Inorganica Chimica Acta, 142 (1988) 285–289

Thermodynamics of the Complex Formation in Pyridine between Gold(I) and Ligands Coordinating via N, P, As or Sb

STEN AHRLAND* and STEFANIA BALZAMO**

Inorganic Chemistry 1, Chemical Center, University of Lund, P.O. Box 124, S-221 00 Lund, Sweden

(Received June 8, 1987)

Abstract

The thermodynamics of complex formation between gold(I) and the ligands tricyclohexylphosphine, triphenylamine, -phosphine, -arsine, and -stibine has been determined in pyridine solution by potentiometric and calorimetric measurements. As expected, the very soft gold(I) displays a more marked stability (b)-sequence $N \ll P > As > Sb$ than its lighter, and less soft, congener silver(I). Like all complexes of these ligands so far studied, the present ones are strongly enthalpy stabilized while the entropy changes are generally unfavourable. The stepwise entropy changes show quite peculiar differences between the various ligands, however. The thermodynamics of these complexes is in striking contrast to that of the gold(I) halido complexes in pyridine which are strongly entropy stabilized, while the enthalpy changes are small.

Introduction

The monovalent d^{10} acceptors copper(I), silver(I) and gold(I) are typically soft acceptors, their softness increasing in the order mentioned [1–3]. They are situated centrally in the triangular area of the periodic system populated by soft acceptors; gold(I) seems in fact to be the softest metallic Lewis acid existing, at least in a non-zero oxidation state. It thus occupies a rather unique position, with the bonding properties typical of soft acceptors developed to an extreme degree.

For ligand atoms of the nitrogen group, the affinity sequence towards soft acceptors is $N \ll P > As > Sb > Bi$. This has been amply proved for copper(I) and silver(I) of the present series of acceptors [4–6], and also for the divalent d^{10} acceptor mercury(II) [4]. Generally, the triphenyl derivatives Ph_3X, X = N, P, As, Sb, Bi, have been applied as ligands, as they are stable solids that can be easily handled. Naturally, however, the donor properties of the ligand atom depend upon its atomic environment. Thus, if the phenyl groups are changed for alkyl ones, the electron density on the ligand atom will increase, as electrons are no longer drawn into aromatic systems. As a consequence, aliphatic phosphines will be stronger donors than aromatic ones. The magnitude of such effects upon the stabilities of the complexes formed has also been measured [7, 8].

It follows from the introductory statements that the affinity sequence written above should be more marked for gold(I) than for any other acceptor of non-zero charge. The present study has been undertaken in order to substantiate this in a quantitative way. In addition, the difference in affinity between the aromatic triphenylphosphine and the non-aromatic tricyclohexylphosphine (Cy_3P) has been measured.

A special reason for the investigation of the affinity between gold(I) and various phosphines is further that gold(I) phosphine complexes have been found to possess interesting properties as anti-inflammatory drugs, with less side-effects than the gold(I) compounds so far used for this purpose [9].

The previous studies of the copper(I) complexes were undertaken in dimethyl sulfoxide (DMSO) [4], those of the silver(I) complexes in pyridine [6] as well as in DMSO [5]. In those solvents both the ligands and the complexes formed are easily soluble which is not the case for example in water. For the present measurements, pyridine has been chosen as a solvent, for the following reasons. For pyridine, extensive data exist not only for the N-group complexes of silver(I), but also for the halide complexes of both silver(I) and gold(I) [10, 11]. It is also easy to prepare a solution of the gold(I) pyridine solvate. Moreover, this solvate is known to be tetrahedrally coordinated in solution [11]. The circumstance that the structure of the initial reactant has been determined very much facilitates the interpretation of the thermodynamic data obtained.

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*Author to whom correspondence should be addressed.

**Present address: Department of Chemistry, University of Rome 'La Sapienza', P.le Aldo Moro 5, I-00185 Rome, Italy.

0020-1693/88/$3.50

The stabilities of the complexes formed have been determined potentiometrically, by means of the gold electrode, while the heats of reaction have been found calorimetrically. In both cases, the procedures have been analogous to those used for the silver(I) complexes [10]. The entropy changes have been calculated from the changes of enthalpy and free energy found.

