Antimony as a Donor Atom in Silver Coordination Chemistry: Synthesis, IR Spectra and Structure of the Silver(I) Cyanoximate Complexes with Triphenylstibine and Triphenylphosphine Model Compounds

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Silver(I) cyanoximate complexes Ag$\{$ONC(CN)-R$\}$ (R = COPh, $\{L^1\}$; COC$(CH_3)_3$, $\{L^2\}$; benzothiazol-2-yl, $\{L^3\}$) with triphenylphosphine and -stibine of compositions Ag$(PPh_3)_n\{L\}$ (n = 2, 4) and Ag$(SbPh_3)_n\{L\}$ (n = 3 for $\{L^1\}$ and $\{L^2\}$, n = 2 for $\{L^3\}$) were synthesized by the reaction of the components in acetonitrile solution and characterized by elemental analyses and IR spectroscopy. The crystal structures of Ag$(SbPh_3)_3\{L\}$ (L = $\{L^1\}$ (**1**), $\{L^2\}$ (**2**), Ag$(SbPh_3)_2\{L^3\}\cdot CH_3CN$ (**3**) and Ag$(PPh_3)_2\{L^1\}\cdot CH_3CN$ (**4**), have been determined by X-ray diffraction. For all the compounds examined the coordination environment of the silver atom has the geometry of a distorted terahedron ([AgP$_2$NO] (**4**); [AgSb$_3$N] (**1**), (**2**); [AgSb$_2$N$_2$] (**3**)). The *bis* adducts Ag$(EPh_3)_n\{L\}$ adopt molecular structures, in which the organic anions are coordinated in bidentate chelate fashion *via* the nitroso nitrogen atom and the oxygen (nitrogen for $\{L^3\}$) atom of the substituent R. In the *tris*-stibino complexes (Ag-Sb 2.670(4) - 2.7748(8) Å; Sb-Ag-Sb 108.87(4) - 115.00(2)°) the cyanoximates are unidentate ligands and coordinated *via* the nitroso nitrogen atoms (Ag-N *ca.* 2.35(1) Å). The different behaviour of N,O and N,N chelating cyanoximes under the same conditions suggests, that the Sb donor triphenylstibine is able to substitute the oxygen atoms in the silver(I) coordination sphere, but not the nitrogen ones. This causes the formation of 1:3 adducts of Ag$\{L\}$ with SbPh$_3$ for N,O donors $\{L^1\}$ and $\{L^2\}$, and only 1:2 for N,N donor anionic $\{L^3\}$.

Introduction

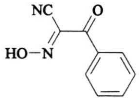
Trisubstituted phosphines and arsines represent are among the most common types of ligands in the coordination chemistry of copper(I), silver(I) and gold(I) [1], and a large number of triphenylphosphine and -arsine complexes M$(EPh_3)_n\{X\}$ (M = Cu, Ag, Au; E = P, As; n = 1 to 4) have been characterized [1 - 3]. The donor abilities of triphenylstibine and, especially, triphenylbismuth are much weaker and their coordination compounds are stable only under special conditions e. g. because of extremely low nucleophilic properties of the counter anions in complexes of composition [Ag$(SbPh_3)_4$]$\{X\}$ (X = ClO_4^-, BF_4^-), Ag$(BiPh_3)\{ClO_4\}$ [4] or [Ag$(SbPh_3)_2\{C_2B_9H_{12}\}]_2$ [5], all prepared from low-basic solvents as diethyl ether and CH_2Cl_2. The factors affecting the formation and stoichiometry of these complexes are not always obvious and it is difficult to predict the stability of inherently weak coordination bonds (*c.f.* Ag-Sb; Ag-Bi) in the presence of usual N,O donor ligands, such as NO_2^-, $(NC)_2CNO^-$, oximes, and dioximes. In this context it was of special interest to synthesize the triphenylstibine and -bismuth complexes of silver(I) cyanoximates Ag$\{$ONC(CN)-R$\}$ (R = functional groups such as cyano, carbamoyl, keto groups, and N-heteroaryls) [6]. In these cases the donor atom sets available for coordination are N_2O_2, N_2O_3, N_3O *etc.* [7] and it was possible to establish some regularities for the formation of Ag-M (M = Sb, Bi) bonds compared to Ag-N and Ag-O bonds. Earlier, we have reported the crystal structure of a polymeric silver(I) benzoylcyanoximate $Ag\{ONC(CN)C(O)Ph\}$ and found that the silver atom is coordinated with both the nitrogen atoms of nitroso and cyano groups (Ag-N 2.18, 2.25 Å) and oxygen atoms of nitroso and carbonyl groups $[AgN_2O_3]$ [8]. The coordination modes of benzoylcyanoximates in metal complexes and the structure of benzoylcyanoximate compounds have been reviewed recently [7].

Following these investigations we were successful in the preparation of 1:2 and 1:3 adducts in the system silver(I)cyanoximate – triphenylstibine, and herein we describe the syntheses and results of X-ray studies of three new $Ag(SbPh_3)$ complexes and the model triphenylphosphine compounds.

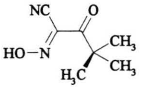
Experimental

Preparation of coordination compounds

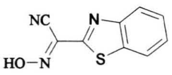
The following oximes, containing functional groups of different steric and donor properties, were used for the study:



$H(L^1)$



$H(L^2)$



$H(L^3)$

Preparations of benzoylcyanoxime $H(L^1)$ [9], pivaloylcyanoxime $H(L^2)$ [10], (benzothiazol-2-yl)cyanoxime $H(L^3)$ [11] and their silver salts $Ag\{L\}$ [7, 8] were as described previously. Triphenylstibine was prepared by the standard Grignard procedure.

