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Formation of Gold(I) Halide and Thiocyanate Complexes in Pyridine and Acetonitrile and the Structures of Gold(I) Solvates in These Solvents. A Thermodynamic and EXAFS Spectroscopic Study

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The thermodynamics of the formation of gold(I) halide and thiocyanate complexes in pyridine and acetonitrile has been studied by means of potentiometric and calorimetric measurements at 25 °C. All solutions contained 0.1 M tetraethylammonium ions; perchlorate was used as a supplementary anion. Changes of free energies, enthalpies, and entropies could be determined for the two mononuclear complexes formed in each system, except for the iodide and thiocyanate complexes in acetonitrile, where only the formation of the second complex could be studied. The solubility was too low for the neutral thiocyanate complex, and gold(I) was reduced when the iodide/gold ratio was <2. The complexes are much less stable in pyridine than in acetonitrile, certainly due to the stronger solvation of Au^+ in the former solvent. The formation reactions are characterized by very large entropy gains. These are moreover much the same as those in the corresponding copper(I) and silver(I) systems, where the complex formation is known to involve a rearrangement of a tetrahedral solvate into a complex with only two tightly coordinated ligands. An analogous lowering of the coordination number therefore most probably takes place in the case of gold(I), in spite of the fact that the crystallized solvates are two-coordinated. Structural studies of gold(I) solutions by means of the EXAFS technique have fully confirmed this inference for both solvents. The Au–N distances are 2.16 and 2.19 Å in pyridine and acetonitrile, respectively, which is about 0.2 Å longer than in the corresponding two-coordinated solid solvates. Similar differences in metal–ligand distance are found between two- and four-coordinated complexes of other d^{10} acceptors, not only for the monovalent copper(I) and silver(I) but also for the divalent mercury(II). In pyridine and acetonitrile solutions, gold(I) thus certainly exists as a tetrahedral solvate.

Introduction

This study is part of an extensive investigation of the solvation and complex formation of the monovalent d^{10} acceptors copper(I), silver(I), and gold(I) in solvents of various donor properties. These acceptors command a special interest as forming the central group in the triangular area of soft acceptors found among the transition metals of the periodic system.[2] They are thus prone to form markedly covalent bonds with a variety of soft donors. This tendency increases strongly within the period, which implies that gold(I) might be considered as the archetype of a soft acceptor.[3] The present study deals with the formation of halide and thiocyanate complexes of gold(I) in the solvents pyridine and acetonitrile, as well as with the structures of the gold(I) solvates present in these solvents in the absence of coordinating ligands.

Analogous studies have already been conducted of the lighter congeners copper(I) and silver(I). The thermodynamics of the formation of copper(I) halide and thiocyanate complexes has been investigated in water,[4] dimethyl sulfoxide (Me_2SO),[5] acetonitrile,[6] pyridine,[7] and tetrahydrothiophene (THT)[8] by a combination of potentiometric and calorimetric measurements. In water, the disproportionation of copper(I) into copper(II) and copper(0) prevents a complete determination of the thermodynamics. The disproportionation is also appreciable in Me_2SO, and air oxidation easily occurs. In the solvents acetonitrile, pyridine, and THT, however, copper(I) is so strongly solvated relative to copper(II) that no disproportionation takes place. Further, the strong solvation of copper(I) in aprotic solvents makes the neutral complexes CuL, L = Cl, Br, I, SCN, sufficiently soluble for calorimetric measurements, which demand metal concentrations in solution of at least a few millimolar. For silver(I), the low solubility of AgL in all but the most strongly solvating solvents has restricted the investigations to pyridine[7] and THT solutions.[8]

In the copper(I) halide systems investigated in acetonitrile[6] and pyridine[7] two mononuclear species, CuL and CuL_2^-, L = Cl, Br, I, are formed in the concentration range studied. With thiocyanate, a third mononuclear copper(I) complex is formed in acetonitrile. Silver(I) in pyridine forms three mononuclear complexes with chloride and bromide and two with iodide and thiocyanate, besides dimeric complexes Ag_2L^+, L = Cl, Br, I, SCN. For the formation of the first two complexes, very large entropy increases are found, which indicate that the reactions involve a decrease of the coordination number of the acceptors. The solid acetonitrile and pyridine solvates of copper(I) and silver(I) are found to be regular tetrahedra.[9-11] An X-ray absorption spectroscopy study of the copper(I) solvates showed that both XANES (X-ray absorption near edge structure) and EXAFS (extended X-ray absorption fine structure) are almost identical for the solvates in solid form and in solution.[12] This means that the copper(I) pyridine and acetonitrile solvates are tetrahedral also in solution. For both solvates, the Cu–N distance is moreover practically the same in solution as that in the solid phase (cf. Table V). Likewise, LAXS (large-angle X-ray scattering) studies of the silver(I) solvates in pyridine and acetonitrile solutions have shown that these solvates have the same structure as the solid solvates that can be crystallized from such solutions; again, the bond distances are practically the same in the solutions as in the phases[13,14] (cf. Table V). EXAFS studies of the dihalocuprate(I) complexes in acetonitrile have shown that no solvent molecules are present in the inner coordination sphere; the same most probably applies also to pyridine.[15] The coordination is therefore most probably linear. For $CuCl_2^-$ and $CuBr_2^-$, this is unequivocally confirmed by the fact that the bond distances Cu–Cl = 2.11 Å and Cu–Br = 2.22 Å are practically the same as those found in

