The Synthesis of Several Gold Chelates[1]

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Very few papers have, until recently, been published reporting on the synthesis of gold chelates.[2,3] In this paper, the synthesis of several gold chelates will be reported. In each case, the gold chelate was obtained by the addition of an ethanolic or an aqueous solutions of chloroauric acid to an ethanolic solution of a ligand. Seven chelates were obtained in a crystalline state, and two as powder. They may be classed roughly into three groups (see Fig. 1). It is well known that aurous gold always appears to be two-covalent, while auric gold is always four-convalent and the four valencies are coplanar with the gold atom.[4,5] Considering the above facts, and the results of paper ionophoresis and the analytical data, it seems most reasonable to assume that one of two gold atoms in the chelate

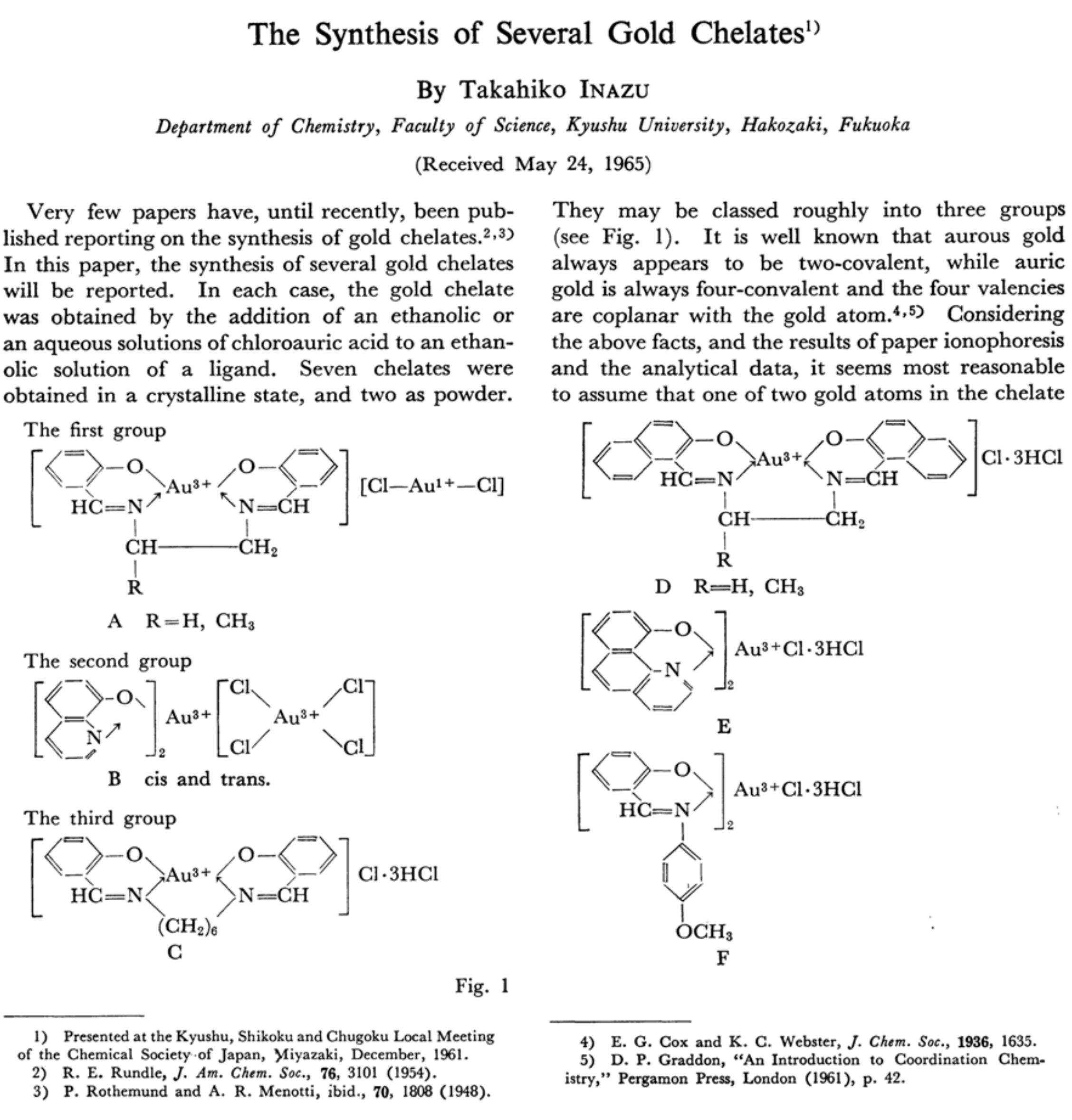

Fig. 1

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[1] Presented at the Kyushu, Shikoku and Chugoku Local Meeting of the Chemical Society of Japan, Miyazaki, December, 1961.

[2] R. E. Rundle, *J. Am. Chem. Soc.*, **76**, 3101 (1954).

[3] P. Rothemund and A. R. Menotti, ibid., **70**, 1808 (1948).

[4] E. G. Cox and K. C. Webster, *J. Chem. Soc.*, **1936**, 1635.

[5] D. P. Graddon, "An Introduction to Coordination Chemistry," Pergamon Press, London (1961), p. 42.

