

A Molecular Bis(isocyanide)silver(I) Nitrate Complex

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Bis(*p*-tolylsulfonylmethylisocyanide)silver nitrate is obtained from the reaction of the isocyanide ligand with silver nitrate in chloroform regardless of the applied ratio of the reactands (1:1 or 2:1). The crystal structure of the product has been determined. In the complex molecule with C_2 symmetry, the nitrate anion is attached to the silver center as an η^2 -chelating ligand. Owing to this approach of the NO_3 ligand, the RNC-Ag-CNR axis ($\text{R} = 4\text{-Me-C}_6\text{H}_4\text{-SO}_2\text{-CH}_2$) is bent [from 180 to $162.1(2)^\circ$], but the geometry of the nitrate is not significantly distorted, suggesting only weak coordinative bonding. The structure is thus intermediate between that of a molecular complex with a tetrahedral coordination and that of an ionic compound with linear coordination of the silver center.

Key words: Isocyanide Complex, Silver(I) Complex, Nitrate Complex

Introduction

Isocyanide complexes of *gold(I)* of the types $(\text{RNC})\text{AuX}$, $[(\text{RNC})\text{AuL}]^+ \text{X}^-$ and $[(\text{RNC})\text{Au}(\text{CNR})]^+ \text{X}^-$ are currently receiving considerable interest owing to the linear “rigid-rod” structures of their molecules and cations, respectively [1–4]. These structures with strictly two-coordinate Au^+ centers are an excellent basis for the construction of supramolecular frameworks and mesogenic phases, not only assembled *via* standard coordinative bonding, but also supported by Au-Au aurophilic interactions. Many of these aggregates are strongly luminescent, and their photophysical properties can be tuned by selecting appropriate substituents R , auxiliary ligands L and counterions X [5–32].

In several studies of *gold(I)* isonitrile complexes $(\text{RNC})\text{AuX}$ it has been shown that the introduction of the nitrate ligand ($\text{X} = \text{NO}_3$) leads to unusual organizational patterns, very different e. g. from those of the corresponding halides ($\text{X} = \text{Cl}, \text{Br}, \text{I}$). In the aggregates, the linearity of the $\text{N} \equiv \text{C-Au-O}$ axis is always retained and the flat nitrate groups appear to be readily accommodated in the oligomers or polymers [16, 17, 20, 22].

The structures of the *silver(I)* complexes $(\text{RNC})\text{AgX}$, $[(\text{RNC})\text{AgL}]^+ \text{X}^-$ and $[(\text{RNC})_2\text{Ag}]^+ \text{X}^-$ are more flexible, with the Ag^+ centers becoming three- or four-coordinate through significant interactions with additional donor sites of the ligands L or

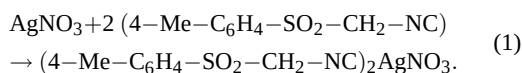
the counterions X . Complexes with trigonal-planar three- and tetrahedral four-coordination are in fact most common, while linear two-coordination of silver(I) by isocyanide ligands is more the exception [33–42]. Recent examples include a series of (isocyanide)silver(I) carboxylates where the RCOO^- groups are in O, O' -bridging positions between silver(I) centers [43]. Similar structural characteristics were found for related complexes with tertiary phosphine ligands [44–47].

In the course of preparative studies in the chemistry of gold(I)/silver(I) isocyanide complexes we have recently obtained and investigated a compound, in which AgNO_3 is the central unit of a 1:2 complex with the ligand $4\text{-Me-C}_6\text{H}_4\text{-SO}_2\text{-CH}_2\text{-NC}$. This isocyanide is commercially available and has been employed as a ligand in earlier studies [48], but structures of the complexes have become known only recently [30]. The title complex has an interesting structure which is reported in this contribution.