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the strictly linear ions present in the solids $[(C_4H_9)_4N][CuCl_2]$ and $[(C_4H_9)_4N][CuBr_2)$.[16] No solid containing CuI_2^- has so far been found, but the short bond distance Cu–I = 2.49 Å in dilute acetonitrile solution again strongly indicates a linear complex.

For gold(I), the disproportionation in aqueous solution is even more extensive than that for copper(I). The reaction $3Au^+ \rightleftarrows Au^{3+} + 2Au(s)$ is displaced so far to the right that the disproportionation constant $K_D = [Au^{3+}]/[Au^+]^3$ (M^{-2}) is difficult to determine. In principle, K_D can be calculated from the standard potentials $E_{01}°$ and $E_{03}°$ of the couples $Au(s)/Au^+$ and $Au(s)/Au^{3+}$, according to $\ln K_D = [(E_{01}° - E_{03}°)/RT](3F)$. As neither $E_{01}°$ nor $E_{03}°$ can be directly determined by emf measurements, the values arrived at depend upon more or less accurate assumptions. For $E_{01}°$, the situation is further complicated by the disproportionation of Au(I). The most elaborate attempt,[17] where the Edwards equation is applied in order to account for the special chemical character of the acceptors involved, results in $E_{01}° = 1.83$ V and $E_{03}° = 1.52$ V, corresponding to a value of $\log K_D = 15.7$. Compared to the classical values[18] of $E_{01}° = 1.68$ V and $E_{03}° = 1.50$ V, corresponding to $\log K_D = 9.1$, the present value of the $E_{01}°$ is thus considerably higher, while the values of $E_{03}°$ do not differ much.

In aprotic solvents, on the other hand, the monovalent state completely predominates. For acetonitrile, this was realized qualitatively by the preparation[19] of the stable solid solvate $Au(CH_3CN)_2ClO_4$, the structure of which is under investigation.[20] Later, it was quantitatively shown[21] that, in the absence of complexing ligands, Au^+ was formed in acetonitrile at the anodic oxidation of Au(s). No Au^{3+} ions are formed even at extremely high oxidation potentials.[22] In the presence of chloride, the complex $AuCl_2^-$ is formed at fairly low potentials, while the further oxidation to $AuCl_4^-$ requires much higher potentials.[21] The Au^+ ion is also formed in Me_2SO by anodic oxidation of Au(s).[23] Values of 1.49[23] and 1.41 V[24] (relative to the normal hydrogen electrode in Me_2SO) have been found for the $Au(s)/Au^+$ couple in Me_2SO. From the free transfer energy of the proton from water to Me_2SO[25,26] $\Delta G_{tr}° = -18.8$ kJ/mol, it follows that the potential of the normal hydrogen electrode in Me_2SO is −0.20 V on the conventional scale, i.e. referred to $E°(H_2(g)/H^+) = 0$ in aqueous solution. On this scale, $E_{01}° = 1.21$ V in Me_2SO (using the lower value, 1.41 V, of those reported above). This $E_{01}°$ value is much lower than the value in water, reflecting the stabilization of Au^+ due to the stronger solvation in the aprotic solvent. A further oxidation of Au^+ does not occur before Me_2SO is oxidized. As might be expected, a similar stabilization of gold(I) takes place also in pyridine, as will be shown below.

Experimental Section

Materials. Solvents were purified as previously described.[6,7] A solution of gold(I) perchlorate in acetonitrile was prepared by oxidation of gold foil with nitrosyl perchlorate.[19] The exact concentration of gold(I) was determined from the equivalence points found in the potentiometric measurements. Since the gold(I) concentration decreases on exposure to light and moisture, preparation and storing of the solutions were performed in a drybox placed in a dark room. A pyridine solution of gold(I) perchlorate was prepared by addition of pyridine to the gold(I) acetonitrile solution and subsequent evaporation of the acetonitrile under reduced pressure at room temperature. A complete exchange of acetonitrile for pyridine could be achieved as gold(I) has a markedly higher affinity for pyridine than for acetonitrile.[21] The tetraethylammonium salts were dried and analyzed as described elsewhere.[6]

Thermodynamic Measurements. The thermodynamic measurements were carried out at 25 °C. As previously, the ionic medium contained 0.1 M $(C_2H_5)_4N^+$, with perchlorate as the supplementary anion.[6,7]

