

## Clusters of Gold Compounds with 1,2-Bis(diphenylphosphino)ethane

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Received July 29, 1967

New cluster gold compounds with 1,2-bis(diphenylphosphino)ethane (DPE) are described. These belong to the following types: (1) The ionic brown compounds  $[Au_6(DPE)_2X]Y$  in which  $X = Cl^-, Br^-, I^-, SCN^-$ ;  $Y = Cl^-, Br^-, I^-, SCN^-, ClO_4^-, PF_6^-$  and  $BPh_4^-$ . (2) The polymeric red violet non-ionic compounds  $[Au_6(DPE)_2X_2]_n$ . (3) The ionic green compounds  $[Au_6(DPE)_3]X_2$ . Conductivity measurements, infrared spectra and exchange reactions seem to indicate in these compounds the presence of gold clusters of six atoms.

## Introduction

We reported previously the preparation and properties of the cluster gold compounds with triphenylphosphine (P)<sup>1</sup> and with ethyldiphenylphosphine (L)<sup>2</sup> and the first results using 1,2-bis(diphenylphosphino)ethane (DPE) as ligand.<sup>3</sup> The latter has basicity of the same order as L, but different steric requirements and can act both as bidentate bridging and as a chelating ligand.

The gold(I) complexes with DPE, which are the starting materials for the preparation of the gold cluster compounds, are of a different type than the complexes with monodentate phosphines: we have prepared both non-ionic bridged compound:



and ionic derivatives



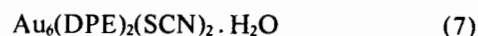
The reduction of dinuclear compound (1) with sodium tetrahydridoborate, in ethanol solution, gave a red-brown substance corresponding to:



This compounds, in which the average oxidation number of gold is 1/3, is of a different type than the triphenylphosphine derivative  $[Au_5P_4]Cl$ , and it differs

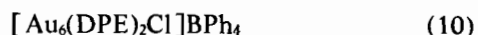
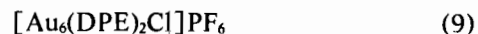
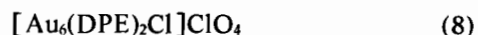
also from the ethyldiphenylphosphine compound, although it has the same ratio of 6/4/2 between gold/phosphorus/chlorine because of its conductivity ( $100 \Omega^{-1} \text{ cm}^{-1}$  in  $10^{-3}$  molar nitromethane).

Compound (4) reacts with strong nucleophilic anions such as bromide, iodide and thiocyanate exchanging completely the two chlorines giving the red-brown compounds (5), (6) and (7) respectively:



which also give conducting solutions in nitromethane.

On the other hand, compound (4) reacts with anions of low nucleophilicity as perchlorate, hexafluorophosphate and tetraphenylborate to give (8), (9) and (10), respectively

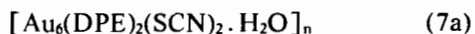
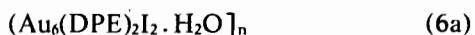
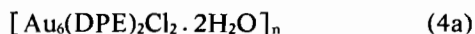


and compound (7) reacts with lithium perchlorate to give:

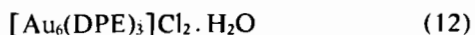


All these compounds behave in nitrobenzene solution as uni-univalent electrolytes.

Compounds (4), (5), (6) and (7) isomerize slowly in dichloromethane solution giving red-violet precipitates (4a), (5a), (6a) and (7a), which are practically insoluble in all common organic solvents:



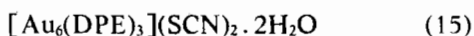
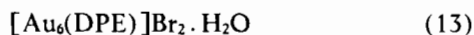
These react further with an excess of DPE in dichloromethane to give the soluble green compounds (12), (13), (14) and (15):



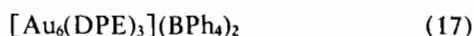
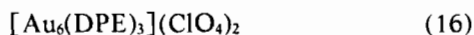
(1) L. Malatesta, L. Naldini, G. Simonetta and F. Cariati, *Coord. Chem. Reviews*, Elsevier, Amsterdam, 255 (1966).

(2) F. Cariati, L. Naldini, G. Simonetta and L. Malatesta, *Inorg. Chim. Acta*, 1, 24 (1957).

(3) L. Naldini, F. Cariati, G. Simonetta and L. Malatesta, *Chem. Comm.*, 647 (1966).