The silver complexes were synthesized by reacting $Ag\{L\}$ and $SbPh_3$ in acetonitrile solution. All experiments were carried out in air. For both the N,O chelating cyanoximates, $\{L^1\}^-$ and $\{L^2\}^-$, even with a 1:2 molar ratio of $Ag\{L\}$ and $SbPh_3$ in the reaction mixture, the complexes of composition $Ag(SbPh_3)_3\{L^1\}$ (**1**) and $Ag(SbPh_3)_3\{L^2\}$ (**2**) were isolated, while (benzothiazol-2-yl)cyanoximate for any molar ratio $Ag\{L\}$ / $SbPh_3$ in the solution yielded only the 1:2 adduct $Ag(SbPh_3)_2\{L^3\}\cdot CH_3CN$ (**3**). We were neither successful in the preparation of 1:2 complexes for both the anions $\{L^1\}^-$ and $\{L^2\}^-$, nor in the synthesis of the ionic 1:4 derivatives $[Ag(SbPh_3)_4]\{L\}$.

The interaction in the system $Ag\{L\}$ – PPh_3 differs dramatically and leads to coordination compounds of the types $Ag(PPh_3)_2\{L\}$ and $Ag(PPh_3)_4\{L\}$. We have not observed formation of 1:3 adducts with triphenylphosphine and the reaction using this stoichiometry yields the mixture of 1:2 and 1:4 complexes. The silver(I)-triphenylphosphine 1:3 complex, however, was reported for another cyanoxime, dicyanamide $ONC(CN)_2^-$, which may not act as a chelate [3]. Thus it may be assumed, that the $Ag(PPh_3)_3^+$ core itself is unstable towards the chelating ligands and tends to dismutate into $[Ag(PPh_3)_2\{chelate\}]$ and $[Ag(PPh_3)_4]^+$.

*Tris(triphenylstibine)benzoylcyanoximatosilver(I) $Ag(SbPh_3)_3\{L^1\}$ (**1**)*

To a solution of 0.141 g (0.5 mmol) of $Ag\{L^1\}$ in hot acetonitrile (20 ml) 0.353 g (1 mmol) of $SbPh_3$ was added. The mixture was stirred for 10 min, filtered and allowed to stand at r. t. for a few days. Then large red-violet crystals of the complex were collected and dried in air. Yield 0.415 g (62%). The compound is soluble in acetonitrile, DMF and decomposes in water. The syntheses of $Ag(SbPh_3)_3\{L^2\}$ (**2**) and $Ag(SbPh_3)_2\{L^3\}\cdot CH_3CN$ (**3**) complexes were carried out in a similar fashion and 1:2 complexes with triphenylphosphine (*cf.* $Ag(PPh_3)_3\{L^1\}\cdot CH_3CN$ (**4**)) were prepared analogously starting with PPh_3.

*Tetrakis(triphenylphosphine)silver(I) pivaloylcyanoximate $[Ag(PPh_3)_4]\{L^2\}$ (**7**)*

To a solution of 0.131 g (0.5 mmol) of $Ag\{L^2\}$ in hot acetonitrile (20 ml) 0.524 g (2 mmol) of PPh_3 was added. The mixture was stirred for 10 min, filtered and the transparent yellow solution obtained was evaporated to a volume of about 10 ml and cooled to r. t. The yellow prismatic crystals of the complex deposited were filtered off and washed with cold acetonitrile. The yield was 0.458 g (70%). The compound is soluble in hot acetonitrile and DMF.

The analytical data of the complexes are presented in Table I.

Measurements

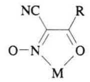
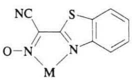
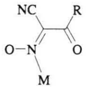
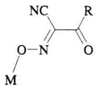
IR spectra were recorded on a Carl Zeiss (Jena) UR-10 spectrometer in KBr pellets (400 - 4000 cm^{-1}). The characteristic IR absorptions of the silver complexes, alkali metal salts and tetraphenylantimony compounds are presented in Table II.

Lattice parameters and the orientation matrix for data collection were obtained from least squares refinement of the setting angles of 24 reflections with $12 < \theta < 15°$. Intensity data were collected at 293(2) K using graphite-monochromatized MoKα radiation ($\omega/2\theta$ scans, λ = 0.71073 Å). Table III lists details of cell parameters, data acquisition and structure refinement. Corrections for Lorentz and polarisation effects were applied.

Table I. Analytical data of the silver(I) cyanoximate complexes.

Compound	Colour	Formula	FW	— Found [%] –			— Calcd [%] —		
				C	H	N	C	H	N
1 $Ag(SbPh_3)_3\{L^1\}$	red-violet	$C_{63}H_{50}AgN_2O_2Sb_3$	1340.2	56.02	3.80	2.12	56.46	3.76	2.09
2 $Ag(SbPh_3)_3\{L^2\}$	yellow	$C_{61}H_{54}AgN_2O_2Sb_3$	1320.2	55.11	4.01	2.13	55.49	4.12	2.12
3 $Ag(SbPh_3)_2\{L^3\}\cdot CH_3CN$	yellow-brown	$C_{47}H_{37}AgN_4OSSb_2$	1057.2	52.90	3.30	4.94	53.39	3.53	5.30
4 $Ag(PPh_3)_2\{L^1\}\cdot CH_3CN$	red-violet	$C_{47}H_{38}AgN_3O_2P_2$	846.6	66.40	4.31	4.61	66.67	4.52	4.96
5 $Ag(PPh_3)_2\{L^2\}$	pink	$C_{43}H_{39}AgN_2O_2P_2$	785.6	65.92	5.07	3.68	65.74	5.00	3.57
6 $Ag(PPh_3)_2\{L^3\}$	yellow-brown	$C_{45}H_{34}AgN_3OP_2S$	834.6	65.01	4.13	5.31	64.75	4.11	5.04
7 $Ag(PPh_3)_4\{L^2\}$	yellow	$C_{79}H_{69}AgN_2O_2P_4$	1310.1	71.65	5.54	2.08	72.42	5.31	2.14

Table II. Vibrational frequences in the infrared spectra and their assignments, cm^{-1}.