(a) Potentiometric Measurements. Data for the calculation of stability constants were obtained by titration of gold(I) solutions with solutions of the ligand concerned. The initial concentration of gold(I) was within the range $0.1 \leq C_M \leq 3.3$ mM in acetonitrile and $1.2 \leq C_M \leq 2.6$ mM in pyridine. The total ligand concentration, C_L, never exceeded 6 mM in any titration. The emf's were measured by a gold electrode in the gold(I) solution, with a silver electrode, Ag(s)/10 mM Ag^+, as reference. In solutions containing no coordinating ligand, the emf varied with the gold(I) concentration according to Nernst's law. The liquid-junction potentials were assumed to be negligible. In pyridine all titrations and in acetonitrile the chloride and bromide titrations were performed as previously described.[6] In acetonitrile, the iodide caused a reduction of Au^+ for iodide/gold ratios <2. However, by addition of aliquots of gold(I) solution to the ligand solution, the stability of the second complex could be established. The neutral thiocyanate complex was precipitated in acetonitrile solution, so that also in this system only the stability of the second complex could be determined.

(b) Calorimetric Measurements. An automatic titration calorimeter was used.[27] To an initial volume of 60 mL of gold(I) solution were added aliquots of ligand solution, and the changes of thermistor resistance, ΔR, were measured. The heat evolved, $Q > 0$, or consumed, $Q < 0$, is calculated from $Q = \epsilon_v(\Delta R - \Delta R_{dil})$ where ΔR_{dil} is the change of thermistor resistance due to the heat of dilution of the ligand. The calibration constant, ϵ_v, depends upon the volume, V mL, according to $\epsilon_v = a + bV$ J Ω^{-1}. The values of a and b depend upon solvent and apparatus. They were determined from measurements of a calibration resistance at various volumes.[28] The initial concentrations of gold(I) were $1 \leq C_M \leq 8$ mM in acetonitrile and $1 \leq C_M \leq 9$ mM in pyridine. For Au^+, the heat of dilution was negligible in both solvents for the concentration ranges used. The total ligand concentrations were <18 mM. In acetonitrile, the heat of dilution was 0.08 J mL^{-1} for $(C_2H_5)_4NCl$ but negligible for the other $(C_2H_5)_4N^+$ salts. In pyridine, the heats of dilution were negligible for all ligands used. No measurements involving iodide and thiocyanate were done in acetonitrile due to difficulties in performing back-titrations with the air-sensitive gold solution.

(c) Calculations. The computer program EMK[29] was used for the numerical calculations of the stability constants. These were then used as fixed parameters in the program KALORI[30] for the calculation of the enthalpy changes.

EXAFS Measurements. (a) Data Collection and Analysis. X-ray absorption data were collected at the Stanford Synchrotron Radiation Laboratory (SSRL) by using an unfocused 8-pole wiggler beam line (IV-1) under dedicated conditions (3.0 GeV, 20–50 mA). The radiation was monochromatized by a Si(220) double-crystal monochromator. The spectra were measured in transmission mode with an average of four scans collected per sample. The X-ray absorption spectra were converted to an energy scale with the internal calibration method[31] assigning the first inflection point of the gold L_{III} edge of gold foil as 11 912 eV. The data reduction was performed by using standard procedures for preedge subtraction, spline-fit and subtraction, normalization, and Fourier filtering.[32,33] The normalized background-subtracted data were converted to k space by assuming a threshold energy (E_0) of 11 930 eV. The photoelectron vector k is defined as $k = (2m_e(E - E_0)/h^2)^{1/2}$, where m_e is the electron mass and h is Planck's constant. The curve-fitting analysis of the EXAFS spectra utilized a parametrized expression for the phase shift and amplitude, which were determined from EXAFS measurements of a model compound.[32,33] All curve fitting was based on least-squares minimization using k^3-weighted data. Fourier filtering was used to isolate the first backscattering shell. In the fits, the distance, the Debye–Waller factor, and the number of atoms in each given shell were allowed to vary.

(b) Model Compound. Solid $KAu(CN)_2$ was used as a model compound for obtaining phase and amplitude parameters. The crystal structure of $KAu(CN)_2$ has been determined, but the Au–C distance

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Table I. Overall Stability Constants (β_j/M^{-j}) of Gold(I) Halide and Thiocyanate Complexes in Acetonitrile and Pyridine at 25 °C, Ionic Medium 0.1 M $(C_2H_5)_4NClO_4$[a]

	ligand				
	Cl^-	Br^-	I^-	SCN^-	ref
			Pyridine		
β_1	$(2.43 \pm 0.10) \times 10^5$	$(1.93 \pm 0.03) \times 10^5$	$(1.81 \pm 0.11) \times 10^6$	$(4.25 \pm 0.03) \times 10^4$	*b*
β_2	$(1.31 \pm 0.07) \times 10^9$	$(2.49 \pm 0.05) \times 10^9$	$(7.9 \pm 0.4) \times 10^{11}$	$(2.30 \pm 0.20) \times 10^8$	*b*
NP	76	76	76	76	
			Acetonitrile		
β_1	$(8.8 \pm 0.9) \times 10^{11}$	$(1.2 \pm 0.2) \times 10^{12}$			*b*
β_2	$(1.1 \pm 0.2) \times 10^{20}$	$(5.1 \pm 1.0) \times 10^{20}$	$(1.0 \pm 0.5) \times 10^{23}$	$(9.8 \pm 4.1) \times 10^{19}$	*b*
NP	154	105	23	31	
β_1	1.4×10^{12}	9.5×10^{11}			21
β_2	8.7×10^{19}	1.2×10^{20}		1.5×10^{20}	21
β_1	1×10^{12}				22
β_2	3×10^{20}		6×10^{23}		22, 39