Results

The preparative experiments aimed at the synthesis of both 1:1 and 1:2 complexes of AgNO_3 with *p*-tosylmethylisocyanide. However, the reactions with both stoichiometries in chloroform as a solvent were found to give only the 1:2 complex. With the 1:1 stoichiometry, one half of the ligand was recovered and the yield of the 1:2 complex accordingly was close to

50% (equ. (1)). While AgNO_3 is only sparingly soluble in chloroform, it dissolves rapidly upon addition of the isocyanide, and colourless crystals are formed after completion of the reaction. The product can be redissolved in acetone, and from these solutions single crystals of the complex can be grown upon careful layering with pentane at room temperature (m. p. 162°C with decomposition).



Solutions of the complex in chloroform- d_1 show the expected sets of signals in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra. The isocyanide carbon atoms give rise to a broad resonance at δC 165 ppm, with the multiplicity arising from the couplings $J(^{14}\text{N}-^{13}\text{C})$ and $J(^{109/107}\text{Ag}-^{13}\text{C})$ which remain unresolved owing to ligand exchange processes in solution. In the FAB mass spectrum (*p*-nitrobenzyl alcohol matrix) the cation $[(p\text{-TosCH}_2\text{NC})_2\text{Ag}]^+$ is detected at m/z 498 (83%), with $[(p\text{-TosCH}_2\text{NC})\text{Ag}]^+$ (100%) as the parent ion. The solid (in KBr) shows an IR absorption $\nu(\text{NC})$ at 2197.5 cm^{-1} , very similar to the reference value of 2195 cm^{-1} reported for $[(p\text{-Tol})\text{NC}]_2\text{AgNO}_3$ [35].

Crystals of the complex (from acetone/pentane) are monoclinic (space group $C2/c$, $Z = 4$). The unit cell contains some sub-stoichiometric, residual solvent, which was found to be disordered. Cation and anion of the complex are not separated. The nitrate group is attached symmetrically to the silver atom as an $\text{O},\text{O}'\text{-}\eta^2$ chelating ligand. The ion-pair has crystallographically imposed C_2 symmetry with the twofold axis passing through the silver atom and the atoms N11 and O12 of the nitrate group (Fig. 1).

The configuration of the complex cation shows a bending of the $\text{C1-Ag1-C1}'$ axis away from the 180° angle to a value of $162.1(2)^\circ$ which is clearly due to the approach of the nitrate anion. The Ag-O1 distances are $2.571(2)\text{ \AA}$ long, which is in good agreement with standard values for bonding Ag-O contacts. The N-O bond lengths of the nitrate anion are different with N11-O11 (coordinated) at $1.252(3)$ and N11-O12 (non-coordinated) at $1.244(4)\text{ \AA}$ as expected for η^2 -coordinated nitrate, but the deviations of the O-N-O angles from 120° are very small: $120.5(2)$, $118.9(3)^\circ$.

The coordinated isocyanide has distances $\text{Ag1-C1} = 2.106(4)$ and $\text{C1-N1} = 1.133(4)\text{ \AA}$, and angles $\text{Ag1-C1-N1} = 169.7(3)^\circ$ and $\text{C1-N1-C2} = 175.5(3)^\circ$.