These new compounds behave as uni-bivalent electrolytes in nitromethane and in nitrobenzene solution. The ionic nature of the complexes is confirmed by the exchange reaction with bulky non-nucleophilic anions as perchlorate and tetraphenylborate to give:



which contain the same cationic species as compounds (12)-(15).

### Experimental Section

The IR spectra have been recorded with Perkin Elmer model 237 and 621 spectrophotometers. The magnetic susceptibilities have been determined at room temperature by the Gouy balance and all the compounds were found diamagnetic.

(3) *Bis[1,2-bis(diphenylphosphino)ethane]gold tetraphenylborate.* From bis[1,2-bis(diphenylphosphino)ethane]gold chloride (2) (0.1 mmole, 103 mg) dissolved in ethanol (50 ml) and sodium tetraphenylborate (0.1 mmole, 34.2 mg). The white crystals were recrystallized from dichloromethane and ethanol as above.

(4)  $\mu$ -chloro-di- $\mu$ -bis[1,2-bis(diphenylphosphino)ethane]hexagold chloride-2 aquo. From  $\mu$ -[1,2-bis(diphenylphosphino)ethane]bis(chlorogold) (1) (9.7 mmoles, 10.0 g) suspended in ethanol (300 ml) on treating drop by drop with an ethanol solution of sodium tetrahydridoborate (19.4 mmoles, 0.73 g). The brown solution filtered from solid sodium chloride was precipitated by hexane. The brown precipitate was recrystallized from dichloromethane and hexane as above.

(4a) *Polymeric di- $\mu$ -(dichloro)di- $\mu$ -bis[1,2-bis(diphenylphosphino)ethane]hexagold .2 aquo.* Obtained from the solution of hexanuclear chloride (4) (0.96 mmoles, 2 g) in ethanol (100 ml) after 30 hours at room temperature, as a red-violet insoluble compound.

(5)  $\mu$ -bromo-di- $\mu$ -bis[1,2-bis(diphenylphosphino)ethane]hexagold bromide aquo. From a solution of hexanuclear chloride (4) (1.9 mmoles, 4.0 g) in ethanol

Table I.

		C	H	Au	Cl, N	O	P	m.p. °C
(1)	$\text{Au}_2(\text{DPE})\text{Cl}_2$	36.3 (36.2)	2.80 (2.78)	44.8 (45.6)	8.25 (8.22)		7.30 (7.18)	291
(2)	$[\text{Au}(\text{DPE})_2]\text{Cl}$	59.2 (60.7)	4.45 (4.66)	19.2 (19.2)				245
(3)	$[\text{Au}(\text{DPE})_2]\text{BPh}_4$	69.8 (69.5)	4.97 (5.17)	15.0 (15.0)				208
(4)	$[\text{Au}_6(\text{DPE})_2\text{Cl}]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$	30.5 (29.9)	2.45 (2.49)	56.5 (56.7)	3.34 (3.40)	1.60 (1.53)	5.90 (5.95)	202
(4a)	$[\text{Au}_6(\text{DPE})_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$	30.3 (19.9)	2.40 (2.49)	56.3 (56.7)	3.25 (3.40)	1.59 (1.53)		210
(5)	$[\text{Au}_6(\text{DPE})_2\text{Br}]\text{Br} \cdot \text{H}_2\text{O}$	28.8 (28.9)	2.30 (2.32)	54.6 (54.8)		0.80 (0.74)		205
(5a)	$[\text{Au}_6(\text{DPE})_2\text{Br}_2] \cdot \text{H}_2\text{O}$	30.9 (28.9)	2.40 (2.32)	54.8 (54.6)		0.83 (0.74)		252
(6)	$[\text{Au}_6(\text{DPE})_2\text{I}]\text{I} \cdot \text{H}_2\text{O}$	27.6 (27.7)	2.18 (2.22)	52.4 (52.5)		0.70 (0.71)		194
(6a)	$[\text{Au}_6(\text{DPE})_2\text{I}_2] \cdot \text{H}_2\text{O}$	27.14(27.7)	2.17 (2.22)	52.7 (52.5)		0.69 (0.71)		215
(7)	$[\text{Au}_6(\text{DPE})_2\text{SCN}]\text{SCN} \cdot \text{H}_2\text{O}$	29.9 (30.7)	2.26 (2.36)	56.5 (55.9)	1.20 (1.32)	0.70 (0.76)		193
(7a)	$[\text{Au}_6(\text{DPE})_2(\text{SCN})_2] \cdot \text{H}_2\text{O}$	29.6 (30.7)	2.16 (2.36)	56.4 (55.9)	1.25 (1.32)	0.73 (0.76)		210
(8)	$[\text{Au}_6(\text{DPE})_2\text{Cl}]\text{ClO}_4$	29.3 (29.9)	2.17 (2.27)	54.9 (55.9)				218
(9)	$[\text{Au}_6(\text{DPE})_2\text{Cl}]\text{PF}_6$	29.2 (28.9)	2.12 (2.22)	54.3 (54.7)				208
(10)	$[\text{Au}_6(\text{DPE})_2\text{Cl}]\text{BPh}_4$	39.3 (39.1)	3.04 (2.91)	50.6 (50.7)				205
(11)	$[\text{Au}_6(\text{DPE})_2\text{SCN}]\text{ClO}_4$	30.0 (30.4)	2.23 (2.25)	55.4 (55.5)	0.69 (0.66)			207
(12)	$[\text{Au}_6(\text{DPE})_3]\text{Cl}_2 \cdot \text{H}_2\text{O}$	38.0 (37.9)	2.92 (3.00)	47.7 (47.9)		0.58 (0.65)		210
(13)	$[\text{Au}_6(\text{DPE})_3]\text{Br}_2 \cdot \text{H}_2\text{O}$	36.5 (36.6)	2.72 (2.89)	46.1 (46.3)		0.60 (0.62)		195
(14)	$[\text{Au}_6(\text{DPE})_3]\text{I}_2 \cdot \text{H}_2\text{O}$	35.4 (35.3)	2.75 (2.79)	44.4 (44.6)		0.57 (0.60)		177
(15)	$[\text{Au}_6(\text{DPE})_3](\text{SCN})_2 \cdot 2\text{H}_2\text{O}$	37.6 (37.9)	3.12 (3.00)	46.9 (46.75)	0.98 (1.10)	1.20 (1.26)		210
(16)	$[\text{Au}_6(\text{DPE})_3](\text{ClO}_4)_2$	36.2 (36.3)	2.78 (2.79)	46.0 (45.9)				245
(17)	$[\text{Au}_6(\text{DPE})_3](\text{BPh}_4)_2$	50.2 (50.1)	3.73 (3.72)	40.0 (39.2)				213