[a] The limits of error refer to three standard deviations; NP denotes the number of observations (emf's measured) for each system. [b] This work.

Table II. Overall Enthalpies ($\Delta H_{\beta_j}°$/kJ mol^{-1}) for the Formation of Gold(I) Halide and Thiocyanate Complexes in Acetonitrile and Pyridine at 25 °C, Ionic Medium 0.1 M $(C_2H_5)_4NClO_4$[a]

	ligand			
	Cl^-	Br^-	I^-	SCN^-
		Pyridine		
$\Delta H_{\beta_1}°$	1.9 ± 0.9	-0.1 ± 0.9	-7.8 ± 1.6	-4.5 ± 0.7
$\Delta H_{\beta_2}°$	4.9 ± 1.1	0.6 ± 1.7	-6.1 ± 1.5	-3.7 ± 0.8
NP	100	86	85	55
		Acetonitrile		
$\Delta H_{\beta_1}°$	-21.6 ± 1.5	-36.4 ± 1.8		
$\Delta H_{\beta_2}°$	-27.9 ± 3.0	-46.5 ± 3.5		
NP	42	34		

[a] The limits of error refer to three standard deviations; NP denotes the number of observations.

reported is evidently not very precise.[34] In recent years, however, the structures of several other compounds containing the $Au(CN)_2^-$ unit have been precisely determined.[35,36] In these, the Au–C distance is 1.97 Å. Since the structure of the $Au(CN)_2^-$ unit certainly is largely independent of the cation, we have presently presumed this distance also in $KAu(CN)_2$. In principle, a model containing short Au–N distances would of course have been preferable. In practice, however, the well-characterized and easily available $KAu(CN)_2$ might be as good a choice, especially as the difference in scattering power between C and N is small.

(c) Studied Solutions. An ≈60 mM gold(I) perchlorate acetonitrile solution and an ≈40 mM gold(I) perchlorate pyridine solution were prepared by evaporating solvent from the solutions obtained by dissolving gold foil (see Materials).

Results

Thermodynamic Measurements. As the value of $E_{01}°$ for the couple $Ag(s)/Ag^+$ versus NHE in water is known for both solvents, viz. 0.25 V in pyridine[37] and 0.574 V in acetonitrile,[38] the values of $E_{01}°$ for the couples $Au(s)/Au^+$ on the conventional scale can be calculated from the potentiometric measurements. The values found are $E_{01}° = 0.80$ V in pyridine and 1.511 V in acetonitrile, to be compared with the values 1.83 V in water[17] and 1.21 V in dimethyl sulfoxide, quoted above.

In both solvents, two mononuclear complexes are formed in all the systems studied, within the ranges of metal and ligand concentrations presently used. The overall stability constants, β_j, are listed in Table I. The complexes are much more stable in acetonitrile than in pyridine. The values found for the gold(I) halides in acetonitrile agree rather well with those of previous investigations.[21,22,39] The overall enthalpy changes, $\Delta H_{\beta_j}°$, are given in Table II. In pyridine, these are all small; in acetonitrile, they are larger and exothermic.

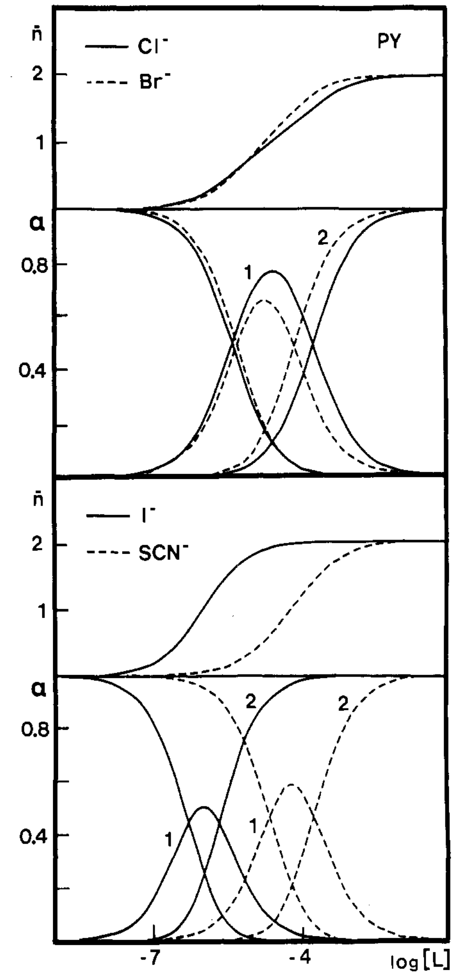

Figure 1. Complex formation and distribution functions of gold(I) halide and thiocyanate species in pyridine.

