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Gold Complexes of Schiff Bases obtained from Salicylaldehyde Derivatives and Alkyl Amines[*1]

Shoichiro YAMADA and Kuniko YAMANOUCHI

Institute of Chemistry, College of General Education, Osaka University, Toyonaka, Osaka

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Gold complexes (abbreviated as $[Au^{III}(X\text{-}SAL \cdot alkyl)_2][Au^{I}Cl_2]$) with salicylideneimine derivatives were prepared as red-brown crystals, where X denotes H, 5,6-benzo and 5-Cl. Since all these complexes are diamagnetic and exhibit similar electronic absorption spectra, the complexes of the $[Au(X\text{-}SAL \cdot R)_2]^+$ type are considered to have a similar configuration, namely a square-planar one. It should be noted that the complexes of the $[Au(X\text{-}SAL \cdot i\text{-}C_3H_7)_2]^+$ type are also planar. The result is found to be similar to that for the palladium(II) and platinum(II) complexes, but different from that for the nickel(II) complexes.

In previous papers, we reported palladium(II) and platinum(II) complexes with salicylideneimine derivatives,[1–3] in order to compare the results with those of the corresponding nickel(II) complexes, which had been studied extensively.[4,5] It seems to be of interest to extend a similar study to gold(III) having a $5d^8$ configuration and to compare the results with those of the corresponding complexes of nickel(II), palladium(II) and platinum(II), which also have a d^8 configuration. No systematic study has ever been carried out on the gold(III) complexes (Fig. 1)[*2] with the Schiff bases, except for a small number of examples.[6] The present paper deals with the results of a study on these gold(III) complexes.

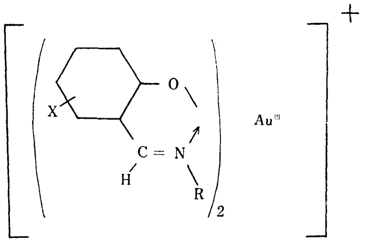

Fig. 1. $[Au^{III}(X\text{-}SAL \cdot R)_2]^+$.

Experimental

Materials. The complexes of the type $[Au^{III}(X\text{-}SAL \cdot R)_2][Au^{I}Cl_2]$ were prepared as red-brown crystals according to the following method.

To an aqueous solution of sodium tetrachloroaurate(III) dihydrate (0.01 mol) were added a solution of salicylaldehyde or its derivative (0.018 mol) in ethanol and a solution of an appropriate amine (0.02 mol) in ethanol. The resulting solution was warmed at about 40°C for about one hour. A brown precipitate formed in the solution was filtered off and recrystallized from suitable organic solvents.

Analytical data of the gold complexes obtained are shown in Table 1. Any attempt to isolate the complexes of the $[Au(X\text{-}SAL \cdot t\text{-}C_4H_9)_2][AuCl_2]$ type according to the method described above has so far been unsuccessful. In this case, the colour change of the solution immediately

TABLE 1. ANALYTICAL DATA OF GOLD COMPLEXES OF THE $[Au(X\text{-}SAL \cdot R)_2][AuCl_2]$

Compound		Calcd, %			Found, %		
X	R	C	H	N	C	H	N
H	C_2H_5	28.40	2.65	3.68	28.35	2.27	3.39
	$n\text{-}C_3H_7$	30.44	3.07	3.55	30.46	2.86	3.50
	$i\text{-}C_3H_7$	30.44	3.07	3.55	30.02	2.97	3.63
	$n\text{-}C_4H_9$	32.33	3.45	3.43	31.46	3.37	3.27
5,6-Benzo	C_2H_5	36.34	2.82	3.26	35.77	2.63	3.15
	$n\text{-}C_3H_7$	37.81	3.17	3.15	36.85	2.84	2.96
	$i\text{-}C_3H_7$	37.81	3.17	3.15	36.97	3.02	3.11
	$n\text{-}C_4H_9$	39.28	3.52	3.05	38.82	3.21	3.09
5-Cl	CH_3	23.96	1.76	3.49	23.84	1.69	3.51

[*1] Presented, in part, at the 19th Symposium on Coordination Chemistry, Sendai, September, 1969.

1) S. Yamada, H. Nishikawa and K. Yamasaki, This Bulletin, **36**, 483 (1963).

2) S. Yamada and E. Yoshida, *ibid.*, **38**, 2179 (1965).

3) S. Yamada and K. Yamanouchi, *ibid.*, **42**, 2543 (1969).

4) S. Yamada, *Coord. Chem. Rev.*, **1**, 415 (1966).