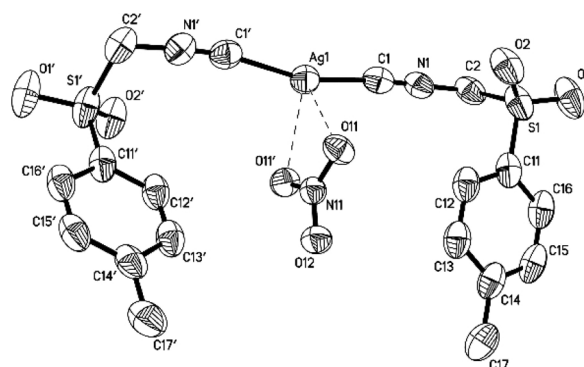


Fig. 1. Molecular structure of bis(*p*-tosylmethylisocyanide)silver(I) nitrate with point group C_2 symmetry (ORTEP, 50% probability ellipsoids, hydrogen atoms omitted). Selected bond lengths [$\text{\AA}$] and angles [$^\circ$]: Ag1-C1 $2.106(4)$, Ag1-O11 $2.571(2)$, S1-O1 $1.435(3)$, S1-O2 $1.440(2)$, S1-C2 $1.795(4)$, S1-C11 $1.744(4)$, N1-C1 $1.133(4)$, N1-C2 $1.415(5)$, N11-O11 $1.252(3)$, N11-O12 $1.244(4)$; $\text{C1-Ag1-C1}'$ $162.08(19)$, Ag1-C1-N1 $169.7(3)$, C1-N1-C2 $175.5(3)$, N1-C2-S1 $110.8(2)$, $\text{O11-N11-O11}'$ $118.9(3)$, O11-N11-O12 $120.53(17)$.

The C1-N1 distance compares well with the value reported for *p*-Tos- CH_2NCAuCl , where $\text{C1-N1} = 1.131(6)\text{ \AA}$ [30]. By contrast, the Ag1-C1 distance of the title compound is very significantly longer than the Au1-C1 reference distance of $1.933(5)\text{ \AA}$ [30], confirming the recently revised order of the standard radii of the coinage metals [49]. All other structural parameters of the isocyanide ligand show no anomalies.

The cation and the complete ion-pair have C_2 symmetry and are thus chiral. The unit cell contains both enantiomers related by a center of inversion.

Discussion

The structure of the title complex appears to represent an intermediate state between a fully ionic extreme with linearly two-coordinate silver in a cation $[\text{RNCaGCNR}]^+$ associated with, but not coordinated to an independent nitrate anion of D_{3h} symmetry on one hand, and an electroneutral complex of tetrahedrally four-coordinate silver ions with the nitrate anion as a chelating ligand of C_{2v} symmetry on the other. This situation reflects the affinity of two-coordinate silver(I) for additional donors including "hard" ligands like NO_3^- . This affinity clearly is aiming not only at trigonal-planar three-coordination, for which the monodentate coordination mode of the nitrate would be sufficient, but rather at four-coordination with chelating nitrate.

And yet the approach of the nitrate anion is not reaching an extreme equilibrium position with tetrahedral angles C-Au-C and C-Au-O: Partly owing to the strain of the four-membered chelate ring, but partly also owing to the reduction of the bond energies of the Au-C bonds associated with the bending of the C-Au-C angle away from linearity, the latter is only compressed to $162.1(2)^\circ$. From the results of an early study of the vibrational spectra of di(*p*-tolylisocyanide)silver(I) nitrate it was concluded that the nitrate resides outside the coordination sphere of the silver atom [36]. However, since the $\nu(\text{CN})$ data are almost the same for the two compounds (2198 vs. 2195 cm^{-1}), an analogous solid state structure can be assumed.

The crystal structure of bis[2,4,6-tri(*t*butyl)phenylisocyanide]silver(I) hexafluorophosphate has been determined and appears to be closely related: the octahedral PF_6^- anion is attached to the silver cation *via* one of its edge to give a molecular structure of C_2 symmetry [39]. The Ag-C and $\text{C}\equiv\text{N}$ distances are $2.075(14)$ and $1.148(17)\text{ \AA}$, respectively, and the C-Ag-C' angle is $156.1(6)^\circ$. This structure confirms the high affinity of two-coordinate silver cations towards anionic ligands including even the poorest donors like CF_3SO_3 or BF_4^- [13]. None of these or other anions [25, 26] becomes attached to the *gold* cations in its 2:1 complexes with isocyanides [1–4].

Because the anions are not tightly bound in compounds of this type, they can be readily mobilized in polar solvents by solvation of the ionic components of the complexes.

Experimental Section

General: The experiments were carried out in dry solvents under nitrogen; Jeol JNM-GX 270 and 400 NMR spectrometers; Finnigan MAT 90 mass spectrometer; Jaseo 460 Plus infrared spectrometer; Kleinfeld Electrothermal IA 9200 melting point apparatus. The reagents were commercially available.