All measurements have been undertaken at 25 °C in the ionic medium used previously [6, 8, 10, 11], *viz.* 0.1 M tetraethylammonium perchlorate.

Experimental

Chemicals

The solutions of gold(I) perchlorate in pyridine were prepared as described elsewhere [11]. They are sensitive to light and moisture and were therefore kept in the dark, in a carefully dried glove-box. As a further precaution, they were prepared afresh before each set of titrations. Triphenylamine, -phosphine, -arsine, -stibine and tricyclohexylphosphine were commercial products of analytical grade. Their solutions are all sensitive to oxygen. They were also prepared afresh before each set of titrations, in a dried glove-box under nitrogen atmosphere. Special care had to be taken in the cases of triphenylstibine and tricyclohexylphosphine.

The tetraethylammonium perchlorate, and the pyridine solvent, were treated as described before [10].

Potentiometric Measurements

Solutions of gold(I) perchlorate, of concentrations $1 \leqslant C_M \leqslant 7$ mM were titrated with solutions of the respective ligand, of concentrations $10 \leqslant C_L \leqslant 100$ mM, except for triphenylamine where the concentration range was $50 \leqslant C_L \leqslant 300$ mM.

The e.m.f.s were measured by gold foil electrodes, using silver electrodes in silver(I) solutions of $[Ag^+]$ = 10 mM as references. The values became stable within 10 min from the addition of ligand, except close to the equivalent point where the potential adjustment took about 30 min. The titrations were performed in a carefully dried glove-box.

Calorimetric Measurements

A titration calorimeter of isothermal jacket type computerized by an ABC80 computer was used [12]. Gold(I) perchlorate solutions (volume 40 ml) of concentrations $5 \leqslant C_M \leqslant 8$ mM were titrated with aliquots of ligand solutions, of concentrations $20 \leqslant C_L \leqslant 300$ mM. The heat evolved was calculated as described before [11]. The heats of dilution were completely negligible for all solutions used.

Calculation of the Stability Constants and Enthalpy Changes

The computer program EMK was used for the numerical calculations of the stability constants [13]. These were used as fixed parameters in a modernized version of the program KALORI [14] for the calculation of the overall enthalpy changes.

Results

The overall stability constants β_j and enthalpy changes $\Delta H^\circ_{\beta j}$ for the complex formation reactions $Au^+ + jL \rightleftharpoons AuL_j^+$ are listed in Table I, with the limits of error indicated. These tend to be largest for the stibine and cyclohexylphosphine systems, *i.e.* for the ligands most difficult to handle. For all the systems, however, the measurements should be precise and accurate enough to give a fairly reliable picture of the thermodynamics of the reactions concerned. In the ranges of metal and ligand concentrations used, the first two mononuclear complexes are formed, except in the amine system. With this ligand only a weak first complex is formed. On the other hand, no formation of complexes beyond the second one is observed in any of the systems investigated. The course of the complex formation reactions is illustrated by the $\bar{n}$-curves presented in Fig. 1.

From the data of Table I the stepwise equilibrium constants K_j and the thermodynamic functions ΔG_j°, ΔH_j° and ΔS_j° for each step of the com-

TABLE I. Overall Stability Constants (β_j (M^{-j})) and Overall Enthalpy Changes ($\Delta H^\circ_{\beta j}$ (kJ mol^{-1})) for the Complex Formation between Gold(I) and the Ligands Ph_3X and Cy_3P in Pyridine[a]

