# The Thiocyanates of Gold and Free Thiocyanogen
## With an Appendix on Gold Chloride

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## SUMMARY

1. *Aurous thiocyanate* in the solid state, as shown already by Cleve, is stable only in the form of double salts. Besides the potassium and silver dithiocyanato-auroates of Cleve we have prepared a new double salt of the same type, viz. *ammonium dithiocyanato-auroate* $NH_4Au(SCN)_2$. The corresponding *dithiocyanato-auroate acid* may be extracted from an aqueous solution by ether; by evaporation of the ethereal solution it remains as a partly decomposed oil.

In aqueous solutions aurous thiocyanate is always present as *dithiocyanato-auroate ion* $Au(SCN)_2^-$. The complexity constant of this complex ion is $10^{22.4}$ times smaller than that of the dicyano-auroate ion.

$$K_{SCN} = \frac{[Au(SCN)_2{}^-]}{[Au^+][SCN^-]^2}; \quad K_{CN} = \frac{[Au(CN)_2{}^-]}{[Au^+][CN^-]^2}; \quad \frac{K_{CN}}{K_{SCN}} = 10^{22.4}.$$

In a solution rich in thiocyanate ions the dithiocyanato-auroate ion is not perceptibly hydrolyzed at $p_H$ 9; in strongly alkaline solution it is decomposed.

The action of ammonia on dithiocyanato-auroates through a reversible reaction leads to formation of Cleve's sparingly soluble, water-susceptible *monammino-aurous thiocyanate* $AuNH_3SCN$. $Au(SCN)_2^- + NH_3 = AuNH_3SCN + SCN^-$.

The dithiocyanato-auroate ion and compounds containing aurous thiocyanate are *colourless*.

2. *Auric thiocyanate.* We are able to corroborate Cleve's statement that auric thiocyanate does not exist in the solid state and we have prepared two new compounds of Cleve's tetrathiocyanato-auriate type, viz. sodium *tetrathiocyanato-auriate* $NaAu(SCN)_4$ and *tetrathiocyanato-auriate acid* $HAu(SCN)_4$, $2H_2O$. The latter acid can be extracted from an aqueous solution with ether and after drying

of the ethereal solution with sodium sulphate it is obtained with two molecules of water.

*Estimation* of auric thiocyanate in the presence of aurous thiocyanate may be accomplished by titration with sulphite till the colour disappears.

In solution auric thiocyanate is present chiefly as tetrathiocyanato-auriate ion $Au(SCN)_4^-$. The complexity constant of this ion is $10^{17.7}$ times as large as that of the tetrachloro-auriate ion.

$$K_{SCN} = \frac{[Au(SCN)_4^-]}{[Au^{+++}][SCN^-]^4}; \quad K_{Cl} = \frac{[AuCl_4^-]}{[Au^{+++}][Cl^-]^4}; \quad \frac{K_{SCN}}{K_{Cl}} = 10^{17.7}.$$

The tetrathiocyanato-auriate ion is strongly reddish-brown. At $\lambda = 578$ m$\mu$ its molar coefficient of extinction is 108, at $\lambda = 546$ m$\mu$ the coefficient is 2.6 times as great, and at 436 m$\mu$ it is nearly 10 times as great.

At thiocyanate ion concentrations exceeding 0.2 *penta-* and *hexathiocyanato-auriate* ions are present in appreciable quantities. The complexity constants of these complex ions are:

$$K_{Au(SCN)_5} = \frac{[Au(SCN)_5^{--}]}{[Au(SCN)_4^-][SCN^-]} = 1.0; \quad K_{Au(SCN)_6} = \frac{[Au(SCN)_6^{---}]}{[Au(SCN)_5^{--}][SCN^-]} = 1.1.$$

The penta- and hexa-complexes are more strongly coloured than the tetra-complexes. At $\lambda = 578$ m$\mu$ the molar coefficient of extinction of the penta-complex is about 218 and that of the hexa-complex about 248.

At small thiocyanate-ion concentrations and hydrogen-ion concentrations the tetrathiocyanato-auriate ion seems to undergo *hydrolysis* according to the following scheme:

$$Au(SCN)_4^- + H_2O \rightleftarrows Au(SCN)_3OH^- + H^+ + SCN^-.$$

However, even at $[H^+][SCN^-] = 0.01$, this hydrolysis amounts to hardly more than 20 per cent.

Very important in connection with the properties of auric thiocyanate is the *dissociation* of the tetrathiocyanato-auriate ion to dithiocyanato-auroate ion and free thiocyanogen $(SCN)_2$:
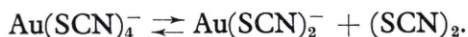
$$Au(SCN)_4^- \rightleftarrows Au(SCN)_2^- + (SCN)_2.$$

At 18° C the dissociation constant has the following value:

$$K = \frac{[Au(SCN)_2^-][(SCN)_2]}{[Au(SCN)_4^-]} = 0.49 \cdot 10^{-4};$$
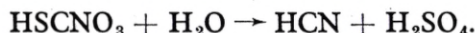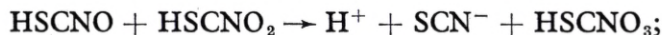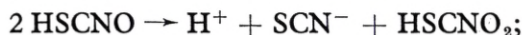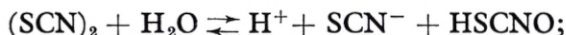
it increases about 8 per cent per degree.