5) R. H. Holm, G. W. Everett, Jr., and A. Chakravorty, "Progress in Inorganic Chemistry," Vol. VII, ed. by F. A. Cotton, Interscience Publishers, New York, N. Y. (1966), p. 83.

[*2] These metal complexes are abbreviated as $[Au(X\text{-}SAL \cdot R)_2]^+$ in this paper.

6) T. Inazu, This Bulletin, **39**, 1065 (1966).

took place, but crystals of the desirable complexes could not be isolated from the solution.

These gold complexes are soluble in acetone, chloroform and ethanol, but insoluble in water. The solubility, however, varies from compound to compound and from solvent to solvent. They are stable to the atmosphere, and do not undergo decomposition when stored in an ordinary sample-tube.

Measurements. Electronic absorption spectra of the gold complexes were determined with a Shimadzu MPS-50L spectrophotometer and a Shimadzu QR-50 spectrophotometer. The solution spectra were determined with ethanol or acetone as a solvent according to the solubility of the complex. The spectrum of the ethanolic solution was found to be nearly the same as that of the acetone solution, when the determination of the spectrum was possible with both solvents.

Diamagnetism of the complexes was detected by the Gouy method.

Electric conductivities of the complexes in acetone were determined with a Toadempakogyo CM-1 conductance bridge.

Results and Discussion

The gold complexes, $[Au(X\text{-}SAL\cdot R)_2][AuCl_2]$, obtained in the present work, which are shown in Table 1, are found to correspond to the empirical formula, $Au(X\text{-}SAL\cdot R)Cl$. The oxidation state of gold in this formula might apparently be plus two. This, however, proves to be incorrect, since these complexes are all diamagnetic; the gold(II) complex, having a d^9 configuration, would be expected to be paramagnetic with one spin-free electron. Thus, we might assume that the complex with the composition $Au(X\text{-}SAL\cdot R)Cl$ be formulated as $[Au^{III}(X\text{-}SAL\cdot R)_2][Au^{I}Cl_2]$, which involves one gold ion in the tervalent and the other in the univalent state. It seems difficult to tell exactly how the reduction of gold(III) to gold(I) has taken place. However, gold complexes of this sort, containing $[Au^{I}Cl_2]^-$ or $[Au^{III}Cl_4]^-$ as a counter-anion, have often been reported in literature;[6,7] the syntheses of the complexes in these reports were also carried out using reactions of a type somewhat similar to those employed in the present work. Electric conductivities of some of the complexes in solution were determined. The values for the acetone solutions, which are shown in Table 2, seem to correspond to the values expected for uni-uni-electrolytes, in agreement with the formulation proposed above for these gold complexes.[7]

Since it is known that the gold(III) ion generally requires a quadri-coordinate planar configuration, the complexes of the $[Au(X\text{-}SAL\cdot n\text{-alkyl})_2]^+$ may reasonably be considered to be planar, no steric hindrance being expected, in this case, against the planar configuration.

TABLE 2. MOLECULAR CONDUCTIVITIES(Λ) OF GOLD COMPLEXES OF THE $[Au(X\text{-}SAL\cdot R)_2]\cdot[AuCl_2]$ TYPE IN ACETONE AT 25°C

Compound		Conc.(mol/l)	Λ (mho)
H	n-C_3H_7	5.15×10^{-4}	144
	i-C_3H_7	6.12×10^{-4}	134
5,6-Benzo	i-C_3H_7	6.50×10^{-4}	132
	n-C_4H_9	7.75×10^{-4}	131
5-Cl	CH_3	5.91×10^{-4}	126

The complexes of the $[Au(X\text{-}SAL\cdot n\text{-alkyl})_2][AuCl_2]$ type in solution show electronic spectra which are similar to each other. Some of the representative spectra are shown in Fig. 2.*[3] In the region shown in Fig. 2, the ion $[AuCl_2]^-$ exhibits almost no absorption, so that the spectra in Fig. 2 may be considered to represent those due to the complexes $[Au(X\text{-}SAL\cdot n\text{-alkyl})_2]^+$. That the spectra are similar to each other indicates that the complexes of the $[Au(X\text{-}SAL\cdot n\text{-alkyl})_2]^+$ type have a similar configuration, namely a square-planar one. The broad absorption band which appears in the region between about 17 and 24 kK may be considered to arise principally from spin-allowed *d-d* transitions in the planar complexes $[Au(X\text{-}SAL\cdot n\text{-alkyl})_2]^+$. The broadness of the band indicates that this band consists of a few components. The intensity of this band seems to be a little too high for the transitions of the pure *d-d* origin, but this finding may be interpreted as due to the considerably high mixing-in of the ligand π-orbitals with the metal *d*-orbitals, as has often been observed with most transition metal complexes with Schiff bases of a similar type. An intense absorption band with its maximum at about 26.7 kK may be considered as due to the internal transitions within the ligands under the influence of the gold(III) ion.