The stepwise stability constants, K_j, are listed in Table III, and the enthalpy changes, $\Delta H_j°$, in Table IV. The latter table also lists the values derived for the changes in free energy, $\Delta G_j°$, and entropy, $\Delta S_j°$. For comparison, corresponding data determined previously[6,7] for silver(I) and copper(I) have also been entered in this table. In pyridine, the stabilities of the first gold complexes follow the mixed sequence $Cl^- > Br^- < I^-$, while the second complexes show a (b) sequence[2] of $Cl^- < Br^- < I^-$. In acetonitrile,

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Table III. Equilibrium Constants (K_j/M^{-1}) for the Stepwise Formation of Gold(I) Halide and Thiocyanate Complexes in Acetonitrile and Pyridine at 25 °C, Ionic Medium $(C_2H_5)_4NClO_4$

	pyridine				acetonitrile	
	Cl^-	Br^-	I^-	SCN^-	Cl^-	Br^-
log K_1	5.38	5.28	6.26	4.63	11.95	12.06
log K_2	3.74	4.12	5.63	3.73	8.08	8.64
K_1/K_2	45	15	4.2	7.9	7340	2650

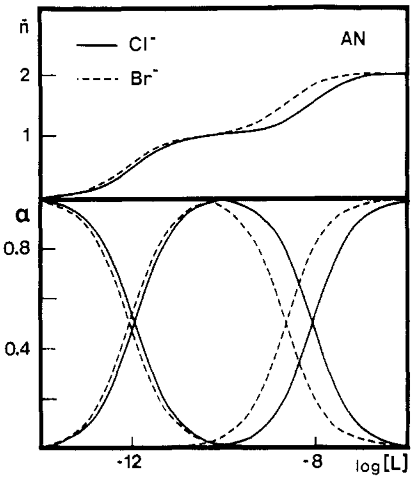

Figure 2. Complex formation and distribution functions of gold(I) chloride and bromide species in acetonitrile.

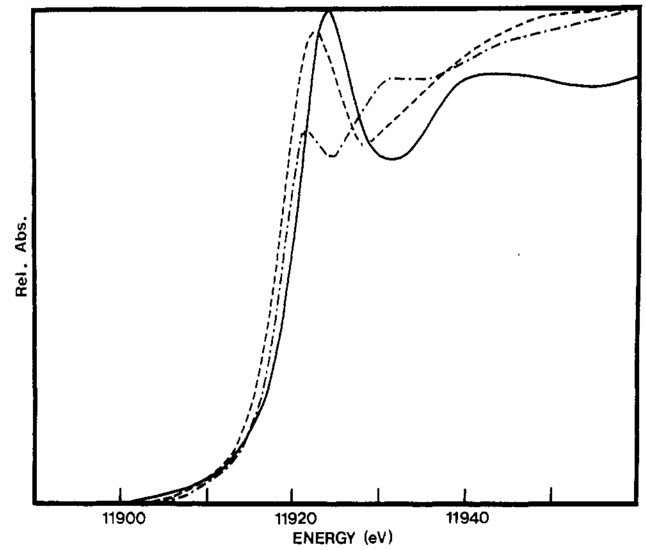

Figure 3. Gold L_{III} absorption edges for $KAu(CN)_2(s)$ (dashed line), $AuClO_4$ in acetonitrile (continuous line), and $AuClO_4$ in pyridine (dotted–dashed line).

both steps display a mild (b) sequence, $Cl^- < Br^-$. The first complexes are strong relative to the second ones in this solvent, as seen from the high K_1/K_2 ratios. In pyridine these values are, on the other hand, not very high. In both solvents, the ratio is larger for chloride than for the other halides. These conditions are also reflected in the complex formation and distribution functions in Figures 1 and 2. In acetonitrile, the large exothermic values of $\Delta H_1°$ contribute substantially to the high stability of the first steps. The entropy terms, $\Delta S_j°$, are all large and positive, with the values for acetonitrile markedly higher than those for pyridine.