	Ph_3N	Ph_3P	Ph_3As	Ph_3Sb	Cy_3P
β_1	6.72 ± 0.22	$(8.74 \pm 0.35) \times 10^9$	$(5.03 \pm 0.15) \times 10^3$	$(4.5 \pm 0.6) \times 10^2$	$(3.56 \pm 0.45) \times 10^9$
β_2		$(2.13 \pm 0.29) \times 10^{13}$	$(6.3 \pm 0.9) \times 10^4$	$(7.9 \pm 1.4) \times 10^4$	$(8.9 \pm 0.7) \times 10^{13}$
$\Delta H^\circ_{\beta 1}$		−69.5 ± 2.0	−17.8 ± 1.0	−6.5 ± 2.2	−85.3 ± 5.1
$\Delta H^\circ_{\beta 2}$		−101.5 ± 3.7	−78.8 ± 8.7	−79.6 ± 2.8	−147.7 ± 7.6

[a] Conditions: Medium 0.1 M Et_4NClO_4; temperature 25 °C. The limits of error refer to three standard deviations.

TABLE II. Equilibrium Constants (K_j (M^{-1})) and Thermodynamic Functions (ΔG_j°, ΔH_j° (kJ mol^{-1}), (ΔS_j° (J K^{-1} mol^{-1})) for the Stepwise Formation of Gold(I) and Silver(I) Complexes with Ligands Ph_3X, Cy_3P and (for Silver(I)) Bu_3P in Pyridine[a]

	Gold(I)					Silver(I)				
	Ph_3N	Ph_3P	Ph_3As	Ph_3Sb	Cy_3P	Ph_3P	Ph_3As	Ph_3Sb	Cy_3P	Bu_3P
$\log K_1$	0.83	9.94	3.70	2.65	9.55	4.31	1.44	1.09	7.19	6.38
$\log K_2$		3.39	1.10	2.24	4.40	2.14			3.91	3.87
$\log K_3$						1.14				2.33
K_1/K_2		3.6×10^6	400	2.6	1.4×10^5	150			1.9×10^3	325
K_2/K_3						10				35
$-\Delta G_1^\circ$	4.7	56.7	21.1	15.1	54.5	24.6	8.2	6.2	41.0	36.4
$-\Delta G_2^\circ$		19.3	6.3	12.8	25.1	12.2			22.3	22.1
$-\Delta G_3^\circ$						6.5				13.3
$-\Delta H_1^\circ$		69.5	17.8	6.5	85	34.4	15.6	11.6	67.9	67.0
$-\Delta H_2^\circ$		32	61	73	63	22.0			23.4	43.0
$-\Delta H_3^\circ$						16.1				38.4
ΔS_1°		−43	11	29	−103	−33	−25	−18	−90	−103
ΔS_2°		−43	−183	−202	−126	−33			−4	−70
ΔS_3°						−32				−84

[a] Conditions: Medium 0.1 M Et_4NClO_4; temperature 25 °C.

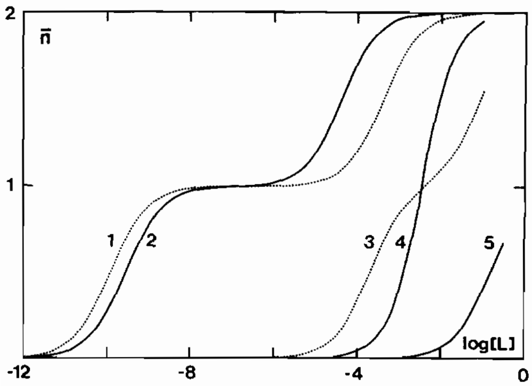

Fig. 1. Complex formation functions in pyridine of the gold(I) systems of Ph_3P (1), Cy_3P (2), Ph_3As (3), Ph_3Sb (4) and Ph_3N (5). Medium 0.1 M Et_4NClO_4, 25 °C.

plex formation reactions have been calculated. These are all listed in Table II. For comparison, the corresponding silver(I) data have also been entered in this Table, with those referring to the tributylphosphine (Bu_3P) system added [6, 8].