Since Beer's law holds for all these complexes in solution, no association of the planar gold(III) complexes is found to take place. This result is similar to that for the corresponding palladium(II) or platinum(II) complexes,[1-3] but different from that for the nickel(II) complexes, in agreement with the current view that the gold(III) ion, like the palladium(II) or platinum(II) ion, has a high tendency to take a quadri-coordinate planar configuration.

For the complexes of the $[Au(X\text{-}SAL\cdot i\text{-}C_3H_7)_2]^+$ type, steric hindrance may be expected to be considerably high against the planar configuration of the complexes. It should be remembered that the corresponding nickel(II) and copper(II) complexes of the $[M(X\text{-}SAL\cdot i\text{-}C_3H_7)_2]$ type were previously

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7) C. M. Harris, *J. Chem. Soc.*, **1959**, 682; C. M. Harris and T. N. Lockyer, *ibid.*, **1959**, 3083.

*[3] It was confirmed that the spectra of these complexes in the solid state are essentially similar to their solution spectra.

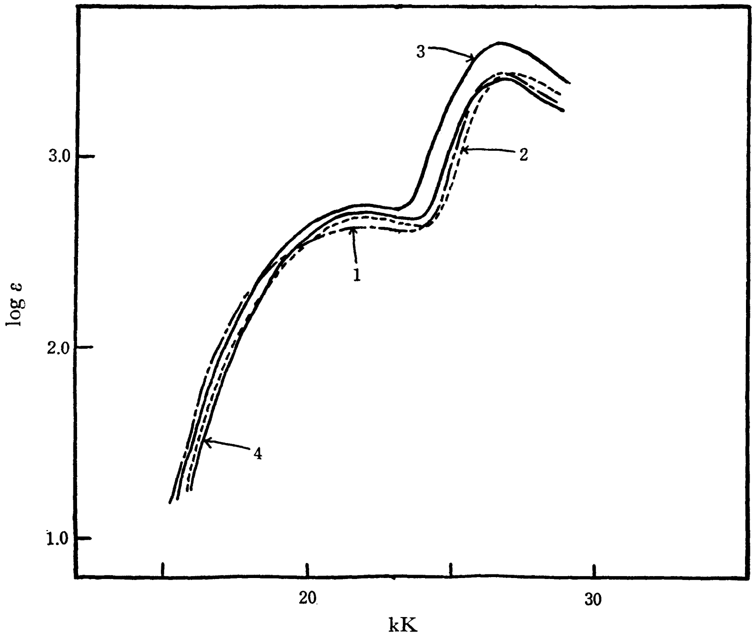

Fig. 2. Electronic absorption spectra of $[Au(X\text{-}SAL\cdot R)_2][AuCl_2]$. 1, X=H, R=$n$-$C_3H_7$, in chloroform; 2, X=H, R=i-C_3H_7, in acetone; 3, X=5,6-benzo, R=i-C_3H_7, in acetone; 4, X=5-Cl, R=CH_3, in acetone.

concluded to be tetrahedral or planar, depending upon X; they are tetrahedral for X=H[8,9] and planar for X=5-Cl and 5,6-benzo.[9] It is considered that the gold(III) complexes of the $[Au(X\text{-}SAL\cdot i\text{-}C_3H_7)_2]^+$ type have a planar configuration, since their spectra are similar to those of the complexes of the $[Au(X\text{-}SAL\cdot n\text{-alkyl})_2]^+$ type. This result with the gold(III) complexes is evidently different from that with the corresponding nickel(II) complexes, both metal ions having a d^8 configuration. This difference between the gold(III) and the nickel(II) complexes may be ascribed principally to the two factors, which are related with the bonding nature and the size of the metal ions, in quite the same way as was previously discussed in the case of the corresponding palladium(II) and platinum(II) complexes.[1-3]

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8) L. Sacconi, "Essays in Coordination Chemistry," ed. W. Schneider, G. Anderegg and R. Gut, Birkhauser Verlag, Basel (1964), p. 148.

9) S. Yamada and H. Nishikawa, This Bulletin, **36**, 755 (1963).