XAS Measurements. (a) Edge Structure. The shapes of the gold(I) L_{III} edges of the three species studied are different (Figure 3). The energy of the gold(I) edge for $KAu(CN)_2(s)$, 11 919 eV, is somewhat lower than those for the gold(I) pyridine and acetonitrile solvates. The differences are 0.8 and 1.6 eV, respectively (Figure 3). This indicates that the effective charge on the gold atom decreases in the sequence acetonitrile > pyridine > cyanide; i.e., the gold–donor bond becomes more covalent in the order expected from previous thermodynamic and spectroscopic measurements.[21,40,41]

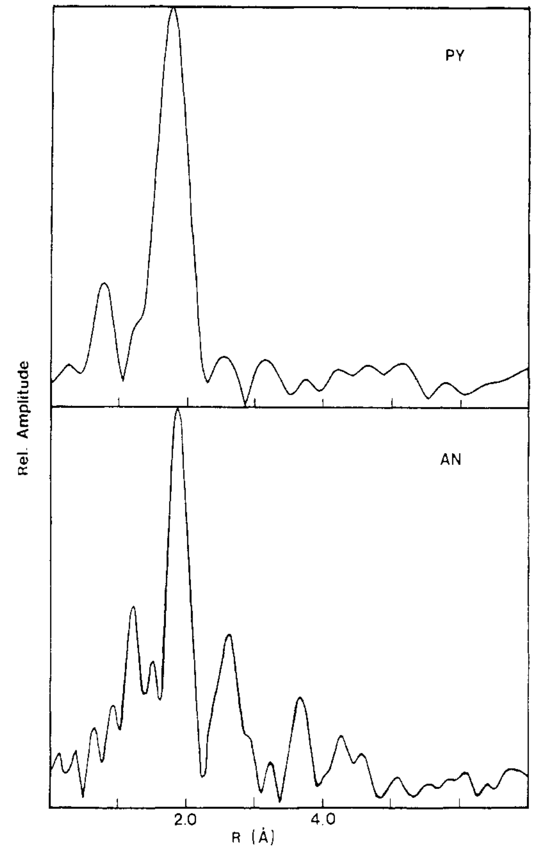

Figure 4. Transforms of gold(I) pyridine and acetonitrile solvates in solution.

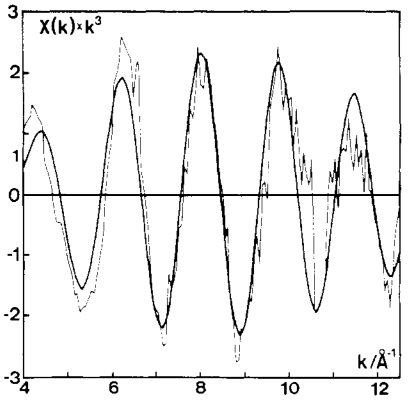

Figure 5. Curve fitting of unfiltered data of the gold(I) pyridine solvate: experimental data, thin line; theoretical model, thick line.

(b) EXAFS. In both the acetonitrile and pyridine solutions, the Fourier transforms of the EXAFS data for gold(I) perchlorate indicate the presence of a single shell of scatterers at 2.1–2.2 Å (Figure 4). On the basis of the chemical properties of these

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Table IV. Thermodynamic Functions ($\Delta G_j°$, $\Delta H_j°$/kJ mol^{-1}; $\Delta S_j°$/J mol^{-1} K^{-1}) for the Stepwise Formation of Copper(I), Silver(I), and Gold(I) Halide and Thiocyanate Complexes in Pyridine and Copper(I) and Gold(I) Complexes in Acetonitrile

	copper(I)				silver(I)				gold(I)			
	Cl^-	Br^-	I^-	SCN^-	Cl^-	Br^-	I^-	SCN^-	Cl^-	Br^-	I^-	SCN^-
Pyridine												
$-\Delta G_1°$	17.6	15.9	15.4	15.0	28.3	28.7	39.2	20.8	30.7	30.1	35.7	26.4
$-\Delta G_2°$	10.9	6.3	~5	6.9	20.6	19.5	18.3	11.0	21.4	23.5	32.1	21.3
$-\Delta H_1°$	-13.0	-10.2	-8.5	-4.7	-1.0	3.3	12.3	1.5	-1.9	0.1	7.8	4.5
$-\Delta H_2°$	-17.3	-20.0		-6.9	-7.6	-6.7	-3.8	-0.1	-3.0	-0.7	-1.7	-0.8
$\Delta S_1°$	103	87	80	66	98	85	90	65	109	101	94	73
$\Delta S_2°$	95	88		46	95	88	74	37	82	81	113	74
$-\Delta G_{\beta_2}°$	28.5	22.1	~20	21.9	48.8	48.2	57.5	31.7	52.1	53.6	67.8	47.7
$-\Delta H_{\beta_2}°$	-30.3	-30.2		-11.6	-8.6	-3.3	8.5	1.4	-4.9	-0.6	6.1	3.7
$\Delta S_{\beta_2}°$	197	175		112	193	173	164	102	191	182	207	148
Acetonitrile												
$-\Delta G_1°$	23.0	19.3	17.9	20.2					68.2	68.8		
$-\Delta G_2°$	31.6	21.8	16.2	20.3					46.1	49.3		
$-\Delta H_1°$	-16.8	-10.5	-8.5	5.4					22	36		
$-\Delta H_2°$	-4.4	-16.7	-12.8	-6.0					6	10		
$\Delta S_1°$	133	100	89	50					156	109		
$\Delta S_2°$	121	129	97	88					134	131		
$-\Delta G_{\beta_2}°$	54.5	41.1	34.1	40.4					114.3	118.2		
$-\Delta H_{\beta_2}°$	-21.1	-27.2	-21.3	-0.6					28	46		
$\Delta S_{\beta_2}°$	254	229	186	138					290	240		

complexes, this shell must represent Au–N scattering. This qualitative interpretation is confirmed by the quantitative curve-fitting analysis. The least-squares refinement of the Au–N distance gave 2.16 and 2.19 Å in the pyridine and acetonitrile solvates, respectively. The estimated uncertainty in these bond lengths is ±0.02 Å.[32,33] The quality of the raw data is shown in Figure 5 as the fit of unfiltered data with a single shell of nitrogens around gold(I) in the pyridine solvate.

