sub> in agreement with the equation



The yellow solid formed in the reaction was identified as silver bromide from its X-ray powder diffraction pattern.

**Reaction of Tetragonal Silver Ketenide with Dinitrogen Tetroxide.**—A solution of N<sub>2</sub>O<sub>4</sub> (2.0 g, 0.022 mol) in benzene (30 cm<sup>3</sup>) at 20 °C was added dropwise over 4 min to a stirred suspension of tetragonal silver ketenide (3.618 g, 0.014 mol) in

benzene (20 cm<sup>3</sup>) at 20 °C in a flask equipped with a gas trap, a serum cap, a dropping funnel, and a magnetic stirrer. An exothermic reaction occurred accompanied by effervescence. Stirring was continued for a total of 5 h. The IR spectrum of a portion of gas transferred by syringe from the reaction flask to a gas cell showed it to contain substantial amounts of CO<sub>2</sub>. The contents of the flask were filtered and the solid washed consecutively with acetone and water. The IR spectrum of the dried solid in the region 650–4000 cm<sup>-1</sup> was identical to that of an authentic sample of AgCN. Yield 1.672 g, 0.0125 mol (Found: Ag, 80.38; C, 9.11; H, 0.66; N, 10.16. AgCN requires Ag, 80.58; C, 8.96; N, 10.46%). The combined filtrate and washings were evaporated to dryness at 100 °C/10 mmHg. The IR spectrum of the white crystalline residue (KBr disc) was identical with that of an authentic sample of AgNO<sub>3</sub> in the region 250–4000 cm<sup>-1</sup>. Yield 2.204 g, 0.013 mol.

*Silver Ketenide–Silver Acetate Complex.*—Silver acetate (16.7 g, 0.01 mol) was suspended in acetic anhydride (300 cm<sup>3</sup>) in a flask equipped with a stirrer and jacketed Vigreux column at the top of which were a thermometer, Perkin triangle and reflux condenser. The contents of the flask were stirred under reflux for 5 h, distillate being continuously removed at high reflux ratio at a rate such that the temperature at the top of the fractionating column was maintained at 139 °C. The volume of distillate was 12 cm<sup>3</sup>. The contents of the reaction flask were cooled to 25 °C, filtered, and the yellow-brown solid in the filter washed consecutively with ethanol, acetone, and pentane and dried *in vacuo* over P<sub>2</sub>O<sub>5</sub>. Yield 12.0 g [Found: Ag, 81.2; C, 10.3; H, 0.34; N, 0.27. (Ag<sub>2</sub>C<sub>2</sub>O)<sub>4</sub>AgO<sub>2</sub>CCH<sub>3</sub> requires Ag, 81.6; C, 10.1; H, 0.25; N, 0.00%]. The IR spectrum of the **EXPLOSIVE** solid as a mull in Nujol showed ketenide absorption bands at 1990vs, 640w and 440s cm<sup>-1</sup> and weak bands attributable to silver acetate at 1510, 660 and 627 cm<sup>-1</sup>, the latter two bands being shoulders of the 640 cm<sup>-1</sup> ketenide band. The IR spectrum of a mull of the solid in hexachlorobutadiene revealed a further absorption band at 1390 cm<sup>-1</sup>, corresponding to the strong band of silver acetate at 1405 cm<sup>-1</sup>. Extending the heating period in the preparation from 5 to 15 h did not lead to a diminution in intensity of the acetate relative to the ketenide absorption, nor did extensive washing of the product with 0.880 ammonia, in which silver acetate is freely soluble. The X-ray powder diffraction pattern of the material differed from that of tetragonal silver ketenide and has not yet been indexed. Electron micrographs showed the solid to consist of bundles of very fine rods, totally different from the flat platelets of tetragonal silver ketenide. The material shows great affinity for small molecules such as H<sub>2</sub>O, O<sub>2</sub> and N<sub>2</sub>. Samples prepared under air or subsequently exposed to air always contain up to ca. 1% of nitrogen. The material, when rigorously dried, almost quantitatively undergoes the same reactions as tetragonal silver ketenide, but reacts more rapidly. Thus it reacts with dil. hydrochloric acid to give silver chloride and acetic acid, and with hydrogen chloride gives ketene and acetyl chloride. Treatment with 5 mol dm<sup>-3</sup> aq AgNO<sub>3</sub> gives the same double salt (Ag<sub>2</sub>C<sub>2</sub>O)<sub>2</sub>·AgNO<sub>3</sub> (X-ray powder diffraction pattern) as is formed from tetragonal silver ketenide under similar conditions. When the material is heated rapidly under argon at reduced pressure it detonates to give carbon suboxide as the major gaseous product, but the gases contain much more carbon dioxide than obtained by detonation of tetragonal silver ketenide.

