

bonds) are 5.508 to 5.647 Å, and thus 0.19 to 0.33 Å longer than the more symmetrical linear three-selenium systems of the triselenocyanate and triselenourea ions.³

The eight-selenium unit can be looked upon as built up of two selenium diselenocyanate molecules, $\text{Se}(\text{SeCN})_2$, bridged together through the selenium atoms of two selenocyanate ions. In the crystals of selenium diselenocyanate, the molecules lie across a crystallographic mirror plane, with the middle selenium atom in the plane; the Se-Se bond lengths are 2.33 Å and the Se-Se-Se angle is 101°. In the present adduct with potassium selenocyanate, the selenium diselenocyanate molecules retain their approximate shape. The Se-Se bonds, on being approached at approximately 180° by selenocyanate ions, become a little longer.

Several rather short $\text{Se}\cdots\text{Se}$ contacts, from 3.34 Å upwards, occur between eight-selenium units.

Details of the structure will be published later.

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The Diisocyanatoargentate Ion

TOR AUSTAD, JON SONGSTAD and
KJELL ASE

*Chemical Institute, University of Bergen,
N-5000 Bergen, Norway*

The univalent silver ion, a B-subgroup ion with d^{10} closed-shell configuration, has a pronounced tendency to occur in linear environment, similarly to Au^+ , Hg^{2+} , and Cu^+ . According to Dunitz and Orgel,¹ this stereochemical behaviour is primarily due to the low d - s separation in these d^{10} ions.

With regard to Ag^+ , which is known to form octahedral, tetrahedral, and linear complexes, the coordination number generally decreases with increasing electron-donor ability of the attached ligands.¹ The Ag^+ ion is known to form complex anions, generally formulated as AgL_2^- , with a series of inorganic and organic anions. The stability of the complex anions is considerably higher in dipolar aprotic solvents than in protic solvents.^{2,3} Furthermore, it appears that the coordination number of silver increases from protic to aprotic solvents.⁴ Several complex silver anions, as $\text{Ag}(\text{IO}_3)_2^-$,⁵ $\text{Ag}(\text{NCO})_2^-$,⁶ $\text{Ag}(\text{NO}_2)_2^-$,⁷ $\text{Ag}(\text{NO}_3)_2^-$,⁸ *etc.*, have been suggested from studies of solubilities and from potentiometric measurements, but no actual salts of these anions have been isolated so far. Salts of the assumed anions, $\text{Ag}(\text{SCN})_2^-$ and $\text{Ag}(\text{SeCN})_2^-$, have been prepared, and a complete crystal structure determination of $\text{NH}_4\text{Ag}(\text{SCN})_2$ ⁹ has shown that the substance consists of AgSCN molecules and ammonium and thiocyanate ions and no ion of type $\text{Ag}(\text{SCN})_2^-$. The same has been found for $\text{KAg}(\text{SeCN})_2$.¹⁰ In these salts there are therefore two different pseudohalide groups, one ionic and one covalently bonded to the silver atom, giving rise to two separate absorptions in the C-N stretching region.¹¹⁻¹³

Recently, Bottger and Geddes¹⁴ have shown that in salts of the general type Me_nNAgL_2 , where L is Cl or Br, there are no discrete AgL_2^- ions in the solids, but effectively infinite chains of tetrahedral AgL_4 units sharing common edges, making anionic units of $(\text{Ag}_2\text{L}_4)_n^{2n-}$. The IR spectra of the salts in dimethyl sulfoxide suggested the presence of discrete anions of type AgL_2^- , but no definite conclusion could be reached whether these anions were bent or linear. Dallinga and Machor¹⁵ have found that the anion AgI_2^- is bent in solution, with the I-Ag-I angle 111°, that is, rather close to the tetrahedral angle. The well-known linear silver complexes, the cation $\text{Ag}(\text{NH}_3)_2^+$ ^{16,17} and the anion $\text{Ag}(\text{CN})_2^-$,^{18,19} are therefore examples more of exceptional than of general coordination behaviour of the univalent silver ion, confirming that only very electron-donating ligands will form linear di-coordinated complexes with the silver ion.¹

We now wish to report the synthesis of salts of the $\text{Ag}(\text{NCO})_2^-$ ion. As pointed out by Norbury,²⁰ the cyanate ion has received relatively little attention as a ligand, probably due to the rather rapid decom-

position of the cyanate ion in water. The use of onium cyanates in aprotic solvents has facilitated the study of the cyanate ion.²⁰

The majority of complexes of the cyanate ion are bonded through nitrogen, and are thus isocyanato complexes; very few cyanato complexes have been reported (Ref. 21 and references therein). A crystal structure determination of silver isocyanate has revealed the presence of *N*-bridged polymers, with *N*-Ag-*N* angles of 180°.²²

Linear coordination at nitrogen is usually found when the isocyanato group is bonded to elements with suitable empty *d*-orbitals, except in the case of trimethylsilyl isocyanate where the Si-N-C angle is 150°.²³ Otherwise, when the -NCO group, as the -NCS group, is attached to hydrogen or carbon, bent molecules are formed.²³ The cyanate ion itself is linear,²³ with the negative charge mainly on the nitrogen end of the anion.²⁴ The pK_a value of isocyanic acid,²⁵ and the nucleophilicity of the cyanate ion toward methyl iodide,²⁶ suggest a considerable electron donating ability of the cyanate ion.