The numbers in parentheses refer to theoretical values.

(1)  $\mu$ -[1,2-bis(diphenylphosphino)ethane]bis(chlorogold). A solution of hydrogen tetrachloroaurate (51.3 mmoles, 10.1 g Au) in ethanol (100 ml) was treated with DPE (51.9 mmoles, 20.4 g). The insoluble white crystals were recrystallized from dichloromethane solution by addition of ethanol.

(2) *Bis[1,2-bis(diphenylphosphino)ethane]gold chloride.* A solution of hydrogen tetrachloroaurate (5.13 mmoles, 1.01 g Au) in ethanol (20 ml) was treated with DPE (10.3 mmoles, 4.10 g). The solution was then evaporated and the residue dissolved in chloroform was precipitated by addition of n-butylether.

(200 ml) with lithium bromide (3.8 mmoles, 0.33 g). The red brown precipitate was filtered and washed with ethanol.

(5a) *Polymeric di- $\mu$ -(dibromo)di- $\mu$ -bis[1,2-bis(diphenylphosphino)ethane]hexagold aquo.* Prepared in the same way as (4a) from (4).

(6)  $\mu$ -iodo-di- $\mu$ -bis[1,2-bis(diphenylphosphino)ethane]hexagold iodide aquo. From a solution of hexanuclear chloride (4) (1.9 mmoles, 4.0 g) in ethanol (200 ml) with lithium iodide (3.8 mmoles, 0.53 g). The red brown precipitate was filtered and washed with ethanol.

(6a) *Polymeric di- $\mu$ -(diiodo)di- $\mu$ -bis[1,2-bis(diphenylphosphino)ethane]hexagold aquo.* Prepared in the same way as (4a) from (4) in dichloromethane.

(7)  *$\mu$ -thiocyanato-di- $\mu$ -bis[1,2-bis(diphenylphosphino)ethane]hexagold thiocyanato aquo.* From a solution of hexanuclear chloride (4) (0.48 mmoles, 1 g) in ethanol (60 ml) with potassium thiocyanate (1.0 mmoles, 97 mg) in aqueous ethanol solution (70%, 10 ml). The red brown precipitate was recrystallized as above.

(7a) *Polymeric di- $\mu$ -(dithiocyanato)di- $\mu$ -bis[1,2-bis(diphenylphosphino)ethane]hexagold aquo.* Prepared in the same way as (4a) from (4) in dichloromethane solution.