*Pyrolysis of Tetragonal Silver Ketenide.*—When heated in a sealed capillary tube at ca. 3 °C min<sup>-1</sup>, silver ketenide progressively darkened in colour and exploded at 304 °C. To establish the nature of the gaseous products, silver ketenide (0.02 g) was placed in a thick-walled Pyrex gas sample tube of an

AEI MS10 mass spectrometer. The tube was connected to the instrument and evacuated. The tap between the tube and instrument was then closed and the lower end of the tube heated gently in a Bunsen flame (**CAUTION**) until the ketenide exploded as evidenced by a slight flash and popping sound and blackening of the inside of the tube. After 1 min the tap between the tube and instrument was opened slowly and the mass spectrum of the evolved gases recorded. The spectrum showed peaks at *m/z* 28, 40, 44 and 68, the latter corresponding to the M<sup>+</sup> ion of carbon suboxide. In a similar pyrolysis silver ketenide (0.02 g) was heated to detonation under argon at a pressure of 0.1 mmHg and the evolved gases transferred to an evacuated gas cell fitted with KBr windows. The IR spectrum showed the gases formed were C<sub>3</sub>O<sub>2</sub>, CO<sub>2</sub> and CO, the latter two in minor amounts. The composition of the solid black residue (Found: Ag, 94.7; C, 4.3; H, 0.01%) has not yet been established.

*Formation of Silver Ketenide from Vinyl Acetate and Silver Acetate.*—A filtered solution of silver acetate (2.5 g, 0.015 mol) in pyridine (20 cm<sup>3</sup>) was added dropwise over 10 min to vinyl acetate (30 cm<sup>3</sup>, 0.32 mol) at 40 °C in a flask fitted with a reflux condenser and thermometer. The mixture was warmed to 75 °C over 20 min. A green precipitate formed and a silver mirror appeared on the walls of the flask. The precipitate was filtered off, washed with acetone and pentane and dried *in vacuo* over KOH. Yield 0.78 g (Found: Ag, 67.02, C, 24.75; H, 1.57; N, 4.00. Ag<sub>2</sub>C<sub>2</sub>O·C<sub>3</sub>H<sub>5</sub>N requires Ag, 64.5; C, 25.09; H, 1.49; N, 4.18%). The IR spectrum of the solid as a mull in Nujol in the region 650–4000 cm<sup>-1</sup> showed absorption bands at 2060m, 2020vs, 1965w, 1588m, 1440s, 740m, 700vs and 640w cm<sup>-1</sup>, indicating that the solid was largely the pyridine complex of silver ketenide, with some tetragonal silver ketenide and a trace of amorphous silver ketenide. GLC analysis of the filtrate showed that acetaldehyde was formed in the reaction.

*Formation of Silver Ketenide from Isopropenyl Acetate and Silver Acetate.*—Reaction as described above, but with isopropenyl acetate (36 cm<sup>3</sup>, 0.32 mol) instead of vinyl acetate yielded a yellow solid, 0.95 g (Found: Ag, 66.4; C, 23.7; H, 1.34; N, 3.76. Ag<sub>2</sub>C<sub>2</sub>O·C<sub>3</sub>H<sub>5</sub>N requires Ag, 64.5; C, 25.09; H, 1.49; N, 4.18%). The IR spectrum of a Nujol mull of the solid showed all the absorption bands of the pyridine complex of silver ketenide and a band at 1965w cm<sup>-1</sup>. GLC analysis of the filtrate showed it to contain acetone (~0.01 mol). The liquor from a blank experiment carried out in the absence of silver acetate also contained acetone (~0.005 mol).

Reactions as above but with ethyl acetate (31 cm<sup>3</sup>, 0.32 mol) and isopropyl acetate (37 cm<sup>3</sup>, 0.32 mol) instead of the unsaturated esters gave no solid products.