Compound	Coordination mode	ν(C≡N)	ν(C=O)	ν(N-O)	$\Delta\nu_{(N-O)}$ [a]
$Ag(PPh_3)_2\{L^1\}\cdot CH_3CN$		2195	1595	1265	+100
$Ag(PPh_3)_2\{L^2\}$		2200	1600	1280	+30
$Ag(PPh_3)_2\{L^3\}$		2195	1495 [b]	1290	+75
$Ag(SbPh_3)_2\{L^3\}\cdot CH_3CN$		2200	1495 [b]	1295	+80
$Ag(SbPh_3)_3\{L^1\}$		2195	1610	1295	+130
$Ag(SbPh_3)_3\{L^2\}$		2210	1630	1280	+30
$(C_6H_5)_4Sb\{L^1\}$ [9]		2210	1628	1130	-35
$(C_6H_5)_4Sb\{L^2\}$ [10]		2210	1662	1130	-120
$Cs\{L^1\}$	ionic	2205	1620	1165	-
$K\{L^2\}$	ionic	2205	1635	1250	-
$Ag(PPh_3)_4\{L^2\}$	ionic	2205	1630	1225	-25
$Cs\{L^3\}$	ionic	2200	1510	1215	-

[a] With respect to those for the ionic alkali metal salts; [b] $-\nu(C=N)$ (benzothiazole).

The structures were solved by direct methods and subsequent Fourier difference techniques.

The structures of **2** and **3** were refined by full-matrix least-squares techniques in the anisotropic approximation. All hydrogen atoms were placed in calculated positions with their isotropic U values set invariant at 0.08 Å^2. In the structure **3** the high thermal motion of atoms of the nitrile group (for N(3) U_{eq} = 0.18(2) Å^2) and the inexact bond angle C(1)-C(3)≡N(3) of 154(4)° indicated possible disorder, but all attempts to use a split-atom model with different partial occupancies were not successful.

An examination of residual electron density features in the structure **1** showed the oximic ligand to be almost equally disordered [57(1) and 43(1)%] over two positions. This may be attributed to the large size of the $Ag(SbPh_3)_3\{L^1\}$ molecules and insensitivity of the packing to the conformations of the coordinated ligand. For the same reason the $Ag(SbPh_3)_3\{L\}$ complexes (**1**) and (**2**) appeared to be actually isostructural (Table III). Resolution of the disorder was possible by introducing a rigid model for the "A" (43(1) %) component of the disordered phenyl group with C-C separations and C-C-C bond angles fixed at 1.39 Å and 120°, respectively. No constraints in bond distances and bond angles were applied for the major component of the disordered phenyl ring, and the carbon atoms C(5-9) and C(5a-9a) were refined isotropically only. The refinement of the disorder model proceeded satisfactorily, and therefore the hydrogen atoms were included in the refinement as fixed contributions with their isotropic U values set invariant at 0.08 Å^2.

Refinements were terminated with all non-hydrogen parameter shifts < 0.05 σ; the weighting schemes were $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $3P = (2F_c^2 + F_o^2)$ and a and b are constants adjusted by the program. All structural calculations were carried out using SHELXS-86 and SHELXL-93 [12, 13]. Convergence was obtained at the values given in Table III.

Further details of the structure determination, atomic coordinates, thermal parameters, and bond lengths and angles can be ordered from Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository numbers CSD-410268 (**1**), CSD-410269 (**2**), CSD-410270 (**3**) and CSD-410271 (**4**).

Results and Discussion

The main vibrational frequencies ν(C≡N), ν(C=O) and ν(N-O) for the compound $Ag(PPh_3)_4\{L^2\}$ do not differ essentially from those of the potassium salt (Table II), suggesting thus an ionic nature of the *tetrakis* complex. Formation of the bulky tetrahedral cation $[Ag(PPh_3)_4]^+$ is a characteristic feature of the Ag^+ – triphenylphosphine system [1]. Unlike this specimen the IR spectra of the compounds $Ag(SbPh_3)_n\{L\}$ (*n* = 2, 3) and $Ag(PPh_3)_2\{L\}$ reveal substantially higher values of ν(NO) as compared to those of the ionic alkali metal cyanox-

Table III. Experimental data for $Ag(SbPh_3)_3\{L^1\}$ (**1**), $Ag(SbPh_3)_3\{L^2\}$ (**2**), $Ag(SbPh_3)_2\{L^3\}\cdot CH_3CN$ (**3**), $Ag(PPh_3)_2\{L^1\}\cdot CH_3CN$ (**4**).