The coordination numbers determined by this curve-fitting method are of limited utility, since the effective coordination number is strongly coupled to the Debye–Waller factor. In particular, long (and presumably weak) bonds will have larger thermal disorder than short (and presumably strong) bonds. Refinements on unfiltered data gave coordination numbers around gold of 2.3 and 3.5 in the gold(I) acetonitrile and pyridine solvates, respectively. Since the model compound, $KAu(CN)_2$, has two short Au–C bonds (1.97 Å), one would expect that the curve fitting would underestimate the coordination number of long (2.16–2.19 Å) Au–N bonds. On the basis of the bond lengths (see below), the true Au–N coordination number is most probably 4. It is not possible to improve on this by selecting a model compound with four light backscatterers coordinated, as no such compound is known.

Discussion

Thermodynamic parameters of the copper(I), silver(I), and gold(I) halide and thiocyanate complexes in pyridine are compared in Figure 6. The enthalpy terms differ considerably, and in particular the values of the copper(I) complexes are more unfavorable than those of the silver(I) and gold(I) complexes. The entropy terms are, on the other hand, favorable for all the systems studied. For a certain ligand, the entropy terms are much the same for all the acceptors. A similar picture emerges for the two systems that can be studied in acetonitrile (Figure 7).

As to the copper(I) and silver(I) systems, the large entropy gains have been ascribed to a combination of two factors.[6,7] First, very large desolvation entropies result from the breakup of well-ordered tetrahedral solvates and the transfer of the solvent molecules to a fairly unstructered bulk solvent. Second, the coordination of halide or thiocyanate ions implies that complexes with only two tightly bonded ligands are formed. The entropy loss of such a process cannot compensate the entropy gain due to desolvation; the decrease of the coordination number results per se in a large net gain of entropy.

For the thiocyanate systems, the entropy terms are throughout smaller than those for the halide systems. As already pointed out,[7] this is certainly mainly due to the lower symmetry of the thiocyanate ion, which brings about a more unfavorable conformation entropy. A halide ion approaching a coordination site is always properly oriented; a thiocyanate ion is not. Upon coordination the thiocyanate ion moreover loses rotational freedom, which further decreases the overall entropy gain.

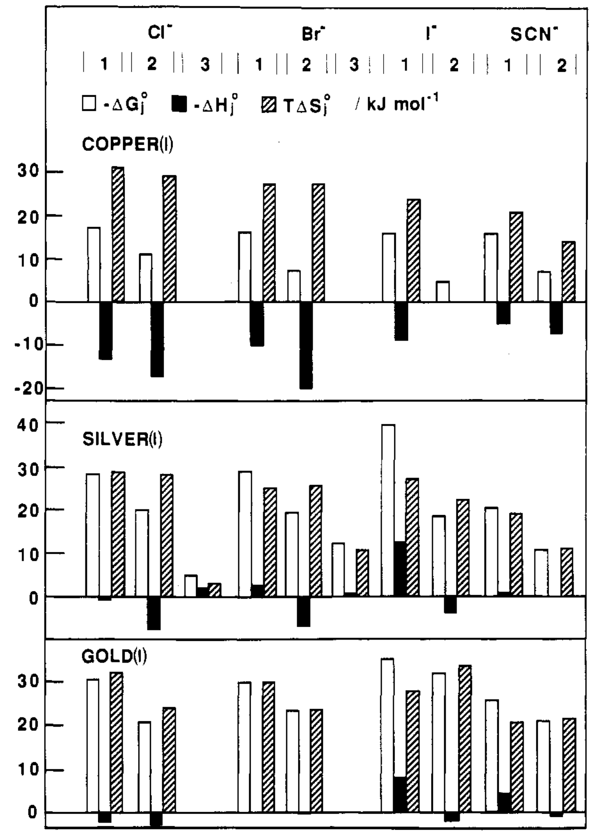

Figure 6. Changes of free energy (white), enthalpy (black), and entropy (hatched) for the consecutive steps of copper(I), silver(I), and gold(I) halide and thiocyanate systems in pyridine.