Preparation: *p*-Tolylsulfonylmethylisocyanide (200 mg, 1.02 mmol) was dissolved in 10 ml of chloroform and added to a suspension of silver nitrate (174 mg, 1.02 mmol) in 10 ml of the same solvent with stirring at room temperature. The reaction flask was protected against light. After 3 h the product was recovered by filtration, washed with diethylether and dried in a vacuum; 286 mg (49% yield). In an experiment with the reagents in the molar ratio 2:1 the yield was almost quantitative. Single crystals were grown from an acetone solution upon layering with pentane, m. p. 162°C with decomposition. $\text{C}_{18}\text{H}_{18}\text{AgN}_3\text{O}_7\text{S}_2$

Table 1. Crystal and structure solution data for bis(*p*-tosylmethylisocyanide)silver(I) nitrate.

$[(^p\text{TolSO}_2\text{CH}_2\text{NC})_2\text{Ag}]\text{NO}_3$	
Empirical formula	$\text{C}_{18}\text{H}_{18}\text{AgN}_3\text{O}_7\text{S}_2$
<i>M</i>	560.34
Crystal system	monoclinic
Space group	C2/c
<i>a</i> / $\text{\AA}$	17.0363(6)
<i>b</i> / $\text{\AA}$	13.8518(4)
<i>c</i> / $\text{\AA}$	11.4364(3)
β / $^\circ$	92.2009(10)
<i>V</i> / $\text{\AA}^3$	2696.81(14)
ρ_{calc} / g cm^{-3}	1.380
<i>Z</i>	4
<i>F</i> (000)	1128
$\mu(\text{Mo-K}\alpha)$ / cm^{-1}	9.39
<i>T</i> / K	143
Refls. Measured	8219
Refls. Unique	2344 [$R_{\text{int}} = 0.073$]
Refined param. / restraints	144 / 0
$R1[I \geq 2\sigma(I)]$	0.0381
$wR2^a$	0.1051
Weighting scheme	$a = 0.0589, b = 3.3507$
$\sigma_{\text{fin}}(\text{max/min})$ / $\text{e}\text{\AA}^{-3}$	0.409 / -0.576

^a $wR2 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$.

(560.34): calcd. C 38.12, H 2.93; found C 38.58, H 3.24. NMR (CDCl_3 , 20°C), ^1H : $\delta = 7.85$ (m, 2H, C_6H_4 -2/4), 7.43 (m, 2H, C_6H_4 -3/5), 2.39 (s, 3H, Me); $^{13}\text{C}\{^1\text{H}\}$: $\delta = 165$ (m, NC), 147.4 (s, C_6H_4 -1), 133.1 (s, C_6H_4 -4), 131.4 (s, C_6H_4 -2/6), 129.8 (s, C_6H_4 -3/5), 62.4 (s, CH_2), 22.6 (s, Me). IR(KBr): 2197.5, $\nu(\text{NC})$. MS(FAB): m/z 498 (83.7, L_2Ag); 303 (100, LAg).

Crystal structure determination: A specimen of suitable quality and size was mounted on the end of a quartz fiber in F06206R oil and used for intensity data collection on a Nonius DIP2020 diffractometer, employing graphite-monochromated Mo- $\text{K}\alpha$ radiation. Intensity data were corrected for absorption effects (DELABS from PLATON). The structure was solved by a combination of direct methods (SHELXS-97) and difference-Fourier syntheses and refined by full matrix least-squares calculations on F^2 (SHELXL-97) [50]. The thermal motion of all non-hydrogen atoms was treated anisotropically. All hydrogen atoms were calculated and allowed to ride on their parent atoms with fixed isotropic contributions. During the structure refinement, the atoms of a solvent molecule were observed but could not be modelled satisfactorily. The SQUEEZE routine in PLATON was used to modify the HKL file. Further information on crystal data, data collection and structure refinement are summarized in Table 1. Anisotropic displacement parameters and tables of interatomic distances and angles have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. The data are available on request on quoting CCDC-291990.

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