	1	**2**	**3**	**4**
Formula	$C_{63}H_{50}AgN_2O_2Sb_3$	$C_{61}H_{54}AgN_2O_2Sb_3$	$C_{47}H_{37}AgN_4OSSb_2$	$C_{47}H_{38}AgN_3O_2P_2$
Formula weight	1340.2	1320.2	1057.2	846.6
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1$
a (Å)	14.558(5)	14.105(3)	11.08(2)	9.184(1)
b (Å)	14.226(4)	14.533(3)	13.54(1)	17.107(1)
c (Å)	27.680(9)	27.480(5)	15.90(2)	13.949(1)
α (°)	90	90	94.2(1)	90
β (°)	94.70(3)	92.46(3)	107.5(1)	106.64(1)
γ (°)	90	90	101.9(1)	90
V (Å^3)	5713(3)	5628(2)	2201(5)	2099.8(3)
Z	4	4	2	2
D_{calc} (g cm^{-3})	1.558	1.558	1.595	1.339
F(000)	2632	2600	1040	868
μ(MoKα) (cm^{-1})	17.84	18.10	17.45	5.97
Diffractometer	Siemens R3m/V	CAD-4 Enraf Nonius	Siemens R3m/V	Stoe STADI-4
$2\theta_{max}$ (°)	40.1	43.9	38.1	58.0
Index ranges	h 0-14, k 0-13, $l \pm 26$	h 0-14, k 0-15, $l \pm 28$	h 0-10, $k \pm 12$, $l \pm 13$	$h \pm 12$, k 0-23, $l \pm 19$
Reflections collected	5513	7222	3634	7160
Unique data (R_{int})	5254 (0.031)	6884 (0.023)	3399 (0.030)	6800 (0.021)
Obs. refls ($I > 2\sigma(I)$)	4404	4997	2696	4186
Data used	5231	6588	3398	5227
Parameters refined	655	622	505	496
R(F), wR(F^2) (obs.)	0.040, 0.093	0.034, 0.086	0.076, 0.194	0.031, 0.076
GOF on F^2	1.069	1.061	1.182	1.084
Largest peak and hole (e Å^{-3})	0.57/–0.38	0.81/–0.77	1.75/–1.45	0.64/–0.40

imates, indicating N-coordination of the nitroso group [7, 14]. A similar increase of ν(NO) was described earlier for cyanoximate complexes of copper(II) and nickel(II) [7, 9], while O-coordination of the nitroso group in organoantimony(V) and organotin(IV) complexes (Table II) effects the shift of ν(NO) to lower wavenumbers [15]. A certain decrease of the ν(C=O) frequencies in the spectra of *bis* phosphine complexes $Ag(PPh_3)_2\{L\}$ ($\Delta_{\nu(C=O)}$ = 25 - 35 cm^{-1}) reflects also the formation of Ag-O=C coordination bonds, so that for these compounds the IR data support bidentate chelate coordination of the cyanoximate anion via the nitroso nitrogen and carbonyl oxygen atoms. Judging by the values of ν(C=N) (benzothiazole) absorptions (Table II), the same suggestions may be made for $Ag(PPh_3)_2\{L^3\}$ and $Ag(SbPh_3)_2\{L^3\}\cdot CH_3CN$. A similar coordination mode was observed earlier for $Cu(H_2O)\{L^1\}_2$ (ν(C=O) and ν(N-O) at 1600 and 1360 cm^{-1}, respectively) [7]. The decrease of the ν(C=O) frequency in the spectra of *tris* stibine complexes $Ag(SbPh_3)_3\{L\}$ is much lower ($\Delta_{\nu(C=O)}$ = 5 - 10 cm^{-1}). This suggests that in $Ag(SbPh_3)_3\{L\}$ complexes the carbonyl groups of the ligands take no part in coordination, or that the Ag-O=C bonds (if present) are essentially ionic. The latter possibility was confirmed earlier for $Cu(4\text{-}MePy)_2\{L^1\}_2$ (ν(C=O) 1600 and 1620 cm^{-1}) [16]. Thus we may conclude that the organic anions in the *bis* complexes $Ag(EPh_3)_2\{L\}$ (E = P, Sb) are coordinated in a bidentate chelate fashion, in the *tris* complexes $Ag(SbPh_3)_3\{L\}$ they are N-monodentate ligands, and in the *tetrakis* complex $Ag(PPh_3)_4\{L_2\}$ the anion is not coordinated.

The IR spectroscopic data agree with the results of the X-ray study. $Ag(PPh_3)_2\{L^1\}\cdot CH_3CN$ adopts a molecular array, the acetonitrile of crystallization is not coordinated. The silver atom is coordinated in a distorted tetrahedron by two phosphorus atoms (Ag-P 2.440(1), 2.441(1) Å; P(1)-Ag-P(2) 126.60(3)°) and the nitroso nitrogen and the carbonyl oxygen atom of the chelating ligand (Fig. 1). A similar environment of the metal atom was proposed also for $Cu(PPh_3)_2\{ONC(CN)C(NH)OCH_3\}$

