Unprecedented μ-1,2,3κ*S* : 4,5κ*N* coordination mode of the thiocyanate anion in two new double salts of silver(I), AgSCN·2AgNO$_3$ and AgSCN·AgClO$_4$

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The double salts AgSCN·2AgNO$_3$ and AgSCN·AgClO$_4$ both feature an unprecedented μ_5-1,2,3κ*S* : 4,5κ*N* coordination mode of the thiocyanate ligand, which generates a two- or three-dimensional network according to the relative coordinating capability of the co-existing nitrate or perchlorate anion.

With the advent of supramolecular chemistry, the coordination concept as applied to metal ions has been extended to polyatomic species such as neutral molecules, organic cations, and anions of various types.[1] In the design of polynuclear metal complexes[2] and the crystal engineering of coordination networks,[3] the possible coordination modes of anionic ligands have to be considered in the synthetic strategy. In this context, it is of interest to determine the highest ligation number[4] (HLN) of simple inorganic polyatomic anions, namely the largest number of coordination bonds that a particular anion can form with neighboring metal centers in its complexes. For example, the HLN of the μ_6-carbonato group in the hexanuclear oxovanadium(IV) cluster $[(VO)_6(CO_3)_4(OH)_9]^{5+}$ is six.[5]

The group 11 metal(I) ions, each having a spherical d^{10} electronic configuration, can in principle serve as ideal probes for obtaining the HLN of small inorganic anions. The synthesis of suitable complexes for such investigations is favored by the tendency of the monovalent coinage metal ions to form aggregates through homoatomic d^{10}–d^{10} interactions.[6,7] Furthermore, silver(I) has distinct advantages over the other members of the coinage triad, as copper (I) is easily oxidized to the +2 oxidation state, and gold(I) has a strong tendency to adopt linear digonal coordination geometry and is also susceptible to disproportionation into Au(III) and Au(0). Our recent studies on the crystal structures of double salts of silver have shown that the cyanide ion has a HLN of four in 3AgCN·2AgF·3H$_2$O,[8] and the azide ion has a HLN of six in AgN$_3$·2AgNO$_3$.[9]

The coordination modes of the ambident thiocyanate ligand[10] in their metal complexes exhibit considerable diversity (Fig. 1), and modes **F**, **H** and **K** are hitherto unknown.[11] Thus far the maximum coordinating capacity of SCN$^-$ involves the formation of two coordination bonds by its nitrogen atom, or three coordination bonds by its sulfur atom, but not simultaneously. Here, we report two novel double salts AgSCN·2AgNO$_3$ **1** and AgSCN·AgClO$_4$ **2**† in which the thiocyanate group exhibits an unprecedented μ_5-1,2,3κ*S* : 4,5κ*N* coordination mode **K** with a HLN of five.

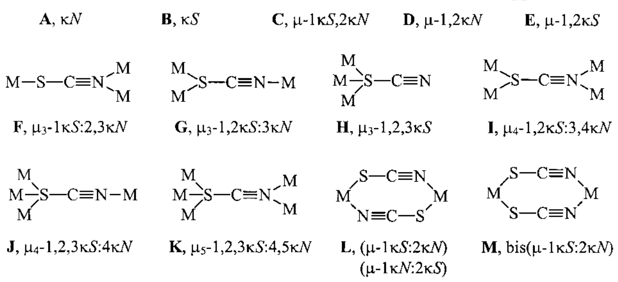
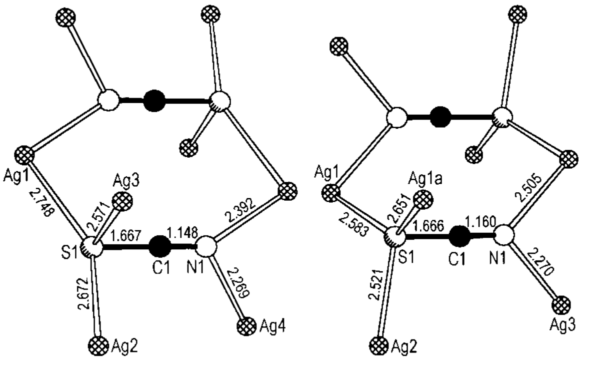


Fig. 1 Possible coordination modes of the thiocyanate ligand.

The crystal structures‡ of both **1** and **2** feature a common centrosymmetric, nearly planar eight-membered (AgSCN)$_2$ ring that has angularly distorted hexagonal geometry, which can be regarded as a basic architectural unit for constructing the coordination network. In each planar heterocycle, there are two 'substituent' silver atoms bonded to each sulfur atom and one 'substituent' silver atom bonded to each nitrogen atom, as shown in Fig. 2. To our knowledge the nearly planar (AgSCN)$_2$ ring moiety with six additional silver atoms attached to it and the resulting μ_5-1,2,3κ*S* : 4,5κ*N* coordination mode of the thiocyanate ligand are both unprecedented.