TABLE I

Chelate[a]	Appearance[b]	Analysis, % Found C	Found H	Found N	Found Cl	Found Au	Calcd. C	Calcd. H	Calcd. N	Calcd. Cl	Calcd. Au
A[c] R=H	Orange y. n.	26.06	2.24	3.84	10.09	53.0	26.25	2.06	3.83	9.70	53.9
A[d] R=CH_3	Pale y. n.	27.57	2.30	3.23		52.11	27.40	2.16	3.76		52.86
B[e]	Dark g. c.	26.26	1.59	3.58		47.81	26.24	1.47	3.40		47.80
B[e]	Amber n.	26.41	1.69	3.53		47.70	26.24	1.47	3.40		47.80
C[f]	Y. brown n.	36.17	3.96	3.92		29.47	36.16	3.79	4.22		29.66
D[g] R=H	Brown p.	40.03	3.16	4.09		27.89	40.07	2.99	3.96		27.81
D[h] R=CH_3	Brown p.	41.73	3.35	3.54		27.20	41.57	3.21	3.88		27.27
E[i]	Dark v. c.	42.35	3.64	3.52	17.70	24.1	42.30	3.52	3.52	17.85	24.8
F[j]	Dark v. n.	42.61	2.50	3.80	19.72	27.2	42.70	2.60	3.84	19.42	27.0

a) Percentages were calculated according to the formula ; c) $C_{16}H_{14}O_2N_2Cl_2Au_2$, d) $C_{17}H_{16}O_2N_2Cl_2Au_2$, e) $C_{18}H_{12}O_2N_2Cl_4Au_2$, f) $C_{20}H_{25}O_2N_2Cl_4Au$, g) $C_{24}H_{21}O_2N_2Cl_4Au$, h) $C_{25}H_{25}O_2N_2Cl_4Au$, i) $C_{28}H_{27}O_4N_2Cl_4Au$, j) $C_{26}H_{19}O_2N_2Cl_4Au$.

b) c=crystals, g=green, n=needles, p=powder, v=violet, y=yellow

molecule of the first group is in a reduced univalent state.[6] In the case of 8-hydroxyquinoline chelates, which belong to the second group, two kinds of crystals, of different colors, were obtained. They may be cis and trans isomers each other. In these chelates, the oxidation states of both golds in the cationic and the anionic parts might be considered to be tervalent[7] on the basis of the analytical data and the paper ionophoresis (Fig. 2, No. 2). The chelates of the third group contain one tervalent gold atom and three molecules of hydrogen chloride in each chelate molecule. All the chelates decomposed spontaneously within a year.

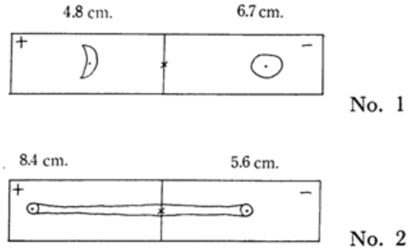

Fig. 2. Paper ionophoresis of gold chelates.

Experimental

The following examples represent the methods of preparing the chelates obtained.

Bis(8-quinolinolato)gold (III) - tetrachloroaurate(III) (B).—A solution of 210 mg. of 8-hydroxyquinoline in 25 ml. of ethanol was mixed with a solution of 300 mg. of chloroauric acid tetrahydrate in 15 ml. of ethanol. After this mixture had stood overnight, a mixture of green crystals and amber needles was obtained. Each of the separated crystals was then collected and washed with a little ethanol. They were slightly soluble in acetone and insoluble in water.

Bis[10-benzo-(h)-quinolinolato]gold(III) - chloride Trihydrogen Chloride (E).—A solution of 85 mg. of chloroauric acid tetrahydrate in 10 ml. of ethanol was mixed with a solution of 127 mg. of a chelating agent[8] in 10 ml. of ethanol. Dark violet needles were immediately formed; these were collected and washed with a little ethanol. They were slightly soluble in acetone and chloroform and insoluble in water.

Paper Ionophoresis.—Tôyô Roshi No. 51 filter paper was used, with a solvent system of acetone-acetic acid-water (1 : 1 : 1 by vol.) (500 V., 2 hr.). The papers were dried in an oven at 120°C, and then left standing overnight. Without further treatment, gray spots of reduced gold were obtained.

N, N' -Disalicylidene-ethylenediaminato-gold(III) - dichloroaurate(I).—(Fig. 2, No. 1).—Two spots were obtained; one spot in the plus region due to $Au(I)Cl_2^-$, and one spot in the minus region due to $Au(III)Ln^+$. (Ln =ligand).

Bis (8 - quinolinolato) gold (III) - tetrachloroaurate(III).—(Amber needles, Fig. 2, No. 2).—Two spots with long tailings were obtained; one spot in the plus region due to $Au(III)Cl_4^-$, and one spot in the minus region due to $Au(III)Ln_2^+$.

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[6] As an example of this type, there is the dimethylglyoxime gold complex, confirmed by X-ray diffraction analysis; cf. Ref. 2.

[7] The α, β, γ, δ-tetraphenyl porphine gold complex also belongs to this type; cf., Ref. 3.

[8] T. Yoshino, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zasshi*), **78**, 108 (1957).