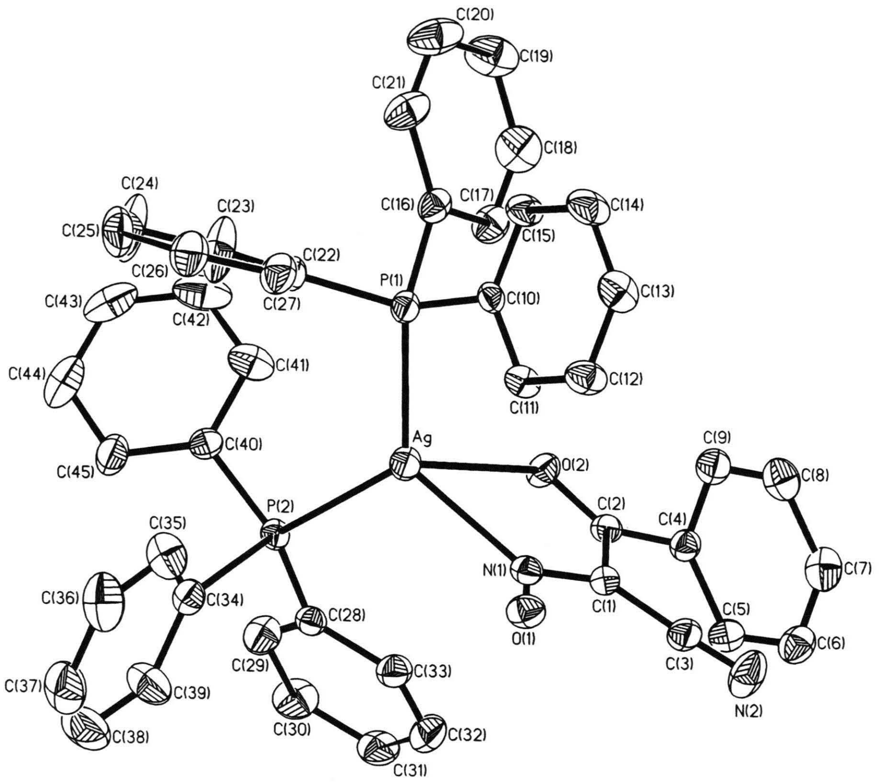


Fig. 1. Perspective view with 40% probability thermal ellipsoids of $Ag(PPh_3)_2\{L^1\}\cdot CH_3CN$ (**4**). Hydrogen atoms and solvate CH_3CN are omitted for clarity. Selected bond lengths and angles (Å,°):

Ag-N(1)	2.341(3)
Ag-P(1)	2.440(1)
Ag-P(2)	2.441(1)
Ag-O(2)	2.515(2)
N(1)-Ag-P(1)	115.0(1)
N(1)-Ag-P(2)	116.1(1)
P(1)-Ag-P(2)	126.60(3)
N(1)-Ag-O(2)	67.49(9)
P(1)-Ag-O(2)	108.87(9)
P(2)-Ag-O(2)	103.74(8)

Table IV. Main geometrical parameters (Å,°) of the benzoylcyanoximate $\{L^1\}$ in **1**, **4**, $2H(L^1)\cdot(18\text{-crown-}6)\cdot 4H_2O$ (**8**) [6], $Rb(18\text{-crown-}6)\{H(L^1)_2\}$ (**9**) [22], $Ph_4Sb\{L^1\}$ (**10**) [9], $Tl\{L^1\}$ (**11**) [8], $Ag\{L^1\}$ (**12**) [8] and $Cu(H_2O)\{L^1\}_2$ (**13**) [7].

	1[a]	**4**	**8**	**9**	**10**	**11**	**12**	**13**
Configuration	*cis-anti*	*cis-anti*	*trans-anti*	*trans-anti*	*trans-anti*	*trans-anti*	*cis-anti*	*cis-anti*
Coordination of ONC	N	N	$NOH{-}{-}{-}OH_2$	NO---H---ON	O	μ^2-O	N,O	N
N(1)-O(1)	1.26(2)	1.259(4)	1.362(2)	1.316(4)	1.30(1)	1.31(1)	1.28(1)	1.249(4)
N(1)-C(1)	1.27(1)	1.342(4)	1.286(2)	1.294(5)	1.32(1)	1.33(1)	1.34(1)	1.340(5)
C(1)-C(2)	1.48(3)	1.455(5)	1.489(3)	1.475(5)	1.47(1)	1.46(1)	1.46(1)	1.442(6)
C(2)-O(2)	1.31(3)	1.227(4)	1.218(2)	1.210(4)	1.22(1)	1.24(1)	1.23(1)	1.253(4)
C(1)-C(3)	1.42(2)	1.443(5)	1.449(3)	1.428(6)	1.45(1)	1.44(1)	1.42(1)	1.449(5)
C(3)-N(2)	1.16(2)	1.134(5)	1.141(9)	1.134(5)	1.15(1)	1.14(1)	1.13(1)	1.129(5)
C(2)-C(4)	1.61(3)	1.488(5)	1.482(2)	1.487(5)	1.48(1)	1.51(1)	1.49(1)	1.468(6)
O(1)-N(1)-C(1)	118(1)	118.0(3)	114.3(2)	114.6(3)	113.2(7)	115.7(8)	117.7(9)	120.7(3)
N(1)-C(1)-C(2)	110(2)	117.3(3)	118.6(2)	119.5(3)	123.7(8)	122.7(8)	118.5(9)	114.8(3)
N-(1)-C(1)-C(2)-O(2)	–1(2)	6.9(8)	153.8(2)	–158.1(8)	177.2(8)	172(1)	–166(1)	1.9(9)

[a] Disordering of the ligand effects in accuracy in the bond lengths and angles; the values are given for the major component.

[3, 17]. The five-membered chelate ring is planar and the deviation of the silver atom from the N(1)C(1)C(2)O(2) mean plane does not exceed 0.050(1) Å. The Ag-N(1) separations of 2.341(3) Å are slightly longer than those found in the structure of $Ag\{L^1\}$ (2.254(8) Å) [8], while the Ag-O(2) bond length is shortened (2.515(2) *versus* 2.670(8) Å) and is comparable to Ag-N(1). A certain unification of the Ag-N and Ag-O separations may be ascribed to an effect of the formation of a genuine chelate ring. At the same time, the structure of $Ag\{L^1\}$ exhibits a typical collinear N,N coordination at the silver atom