*Formation of Silver Ketenide from Phenyl Acetate and Silver Acetate.*—A filtered solution of silver acetate (0.32 g, 0.0018 mol) in pyridine (10 cm<sup>3</sup>) was added to freshly distilled phenyl acetate (5 cm<sup>3</sup>, 0.034 mol) at 22 °C and the mixture heated to 75 °C over 10 min. The fine yellow suspension formed was filtered off, washed with ethanol and pentane and dried *in vacuo*. Yield 0.153 g, 51% (Found: Ag, 65.5; C, 24.30; H, 1.43; N, 3.97. Ag<sub>2</sub>C<sub>2</sub>O·C<sub>6</sub>H<sub>5</sub>N requires Ag, 64.5; C, 25.09; H, 1.49; N, 4.18%). The IR spectrum of a Nujol mull of the solid was that of a mixture of tetragonal silver ketenide and its pyridine complex (major component). GLC analysis of the filtrate showed it to contain significantly more phenol than that from a similar experiment carried out in the absence of silver acetate. In a series of similar experiments but with 4-nitro-, 4-cyano-, 4-methyl- and 4-methoxyphenyl acetate (0.034 mol) instead of phenyl acetate, the yields of silver ketenide pyridine complex obtained were 65, 64, 43 and 31% respectively.

*X-Ray Powder Diffraction Study of Silver Ketenide.\**—The powder sample was spread in a thin layer on plastic film, supported on a 'Nonius' Guinier-type camera with a lithium fluoride monochromator. A proportion of thallos bromide was added to the sample as an internal standard. Spacings between lines on the photograph were measured with a precision microdensitometer, and referred to the thallos bromide spacings, which were calculated from the known cubic parameter of 3.9850 Å.<sup>28</sup> The camera was calibrated to these  $\theta$  values of thallos bromide. The temperature during the exposure was 25 °C. The relative integrated values were measured from patterns obtained in a circular Debye-Scherrer camera, and estimated from the Guinier-type camera patterns in those cases where they were not measurable from the Debye-Scherrer patterns. 29 Lines were observed and measured with the Guinier camera. A further nine lines, at larger angles, were observed, measured and indexed with the circular Debye-Scherrer camera. The powder photographs all showed the special features that (*hko*) lines are sharp whereas reflections from planes having an *l*-component are diffuse. Within the limits observable with the Guinier-type camera there are 48 possible and 29 observed reflections. With three exceptions there is a systematic absence of reflections from planes for which (*h + k*) is odd, and the three exceptions (100, 101, 210), are all very weak. The density of silver ketenide, measured in duplicate by CCl<sub>4</sub> displacement, was 4.45 ± 0.03 g cm<sup>-3</sup>.

*X-Ray Powder Diffraction Study of the Pyridine Complex of Silver Ketenide.\**—The powder sample was mounted as a thin film on a 'Nonius' Guinier-type camera, using  $\alpha$ -quartz as an internal standard. Copper K $\alpha$  radiation was used with a lithium fluoride monochromator. Distances, referred to the observed<sup>29</sup> values for quartz, were measured with a graticule, and the camera was calibrated to the known quartz lines. The temperature during the exposure was 25 °C. The pattern was indexed in the orthorhombic system, only slightly distorted from the tetrahedral. 46 Lines were observed with overlapping of interchanged *h,k* reflection (e.g. 200, 020) for the larger interplanar spacings, and resolution of the two lines for 400 and 040 and beyond. Only reflections for which both *h* and *k* are even are strong and reflections for which either or both *h* and *k* are odd are weak or missing. The density of the solid was measured pyknometrically by displacement of pyridine. The measured value of 2.81 g cm<sup>-3</sup> is in excellent agreement with the value of 2.82 g cm<sup>-3</sup> calculated from the unit cell parameters on the basis of four Ag<sub>2</sub>C<sub>2</sub>O·C<sub>5</sub>H<sub>5</sub>N molecules per unit cell.

*X-Ray Powder Diffraction Study of the 3-Methylpyridine Complex of Silver Ketenide.*—The procedure followed was as described above for the pyridine complex. The density of the 3-methylpyridine complex, measured pyknometrically by displacement of 3-methylpyridine, was 2.68 g cm<sup>-3</sup>. This is higher than the calculated value (2.60 g cm<sup>-3</sup>), and the discrepancy is probably due to irreversible loss of some 3-methylpyridine from the crystal lattice to give the denser silver ketenide. Elemental analysis indicated a 2.5% deficit of 3-methylpyridine. The calculated density for a mixture of 2.5% silver ketenide and 97.5% of its 3-methylpyridine complex is 2.65 g cm<sup>-3</sup>.

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