Also in the gold(I) systems, the complex formation evidently implies the coordination of two tightly bonded ligands. As the entropy gains are very similar, however, these complexes must be formed in processes analogous to those established for the copper(I) and silver(I) complexes, i.e. involving the breakup of

Table V. Bond Distances M–N, M–C, and M–P (Å) in Two- and Four-Coordinated Complexes of Copper(I), Silver(I), and Gold(I) in Solid State (s) and in Solution (sol)

	copper(I)		silver(I)		gold(I)	
donor atom	two	four	two	four	two	four
N (C_5H_5N(s))		2.046 (4)[a]	2.16[b]	2.322 (3)[a]	2.0[c]	
N (C_5H_5N(sol))		2.05 (1)[d]		2.30 (2)[e]		2.16 (2)[f]
N (CH_3CN(s))		1.99 (1)[g]		2.26 (1)[h]	1.96[i]	
N (CH_3CN(sol))		1.99 (1)[d]		2.25 (1)[j]		2.19 (2)[f]
N (MePz)s))[k]	1.88[k]					
N (TMP)(s))[k]	1.87[k]					
C (CN^-(s))			2.13[l]		1.97[m]	
P (PPh_2Me (s))					2.316 (4)[n]	2.449 (1)[o]

[a] Reference 9. [b] Reference 44. [c] References 45, 46. [d] Reference 12. [e] Reference 14. [f] This work. [g] Reference 11. [h] Reference 10. [i] Reference 20. [j] Reference 13. [k] MePz = 1-methylpyrazole, TMP = 1,3,5-trimethylpyrazole; ref 47. [l] Reference 48. [m] References 35, 36. [n] Reference 49. [o] Reference 50.

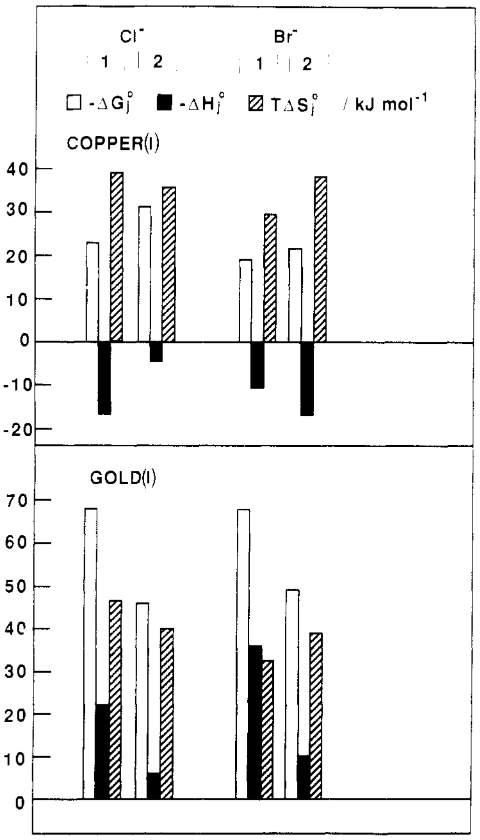

Figure 7. Changes of free energy (white), enthalpy (black), and entropy (hatched) for the consecutive steps of copper(I) and gold(I) chloride and bromide systems in acetonitrile.

tetrahedral pyridine or acetonitrile solvates. The structural investigations confirm this conclusion. From solid to solution, the bonds lengthen by 0.16 and 0.21 Å for pyridine and acetonitrile, respectively (Table V). These increases are just of the magnitude expected for a change from two- to four-coordination, as shown by many well-established examples. Thus, the Ag–N bonds in two- and four-coordinated solid silver(I) pyridine solvates differ by 0.16 Å (Table V). Between the linear pyrazole and the tetrahedral pyridine complexes of copper(I), the difference in the Cu–N bond lengths is about the same, 0.17 Å (Table V). Further, between two- and four-coordinated mercury(II) halides in Me_2SO solution, the Hg–L bonds differ by about 0.18 Å, and much the same difference is found between solid mercury(II) halide complexes.[42] For mercury(II) thiocyanate complexes[43] in Me_2SO, the difference is slightly smaller, 0.14 Å. This is about the same as that found between the two- and four-coordinated solid gold(I) complexes that are formed by diphenylmethylphosphine (Table V).

From the values quoted for copper(I) and silver(I) solvates (Table V), it is also evident that the M–N distances are generally much the same in solution and in the solid state. In any case, the differences are much smaller than those brought about by an increase of the coordination number from 2 to 4. The present comparison of gold(I) solvates in solution and solid phases thus seems justified.

As pointed out above, the positive charge on gold(I) is higher in the acetonitrile than in the pyridine solvate. This implies that acetonitrile is a poorer electron donor than pyridine, as is in fact quite generally found.[40] In spite of this, the M–N distances in the copper(I) and silver(I) solvates are shorter for acetonitrile; in the gold(I) solvates they are about the same for both solvents. This must be due to a less expanded electron cloud on the acetonitrile nitrogen, which allows a closer approach in spite of a weaker bonding.

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Registry No. Au, 7440-57-5; CH_3CN, 75-05-8; pyridine, 110-86-1.

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