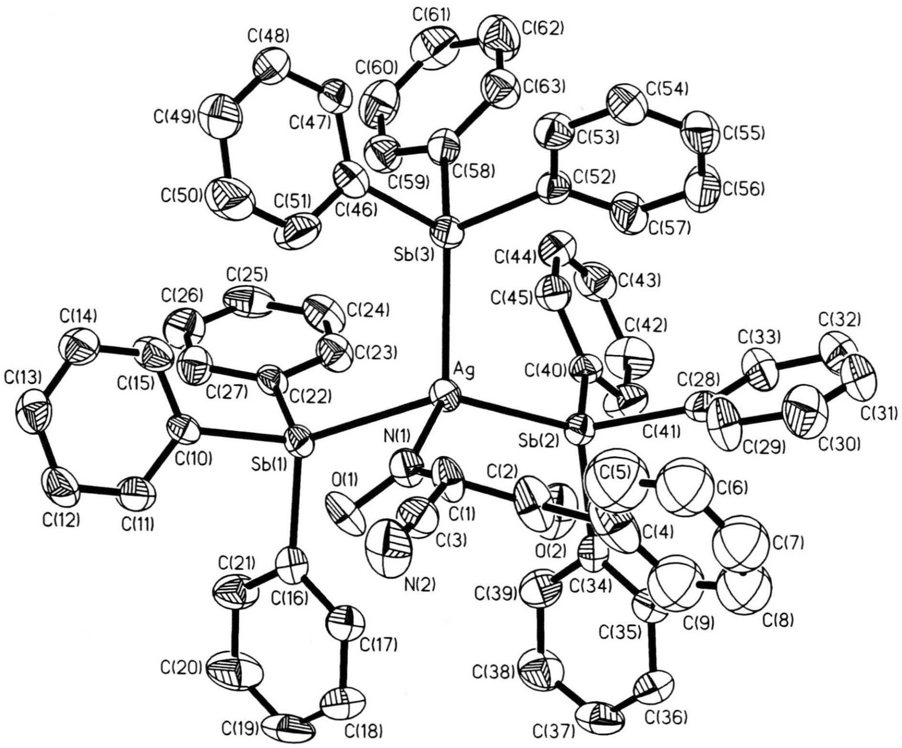


Fig. 2. Molecular structure of $Ag(SbPh_3)_3\{L^1\}$ (**1**) with 40% probability thermal ellipsoids. Only the major orientation of the disordered anion is shown. Selected bond lengths and angles (Å, °): Ag-Sb(1) 2.751(1), Ag-Sb(2) 2.712(1), Ag-Sb(3) 2.721(1), Ag-N(1) 2.349(9), Sb(1)-Ag-Sb(2) 114.84(3), Sb(1)-Ag-Sb(3) 112.08(4), Sb(2)-Ag-Sb(3) 108.87(4), N(1)-Ag-Sb(1) 87.9(3), N(1)-Ag-Sb(2) 124.6(2), N(1)-Ag-Sb(3) 107.0(3).

via nitroso and nitrilic nitrogen atoms, with an additional weak Ag-O bond [1, 8]. The N(1)-Ag-O(2) angles are the same for both compounds (67.49(9) and 67.5(3)° respectively).

The geometrical parameters of benzoylcyanoximate are accurate and allow a direct comparison with the data reported earlier. The C-C, C(3)-N(2) and C(2)-O(2) bond lengths are insensitive to the effects of coordination and are actually the same for all the benzoylcyanoximate species (Table IV). At the same time, coordination of the nitrogen (oxygen) atoms of the oximic group by the metal centers disturbs the electronic structure of the CNO fragment significantly, as reflected by the differences in the bond lengths for main types of coordination compounds (Table IV). The N(1)-O(1) and N(1)-C(1) bond lengths of 1.259(4) and 1.342(4) Å, respectively, are actually the same like those of $Cu(H_2O)\{L^1\}_2$ (1.259(4) and 1.333(5) Å) [7]. These separations suggest a nitroso character C-N=O of the oximic group. The CNO bond angles are almost 120°, while for the O-coordinated benzoylcyanoximate another structure may be proposed, in which the N-O bond lengths are equal to or exceed the C-N one (Table IV). Unfortunately, the disordering and high thermal motion in the structures **1** and **2** preclude any discussion of the anion geometry for these compounds.

The molecular structure of the silver-triphenylstibine complexes and the refined disordering model for coordinated benzoylcyanoximate in **1** are depicted in Fig. 2 - 5. In all the compounds under consideration the coordination polyhedron of the silver atoms is a distorted tetrahedron with nitroso nitrogen (Ag-N at 2.349(9) and 2.359(5) Å) and three antimony atoms [Ag-Sb separations are in the range 2.6898(8) - 2.7748(8) Å] in **1** and **2** [$AgNSb_3$], and two nitrogen and two antimony atoms [Ag-Sb 2.670(4); 2.682(3) Å] in **3** [AgN_2Sb_2]. In the *tris* stibine complexes **1** and **2** all the Sb-Ag-Sb bond angles lie within the range of 108.87(4) - 115.00(2)°, the almost per-

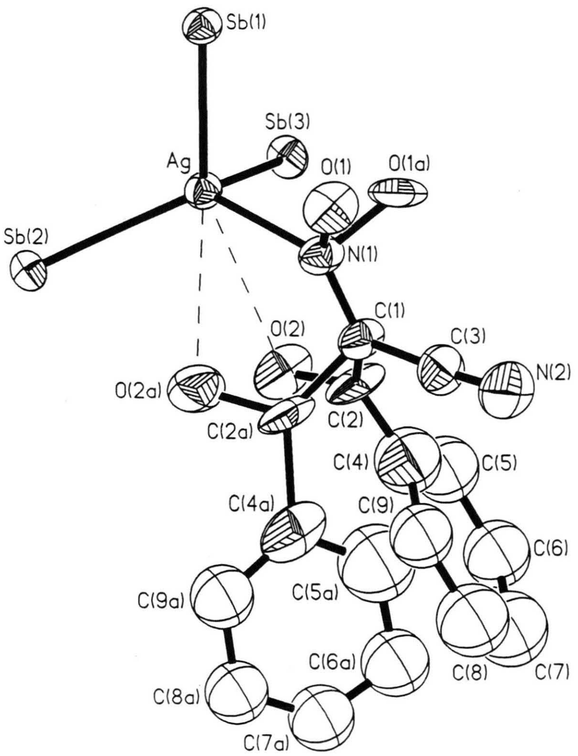


Fig. 3. The refined disordering model of the anion in the structure of **1**. The angle between the two orientations [O(1)-N(1)-O(1a)] is *ca.* 56(2)° ("A" is a minor component [43(1)%]). Ag---O(2), Ag---O(2a) are 2.93(1) and 2.81(1) Å.