In the crystal structure of **1**, the basic architectural units share the S-bonded 'substituent' silver atoms of type Ag2 and Ag3 along the $[1\bar{1}0]$ and [110] directions to generate a corrugated layer (Fig. 3), with the nitrate anions located between adjacent layers. One of the two independent NO$_3^-$ anions functions as a tightly bridged ligand to silver atoms of type Ag1 and Ag4 [average Ag–O 2.445(3) Å], and the other as a loosely bridged one to silver atoms of type Ag2 and Ag4 [average Ag–O



AgSCN·2AgNO$_3$, **1** AgSCN·AgClO$_4$, **2**

Fig. 2 Basic architectural units in **1** and **2**, each consisting of a nearly planar eight-membered (AgSCN)$_2$ ring with six 'substituent' silver atoms.

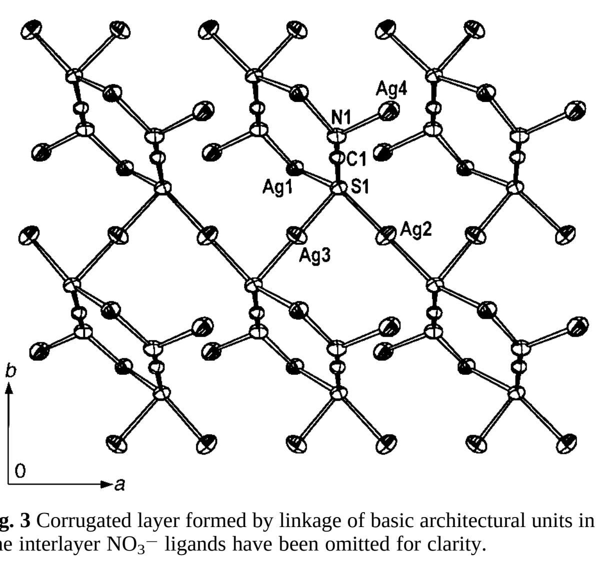


Fig. 3 Corrugated layer formed by linkage of basic architectural units in **1**. The interlayer NO$_3^-$ ligands have been omitted for clarity.

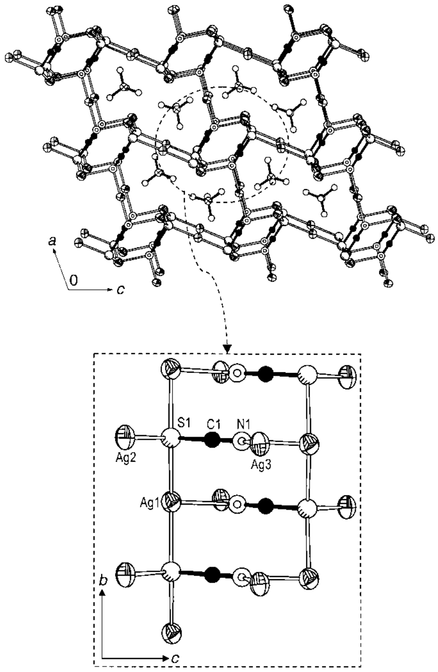


Fig. 4 Crystal structure of **2** viewed along the *b* direction (top), and a hexagonal channel viewed along the *a* direction showing it as a ladder-like chain of fused $(SCN)_2$ rings.

2.579(4) Å], thus linking adjacent layers along the *c* direction into a three-dimensional framework. Interestingly, there co-exist four kinds of coordination modes of silver atoms in **1**, namely linear coordination for type Ag3 atoms at $\bar{1}$ [Ag3–S1 2.571(1) Å], nearly coplanar triangular coordination for type Ag1 atoms [Ag1–N1 2.392(4), Ag1–O2 2.479(3), Ag1–S1 2.748(2) Å, sum of bond angles at Ag1 358.5°], distorted square coordination for type Ag2 atoms at $\bar{1}$ [Ag2–O6 2.566(4), Ag2–S1 2.672(1) Å] and distorted tetrahedral coordination for type Ag4 atoms [Ag4–N1 2.269(4), Ag4–O3 2.411(3) Ag4–O5 2.591(4), Ag4–S1 2.861(2) Å].