Discussion

The measurements confirm that the affinity sequence $N \ll P > As > Sb$ is much more marked for gold(I) than for silver(I). Even in the soft solvent pyridine where monovalent d^{10} acceptors are very strongly solvated [15, 16], gold(I) is able to form very strong phosphine complexes, Table II. Also the other ligand atoms have a higher affinity for gold(I) than for silver(I) but the differences are much smaller than for phosphorus. As to the latter, the difference is moreover especially large for the first step. Still more remarkable, for the second step the affinities are reversed between arsenic and antimony. Evidently, more factors are at play than the strength of the bond Au–X. This is also confirmed by the relatively low stabilities of the Cy_3P complexes. Quite contrary to what is expected, and also found in the case of silver(I), the value of K_1 for Cy_3P is lower than for Ph_3P, Table II. Also the value of K_2 of the gold(I)–Cy_3P system is unexpectedly low, both relative to the gold(I)–Ph_3P and to the silver(I)–Cy_3P system.

Only one quantitative study of the stabilities of complexes formed between gold(I) and ligands Ph_3X in solution seems to have been performed previously, *viz.* by Roulet and Favez [17], in acetonitrile (AN) at −20 °C. As most of their data moreover refer to equilibria $AuCl + Ph_3X \rightleftharpoons AuClPh_3X$ and $AuBr + Ph_3X \rightleftharpoons AuBrPh_3X$, a direct comparison with our results is somewhat difficult. Obviously, however, the complexes are much more stable than in pyridine. This is certainly expected as gold(I) should, like silver(I) and copper(I), be much less strongly solvated in acetonitrile than in pyridine [15, 16].

This conclusion, based on the very exothermic heats of transfer ΔH°_{tr} (AN→ Py) of Ag^+, Cu^+, and the halide complexes CuL and CuL_2^-, is further confirmed by the standard potential E°_{01} (Au(s)/Au^+) which is much higher in AN, 1.511 V, than in pyridine, 0.80 V [11]. For both the chloride and the bromide series the stability sequence is the one expected, $N \ll P > As > Sb$. The differences between the heavier ligand atoms are not very large, however, as is also found for the second step in pyridine, Table II.

For Ph_3P, and also for the mixed aromatic–aliphatic phosphines Ph_2MeP and $PhMe_2P$, not only constants for the equilibria mentioned above, but also values of β_2 have been determined. In all cases, the expected stability sequence $Ph_3P < Ph_2MeP < PhMe_2P$ is found [17].

Indications about the effects that bring about the abnormal affinity relations found in the present investigation are given by the enthalpy and entropy changes, Table II. As expected, the normal stability sequence found for the complexes $AuPh_3X^+$ is due to the enthalpy terms ΔH°_1 which become less exothermic in the order $P > As > Sb$. Also as expected, ΔH°_1 is considerably more exothermic for Cy_3P than for Ph_3P. For the latter pair, this also applies to ΔH°_2. The relatively low stabilities of the Cy_3P complexes is for both steps an entropy effect, probably mainly due to the larger bulk of the aliphatic ligand. Also, an aromatic interaction certainly exists between the rings of pyridine and Ph_3P. This implies that the increase in order brought about by the complex formation would be larger for Cy_3P than for Ph_3P. Consequently, the entropy terms would be more unfavourable for Cy_3P. This should of course also apply to the silver(I) systems, and it does for ΔS°_1, and also for ΔS°_j of the other aliphatic phosphine Bu_3P, but not for ΔS°_2 of Cy_3P, for some unknown reason. For silver(I), however, the difference in ΔH°_1 between Ph_3P and Cy_3P is large enough to make the aliphatic complex the stronger one which is not the case for gold(I).

For the Ph_3X ligands, the values of ΔH°_2 become more exothermic in the order $P < As < Sb$, *i.e.* the trend is just opposite to that found for ΔH°_1. The silver(I) complexes are too unstable in pyridine to allow a comparison, but in DMSO the expected sequence $P > As > Sb$ is found for $-\Delta H^\circ_2$ [5]. Most interestingly, however, the abnormal sequence $P < As < Sb$ appears for silver(I) in DMSO at the third step, ΔH°_3 becoming more exothermic in that order. Neither in pyridine, nor in acetonitrile [17], does gold(I) take this third step with any of these ligands, in the range of [L] available. Seemingly, the gold(I)–phosphorus bond in the first complex, $AuPh_3P^+$, is very strong, also relative to the bonds in the second complex $Au(Ph_3P)_2^+$. The less soft ligand atoms arsenic and antimony do not act in this manner; on the contrary the coordination of a second ligand seems to bring about a stabilization of the whole bonding system. For silver, an analogous effect is found in DMSO, but at the third step [5]. It might be, however, that these abnormal ΔH°_j sequencies at least partly originate in desolvation reactions rather than in special properties of the metal to ligand bonds, as will be discussed below.