fect values for a tetrahedral environment. The distorted tetrahedral coordination is the most common for silver(I) complexes with triphenylphosphine, -arsine and stibine $[Ag(EPh_3)_2\{X\}]$, $[Ag(EPh_3)_3\{X\}]$ and $[Ag(EPh_3)_4]\{X\}$ (E = P, As, Sb) [1].

In $Ag(SbPh_3)_2\{L^3\}\cdot CH_3CN$ the angle Sb-Ag-Sb of 121.2(2)° agrees well with this parameter of $[Ag(SbPh_3)_2\{C_2B_9H_{12}\}]_2$ (118.5(1)°) [5] and is somewhat smaller than the P-Ag-P angles in $Ag(PPh_3)_2$ complexes (126.60(3)° for **4** and 132.83(4)° for dimeric $[Ag(PPh_3)_2\{ONC(CN)_2\}]_2$ [3]). This may be attributed to the longer Ag-Sb separations as compared with the Ag-P data (2.67 - 2.71 Å *versus* 2.42 Å as average of 27 Ag-PPh_3 complexes [2]) and the weaker steric repulsion of the EPh_3 ligands (E = P, Sb) in $Ag(SbPh_3)_2$ complexes. The organic anion is coordinated in a bidentate chelate manner *via* the nitrogen atoms of the nitroso and heteroaryl groups (Fig. 5). Both Ag-N separations [2.36(2) and 2.43(3) Å] are comparable with those found for **1** and **2**. The cyanoxime is actually planar [within 0.10(2) Å] and has a *cis-anti* configuration of the CNO group with respect to the benzothiazole nitrogen atom (torsion angle N(2)-C(2)-C(1)-N(1) is 2(1)°). The *cis* orientation of both nitrogen atoms is stabilized by coordination to the metal center, while the neutral molecule $H(L^3)$ [18] and both the anionic forms $\{L^3\}^-$ and $H(L^3)_2{}^-$ [in $[Cs_2(18\text{-crown-}6)_3]\{H(L^3)_2\}_2\cdot 2H(L^3)\cdot 2H_2O]$ [19] possess the more favourable *trans-anti* configuration. In the five-membered chelate ring the silver atom deviates by 0.33(1) Å from the mean plane N(1)C(1)C(2)N(2). The geometrical parameters of the anion within the values of standard deviation (±0.03 Å) agree with that reported for $[Cs_2(18\text{-crown-}6)_3]\{H(L^3)_2\}_2\cdot 2H(L^3)\cdot 2H_2O$ [19] and $Tl(18\text{-crown-}6)\{H(L^3)_2\}$ [20].

There are no coordinative bonds of the type Ag-O with nitroso groups, and long contacts Ag-O (with the carbonyl group) in structures **1** and **2** are found at 2.81(1), and 2.93(1) and 2.725(6) Å (for two orientations of the disordered ligand), respectively. These distances are essentially longer than the usual values for silver(I) complexes (*ca.* 2.20 - 2.50 Å [1]) and even slightly exceed the Ag-Sb separations in the title compounds. Evidently, these long Ag-O contacts are determined by the structure of the ligands (*trans-anti* configuration of the nitroso group with respect to carbonyl) and may be ascribed to an only weak van der Waals interaction between the atoms. The same observation for the configuration and coordination mode of benzoylcyanoximate $\{L^1\}^-$ was made for $Cu(4\text{-MePy})_2\{L^1\}_2$ [7, 16]. It should be noted in this context that in coordination compounds with N,O donor ligands the silver atom tends to demonstrate preferably N coordination, very often forming two collinear short Ag-N bonds (2.15 - 2.30 Å) [1, 8].

We suppose that weak donor groups such as triphenylstibine may substitute the oxygen atoms in the silver coordination sphere, but not the nitrogen atoms in the AgN_2 chelate ring. The large volume of Sb coordinated triphenylstibine makes the realization of coordination numbers of the silver atom higher than four ($[AgN_2Sb_2]$ or $[AgNSb_3]$) impossible. This is a possible reason for the different behaviour of triphenylphosphine and -stibine in silver(I) cyanoximates. Thus, PPh_3 easily substitutes even the nitroso nitrogen atoms in the silver co-