In the crystal structure of **2**, fusion of the basic architectural units along the *b* direction generates a ladder-like chain, which takes the appearance of a hexagonal column when viewed in the *b* direction (Fig. 4). The hexagonal columns are connected by sharing the S-bonded Ag2 atoms (site symmetry 2) along the *c* direction and the N-bonded Ag3 atoms (site symmetry $\bar{1}$) along the *a* direction to form a three-dimensional channel-type network, as shown in Fig. 4. The perchlorate anions are stacked as a double column within each channel. In contrast to the nitrate anions in **1**, the perchlorate anions in **2** do not directly bond to silver atoms, leading to lower coordination numbers, namely linear coordination for type Ag2 [Ag2–S1 2.521(2) Å] and Ag3 [Ag3–N1 2.270(6) Å] atoms, and trigonal pyramidal coordination for the type Ag1 atom [Ag1–S1 2.583(2) and 2.651(2), Ag1–N1 2.505(6) Å].

The sulfur and nitrogen atoms of the thiocyanate unit in both **1** and **2** are asymmetrically bonded to silver atoms. The Ag–S and Ag–N distances are significantly longer than those found in AgSCN [Ag–S 2.428(11), Ag–N 2.223(28) Å],[12] respectively, but still fall within the range found in many transition metal thiocyanate complexes.[13] The thiocyanate units in both **1** and **2** are essentially linear. The S–C and C≡N distances of the thiocyanate ligands in **1** [S–C 1.669(4), C–N 1.148(5) Å] and **2** [S–C 1.666(2), C–N 1.160(3) Å] are in good agreement with those found in AgSCN [S–C 1.64(3), C–N 1.19(7) Å][12] and many transition metal thiocyanates.[11] In contrast to AgSCN, in which the cations and anions are arranged alternately to form an infinite zigzag chain such that each silver atom is only bound to one nitrogen and one sulfur atom,[12] the thiocyanate unit bridges five silver atoms in both double salts **1** and **2** to form two- and three-dimensional networks, respectively, resulting in a variety of coordination environments around individual silver atoms.

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Notes and references

† *Synthesis*: AgSCN was prepared by mixing aqueous solutions of ammonium thiocyanate and silver nitrate at room temperature. The white precipitate was filtered, washed several times with de-ionized water, and temporarily stored in wet form in the dark.

Synthesis of $AgSCN\cdot 2AgNO_3$ **1**: wet AgSCN was added to 2 mL of a concentrated MeCN solution of $AgNO_3$ (*ca.* 40%) with stirring until saturated at 40 °C. The excess amount of AgSCN was filtered off, and the solution was placed into a desiccator charged with P_2O_5. In the course of two days colorless crystals of $AgSCN\cdot 2AgNO_3$ were obtained in nearly quantitative yield. The compound is stable when immersed in its mother liquor; it is hygroscopic and slowly decomposes in air.

Synthesis of $AgSCN\cdot AgClO_4$ **2**: the above procedure was repeated using EtOH and silver perchlorate instead of MeCN and silver nitrate, respectively. The distinct difference between the two preparations is that the filtrate of **2** turned from colorless to pale purple and the cyrstals of **2** are pale purple.

‡ *Crystal data*: **1**: colorless prism, Siemens P4/PC diffractometer, Mo-Kα radiation (λ = 0.71073 Å), 2275 unique reflections (R_{int} = 0.0247), 1423 of which with $I > 2\sigma(I)$ were considered as observed, triclinic, space group $P\bar{1}$ (no. 2), Z = 2, D_c = 4.256 g cm^{-3}, a = 6.569(5), b = 7.732(1), c = 8.031(2) Å, α = 104.09(1), β = 93.94(4), γ = 90.04(3)°, V = 394.6(3) Å^3, μ = 76.41 cm^{-1}, $R1$ = 0.0394, GOF = 0.990.

2: pale purple plate, Rigaku RAXIS IIC diffractometer, Mo-Kα radiation (λ = 0.710 73 Å), 1086 unique reflections (R_{int} = 0.0862), 1032 of which with $I > 2\sigma(I)$ were considered as observed, Monoclinic, space group $C2/c$ (No. 15), Z = 8, D_c = 3.958 g cm^{-3}, a = 15.294(4), b = 4.766(1), c = 18.278(4) Å,β = 109.89(2)°, V = 1252.7(5) Å^3, μ = 69.55 cm^{-1}, $R1$ = 0.0642, GOF = 1.116. The structures of **1** and **2** were solved by the direct method (SHELXS-86) and refined by full-matrix least squares on F^2 using the Siemens SHELXTL-93 (PC Version) package of crystallographic software. All non-hydrogen atoms were refined with anisotropic thermal parameters. Results of the crystal structure determination (CSD-410622 and 410623) have been deposited at the Fachinformationszentrum Karlsruhe, D-76344, Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de). CCDC 182/1206. See http://www.rsc.org/suppdata/cc/1999/813/ for crystallographic files in .cif format.

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