Due to the very low solubility of alkali cyanates in aprotic solvents,²⁷ tetramethylammonium cyanate and tetraphenylarsonium cyanate were used as sources of the cyanate ion in this work. Freshly prepared silver cyanate was found to dissolve rather rapidly in solutions of these cyanates in acetonitrile. Upon addition of ethyl acetate to the reaction mixtures, the desired products crystallized in high yields.

Tetramethylammonium diisocyanatoargentate was found to decompose slowly on storage, probably due to moisture. This salt as well as the tetraphenylarsonium salt were decomposed rapidly by protic solvents, and by alkali metal cations and other hard Lewis acids, with the formation of silver isocyanate. The salts were very soluble in acetonitrile without any detectable decomposition, while nitromethane and warm acetone caused a rapid precipitation of silver isocyanate.

Tetramethylammonium diisocyanatoargentate, crystallized from acetonitrile upon addition of a small amount of chloroform, occurred as colourless orthorhombic prisms bounded by {001}, {101}, and {011}. Using $MoK\alpha_1$ radiation ($\lambda = 0.70926 \text{ \AA}$), the unit cell dimensions, with standard deviations in parentheses, were found to be, $a = 10.867(6) \text{ \AA}$, $b = 6.614(5) \text{ \AA}$, $c = 13.852(7) \text{ \AA}$.

There are four formula units per unit cell. The density, found by flotation, is 1.775, calc. for $Z = 4$, 1.774 g/cm³. Systematic absences are *Ok**l* when $k + l = 2n + 1$, and *hk**l* when $h = 2n + 1$. The space group is then either *Pna*2₁ (No. 33) or *Pnma* (No. 62). The latter space group, in which the general positions are eight-fold, implies that the tetramethylammonium ion possesses mirror plane symmetry, and that the silver atom lies either in a mirror plane or in a center of symmetry. The determination of the crystal structure is in progress and will be reported later.

The IR spectrum of tetraphenylarsonium diisocyanatoargentate in Nujol showed only one strong peak, at 2200 cm⁻¹, in the C-N stretching region. The tetramethylammonium salt had, in addition, a definite shoulder at ~2180 cm⁻¹, which did not disappear on repeated purification. IR of both salts in acetonitrile using 0.1 cm liquid cells showed only one peak for both salts, at 2195 cm⁻¹, with an integrated intensity of absorption per NCO group of $12 \times 10^4 \text{ M}^{-1} \text{ cm}^{-2}$. This is considerably higher than for the cyanate ion, $5.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-2}$,²⁸ as anticipated for a complex with an N-bonded cyanato group.

These results indicate that in the diisocyanatoargentate ion in these salts, the two cyanato groups are symmetrically bonded to the silver atom through nitrogen. In analogy with other cyanato compounds, the diisocyanatoargentate ion appears to be linear, but with a slight distortion from linearity in the case of the tetramethylammonium salt. Further studies on the diisocyanatoargentate ion are in progress in this laboratory.

Experimental. Acetonitrile was purified as reported previously.²⁸ Chloroform and ethyl acetate were free from ethanol. Solutions of salts of the diisocyanatoargentate ion were carefully shielded from atmospheric moisture.

Potassium cyanate, Baker Analyzed Reagent, was precipitated with methanol from an aqueous solution, made acidic to phenolphthalein, prior to use.

Silver isocyanate, made from potassium cyanate and silver nitrate, was carefully washed with acetone and ether.

Tetramethylammonium bromide, Fluka *purum*, was ground in a mortar under acetone to remove traces of water. The salt was finally washed repeatedly with ether and dried to constant weight.

Tetraphenylarsonium cyanate, made according to Norbury and Sinha,²⁰ was repeatedly dissolved in acetonitrile, some benzene was added, and the solvent mixture was removed in vacuum to ensure a complete removal of hydrated water in order thereby to cause precipitation of the last traces of the potassium salts. Finally, the salt was recrystallized from acetonitrile and dried to constant weight prior to use.

Tetraphenylarsonium diisocyanatoargentate. To 2.1469 g tetraphenylarsonium cyanate in 30 ml acetonitrile was added the equivalent amount of freshly prepared silver isocyanate, 0.756 g, which dissolved rapidly. On addition of some ethyl acetate to the filtered reaction mixture, white needles crystallized. Yield, 2.41 g, 83%. M.p. 155°C. (Found: C 54.84; H 3.61; N 5.23. Calc. for $C_{26}H_{20}N_2O_2AsAg$: C 53.91; H 3.48; N 4.84.)

Tetramethylammonium diisocyanatoargentate. To 30.8 g tetramethylammonium bromide in 300 ml acetonitrile was added 60 g silver isocyanate. The mixture was refluxed for 1 h and then filtered while still warm. To the filtrate was added 5 g silver isocyanate, and the mixture was refluxed for half an hour. After cooling and filtering, the filtrate was evaporated to dryness in vacuum, and the residue dissolved in a minimum amount of acetonitrile. The solution was filtered, and the desired product precipitated by addition of a small amount of ethyl acetate. Yield, 37.3 g, 80%, m.p. 123–124°C.

The combined residues from the filtrations were treated with 500 ml warm acetonitrile and filtered while still warm. Upon cooling, 2.7 g of a white crystalline product separated. This compound had a very limited solubility in acetonitrile. As the Belstein test on halogen was negative, the combustion data suggested this compound to be $Me_4NAg_3(NCO)_4$. (Found: C 16.57; H 2.11; Ag 58.2; N 11.17. Calc. for $C_8H_{12}Ag_3N_5O_4$: C 16.97; H 2.13; Ag 57.2; N 12.55.) The compound showed a very complex spectrum in the 2200 cm^{-1} region and was not further examined.

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