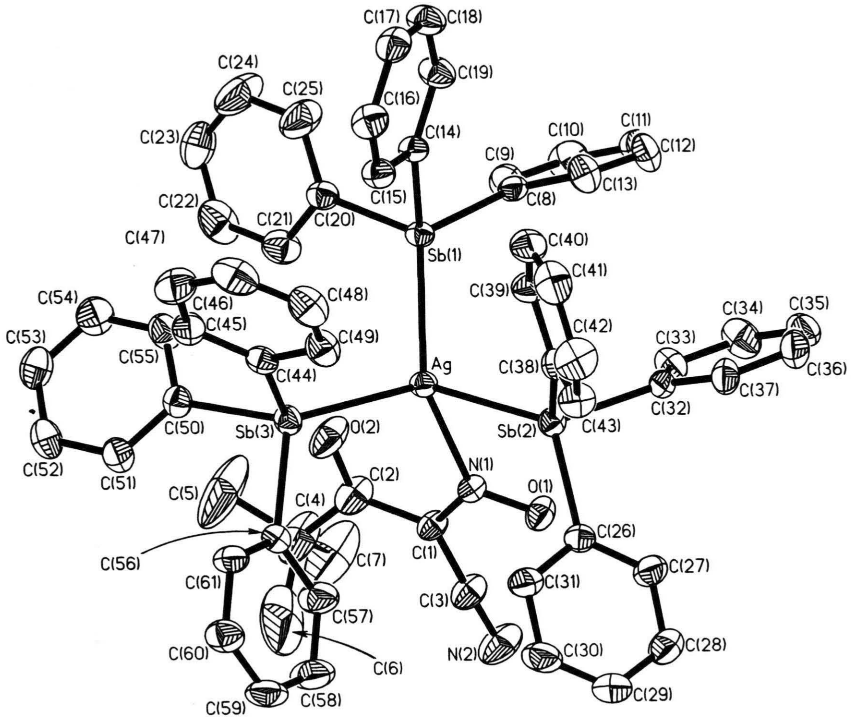


Fig. 4. Molecular structure of $Ag(SbPh_3)_3\{L^2\}$ (**2**), with 40% probability thermal ellipsoids. Selected bond lengths and angles (Å,°):

Ag-N(1)	2.359(5)
Ag-Sb(1)	2.6898(8)
Ag-Sb(2)	2.7748(8)
Ag-Sb(3)	2.7080(8)
O(1)-N(1)	1.265(6)
N(1)-C(1)	1.320(8)
C(1)-C(2)	1.45(1)
N(1)-Ag-Sb(1)	121.7(1)
N(1)-Ag-Sb(3)	113.8(1)
Sb(1)-Ag-Sb(2)	115.00(2)
Sb(3)-Ag-Sb(2)	109.55(3)
O(1)-N(1)-C(1)	118.6(5)
C(1)-N(1)-Ag	125.2(4)

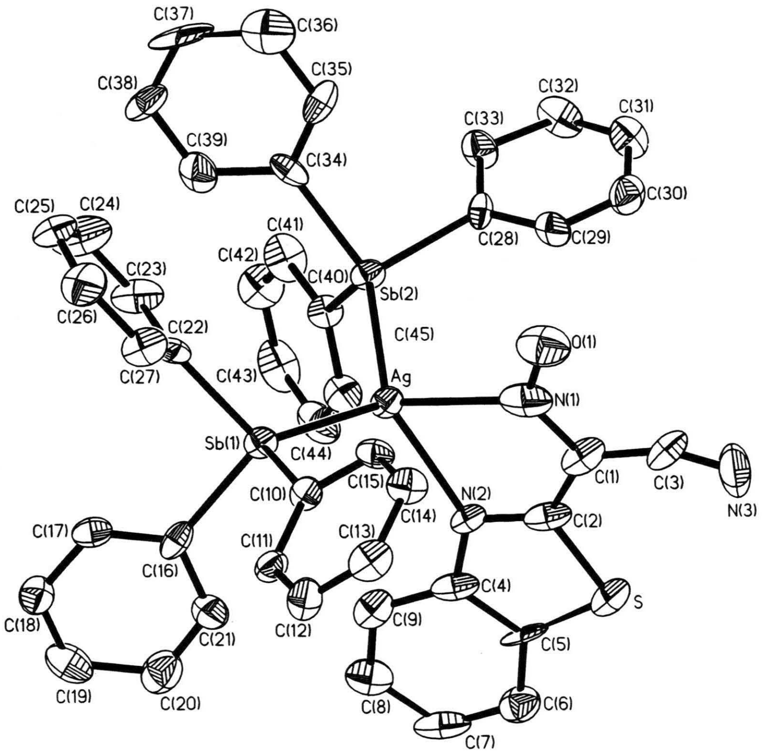


Fig. 5. Molecular structure of $Ag(SbPh_3)_2\{L^3\}\cdot CH_3CN$ (**3**), with 30% probability thermal ellipsoids. Acetonitrile of crystallization omitted. Selected bond lengths and angles (Å,°):

Ag-Sb(1)	2.670(4)
Ag-Sb(2)	2.682(3)
Ag-N(1)	2.43(3)
Ag-N(2)	2.36(2)
O(1)-N(1)	1.19(2)
N(1)-C(1)	1.38(3)
Sb(1)-Ag-Sb(2)	121.2(2)
N(1)-Ag-Sb(1)	113.4(5)
N(1)-Ag-Sb(2)	111.3(4)
N(2)-Ag-Sb(2)	113.5(4)
N(1)-Ag-N(2)	70.5(8)

ordination sphere with formation of $[Ag(PPh_3)_4]^+$, while $[Ag(SbPh_3)_4]^+$ appears to be unstable to N donor nucleophiles. The potentially N,O chelating oximate ions (*c.f.* $\{L^1\}^-$, $\{L^2\}^-$ or carbamoylcyanoximates $\{ONC(CN)C(O)NR_2\}$ ([6, 14]) in the coordination compounds of that type may act as N monodentate groups, and N,N chelating oximates (*c.f.* $\{L^3\}^-$ and 2-pyridylcyanoximate [21]) as N,N bidentate chelating ligands. Therefore, the maximum ratio $SbPh_3/Ag^+$, which may be reached for these systems even in the presence of an excess of triphenylstibine in the reaction mixture, is 3:1 for N,O donor and 2:1 for N,N donor chelating cyanoximates, as confirmed by the present study.

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