3. *Free thiocyanogen* $(SCN)_2$ is to be regarded as a colourless pseudo-halogen situated between bromine and iodine. It is instantaneously liberated from thio-

cyanates by bromine, and in its turn it immediately liberates iodine from iodides. It is extremely unstable; in aqueous solution it is hydrolyzed according to the following scheme:

$$3(SCN)_2 + 4H_2O \rightarrow 5H^+ + 5SCN^- + HCN + H_2SO_4.$$

This gross process is the result of the following 4 partial processes:

$$(SCN)_2 + H_2O \rightleftharpoons H^+ + SCN^- + HSCNO;$$

$$2HSCNO \rightarrow H^+ + SCN^- + HSCNO_2;$$

$$HSCNO + HSCNO_2 \rightarrow H^+ + SCN^- + HSCNO_3;$$

$$HSCNO_3 + H_2O \rightarrow HCN + H_2SO_4.$$

The second of these partial processes controls by its slow rate the reaction velocity for which the following equation has been shown to be valid:

$$\frac{d[(SCN)_2]}{dt} = -k'[HSCNO]^2 = -k\frac{[(SCN)_2]^2}{[H^+]^2[SCN^-]^2}$$

At 18° C the velocity coefficient $k$ has a numerical value of about 5, and the value increases about 11 per cent per degree.

4. *The auto-reduction.* In solution auric thiocyanate by *auto-reduction* is converted into aurous thiocyanate according to the following equation:

$$3Au(SCN)_4^- + 4H_2O \rightarrow 3Au(SCN)_2^- + 5H^+ + 5SCN^- + HCN + H_2SO_4$$
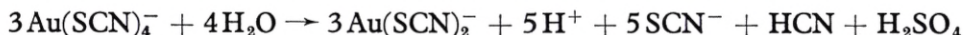
The presence of hydrogen ions, of thiocyanate ions and of aurous thiocyanate strongly depresses the velocity of this autoreduction.

The autoreduction is caused by the instability of the free thiocyanogen arising from dissociation of auric thiocyanate. It has been shown that its rate of reaction can be correctly calculated from the dissociation constant of auric thiocyanate and the velocity of decomposition of free thiocyanogen.

5. *The deposition of gold.* A solution of aurous thiocyanate deposits gold with simultaneous formation of auric thiocyanate according to the following equation:

$$3Au(SCN)_2^- \rightleftharpoons 2Au + Au(SCN)_4^- + 2SCN^-.$$
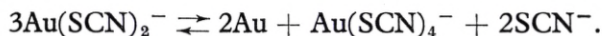
This reaction is reversible, auric thiocyanate dissolving gold with formation of aurous thiocyanate. The *equilibrium constant* of this reversible reaction has the following value:

$$K = \frac{[Au(SCN)_4^-][SCN^-]^2}{[Au(SCN)_2^-]^3} = \text{about } 33.$$

The *velocity* of the gold-dissolving effect of auric thiocyanate, we have not investigated more closely. Concerning the velocity of the reciprocal reaction, the separation of gold from aurous thiocyanate, we have found that with decreasing

concentration of thiocyanate ions it increases rapidly; with decreasing concentration of hydrogen ions it increases slowly. The velocity is catalytically increased by addition of gold powder. In 0.1 $M$ HCl, 0.5 $M$ NaSCN, 0.1 $M$ Au$^I$ at 40° C about half of the gold is deposited during three days.

The joint effect of the autoreduction and the gold deposition is that during a sufficient length of time gold thiocyanate solutions deposit all their gold in metallic form.

6. *The solubility product of sodium auric thiocyanate*, [Na$^+$][Au(SCN)$_4^-$] at 18° C was found to be 0.0005 in a solution 2.2 normal with respect to strong electrolytes and 0.0004 in one 0.6 normal with respect to electrolytes. In the calculation of these values, concentrations were used instead of activities. The solubility product of *potassium auric thiocyanate*, [K$^+$][Au(SCN)$_4^-$], has the value 0.00006 at an electrolyte concentration of 1.4 normal.

7. *Auric chloride.* In a solution of chlorauric acid *in hydrochloric acid* gold is present chiefly as *tetrachloro-auriate ion* AuCl$_4^-$. This ion in solution is hydrolyzed according to the following equation:

$$AuCl_4^- + H_2O = AuCl_3(OH)^- + H^+ + Cl^-.$$

Its *hydrolysis constant* has the following value:

$$K = \frac{[AuCl_3(OH)^-][H^+][Cl^-]}{[AuCl_4^-]} = 0.55 \cdot 10^{-4}.$$

8. The following *standard potentials* have been determined:

| Electrode reaction | Standard potential. $_0E_h$ |
|---|---|
| Au + 2SCN$^-$ = Au(SCN)$_2^-$ + e | 0.689 volts |
| Au(SCN)$_2^-$ + 2SCN$^-$ = Au(SCN)$_4^-$ + 2e | 0.645 – |
| Au + 4SCN$^-$ = Au(SCN)$_4^-$ + 3e | 0.660 – |
| Au + 4Cl$^-$ = AuCl$_4^-$ + 3e | 1.001 – |
| 2SCN$^-$ = (SCN)$_2$ + 2e | 0.769 – |

These values are valid around 18° C. In their calculation ion concentrations were used instead of activities.

9. The value given by *Abegg* and *Campbell* of the *standard potential of gold-aurous ion*, viz. 1.5, is unreliable for in measurements of gold electrode potentials in strong nitric acid saturated with aurous oxide, only the oxidation potential of nitric acid is measured.