The unexpected ΔH°_j sequences are accompanied by very peculiar trends in the entropy changes, Table II. While in the gold(I) phosphine systems the values of ΔS°_1 and ΔS°_2 are negative and of much the same magnitude for the two consecutive steps, the arsine and stibine behave very differently. The values of ΔS°_1 are both positive, while the values of ΔS°_2 are very negative, much more so than for the phosphines. The most positive ΔS°_1 and the most negative ΔS°_2 are found for the stibine. A similar entropy trend is also observed for silver(I) in DMSO, but not before the formation of the third complex [5].

These unusual trends in ΔH°_2 and ΔS°_2 combine to give the peculiar trend $P > As < Sb$ found for K_2, Table II.

The main features of this intricate thermodynamic pattern may be interpreted as follows. The tetrahedral solvates initially present [11] are disrupted as the complexes are formed. Very plausibly, the desolvation taking place at the first step is more extensive, the larger the ligand atom X. If so, the values of ΔS°_1 would increase in the order $P < As < Sb$, just as observed. But if an extensive desolvation has taken place at the first step, little, if any, entropy is to be gained from this source at the second step. The values of ΔS°_2 would then be increasingly unfavourable in the sequence $P > As > Sb$, also as observed. For the arsine and stibine systems, the total entropy loss $\Delta S^\circ_{\beta 2} = \Delta S^\circ_1 + \Delta S^\circ_2$ is almost the same, -172 and -173 J K^{-1} mol^{-1}, respectively. Provided the entropy changes due to other sources do not differ appreciably, this would imply that the total desolvation occurring in the first two steps is much the same for these ligands. The provision made cannot, of course, be strictly true as is obvious already from the different steric requirements of the two ligands. The close agreement is nevertheless striking. The value of $\Delta S^\circ_{\beta 2}$ of the Ph_3P system is much less negative, -86 J K^{-1} mol^{-1}, which might possibly indicate a less complete desolvation of the second phosphine complex.

With the desolvation of the first step increasing in the order $P < As < Sb$, the desolvation enthalpies should also increase in that order. This would further strengthen the trend of ΔH°_1 to become less exothermic in the order $P > As > Sb$. For the second step, on the other hand, the desolvation enthalpies ought to follow the reversed order $P > As > Sb$, which might well result in the abnormal ΔH°_2 sequence actually observed.

Finally, a most characteristic feature of the complexes formed between monovalent d^{10} acceptors and the present ligands, in pyridine as well as in DMSO, is that they are generally strongly enthalpy stabilized while the entropy changes are generally unfavourable. This reflects a weak solvation of acceptors [15, 16] and ligands [18], in combination with strong metal to ligand bonds (especially in the case of the phosphines) and unfavourable conformation entropies of the ligands. The thermodynamics of these complexes offers indeed a striking and informative contrast to that of the halide complexes of the same acceptors in pyridine which are strongly entropy stabilized while the enthalpy changes are either more or less unfavourable, or at least of little importance [11]. This fundamental difference in thermodynamic behaviour is evidently due to two significant differences between the ligands. The halide ions are much more strongly solvated than the N-group ligands [18, 19] and they have much more favourable conformation entropies.

Acknowledgements

We most gratefully acknowledge a grant from the Blanceflour Boncompagni-Ludovisi Foundation which made possible the stay of S.B. at the Chemical Center of the University of Lund. Our sincere thanks are also due to Dr Karin Nilsson for experimental advice and valuable help with the calculations.

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