(8)  *$\mu$ -chloro-di- $\mu$ -bis[1,2-bis(diphenylphosphino)ethane]hexagold perchlorate.* From hexanuclear chloride (4) (1.44 moles, 3.0 g) in ethanol (100 ml) and lithium perchlorate (2.88 mmoles, 0.31 g). The red-brown precipitate was thoroughly washed with ethanol and dried.

(9)  *$\mu$ -chloro-di- $\mu$ -bis[1,2-bis(diphenylphosphino)ethane]hexagold hexafluorophosphate.* From hexanuclear chloride (4) (1.44 mmoles, 3.0 g) in ethanol (100 ml) and ammonium hexafluorophosphate (2.88 mmoles, 0.47 g). The red-brown precipitate was washed as above.

(10)  *$\mu$ -chloro-di- $\mu$ -bis[1,2-bis(diphenylphosphino)ethane]hexagold tetraphenylborate.* From hexanuclear chloride (4) (0.29 mmoles, 0.6 g) in ethanol (60 ml) and sodium tetraphenylborate (0.58 mmoles, 0.2 g). The red-brown precipitate was washed as above.

(11)  *$\mu$ -thiocyanato-di- $\mu$ -bis[1,2-bis(diphenylphosphino)ethane]hexagold perchlorate.* From hexanuclear thiocyanate (7) (0.47 mmoles, 1.0 g) in warm ethanol (50 ml) and lithium perchlorate (0.47 mmoles, 51 mg). The red-brown precipitate was recrystallized from dichloromethane on addition of hexane.

(12) *Tri- $\mu$ -{tris[1,2-bis(diphenylphosphino)ethane]hexagold}dichloride aquo.* A suspension of the polymeric red-violet compound (4a) (1 g) in dichloromethane (100 ml) treated with DPE (187 mg) was stirred until a green solution was obtained. From this the green title compound was precipitated by hexane.

(13) *Tri- $\mu$ -{tris[1,2-bis(diphenylphosphino)ethane]hexagold}dibromide aquo.* Obtained analogously as the above compound (12) from the polymeric red-violet compound (5a) (1 g) suspended in dichloromethane (100 ml) and DPE (183 mg).

(14) *Tri- $\mu$ -{tris[1,2-bis(diphenylphosphino)ethane]hexagold}diiodide aquo.* Obtained analogously as (12) from polymeric red-violet compound (6a) (1 g) suspended in dichloromethane (100 ml) and DPE (175 mg).

(15) *Tri- $\mu$ -{tris[1,2-bis(diphenylphosphino)ethane]hexagold}dithiocyanate-2 aquo.* Obtained analogously as (12) from polymeric red-violet compound (7a) (1 g) suspended in dichloromethane (100 ml) and DPE (188 mg).

(16) *Tri- $\mu$ -{tris[1,2-bis(diphenylphosphino)ethane]hexagold}diperchlorate.* Obtained from hexanuclear dichloride (12) (0.15 mmoles, 370 mg) in ethanol solution and lithium perchlorate (0.15 mmoles, 16.2 mg). The green compound was recrystallized from dichloromethane and hexane.

(17) *Tri- $\mu$ -{tris[1,2-bis(diphenylphosphino)ethane]hexagold}bis(tetraphenylborate).* Obtained from hexanuclear dichloride (12) (0.1 mmoles, 246 mg) in ethanol solution and sodium tetraphenylborate (0.1 mmoles, 34.2 mg). The green compound was recrystallized from dichloromethane and hexane.

## Results and Discussion

Compound (1) is a covalent dicoordinated, dinuclear gold(I) derivative, as it was proved by the lack of conductivity and the IR spectrum which shows a strong band at  $325\text{ cm}^{-1}$ , assigned to the Au-Cl stretching which does not appear in compound (2) (Table II). Compounds (2) and (3), on the contrary, are considered salt-like derivatives of tetracoordinated, chelated gold(I). As a matter of fact, we have no direct evidence that DPE is chelated, but we infer this from the fact that four-coordinate gold(I) compounds have been described with chelating ditertiary phosphines and arsines.<sup>4</sup>

The conductivities of compounds (4), (5), (6) and (7) which roughly correspond to uni-univalent electrolytes and the reaction of (4) and (7) with non-nucleophilic anions to give (7), (9), (10) and (11) derivatives, indicate that the two anions are differently bound in these complexes: one, acting as ligand in the inner sphere, can only be exchanged by nucleophilic anions, whereas the other completely dissociated in solution, can be exchanged with any other anion under appropriate conditions.

The infrared spectrum of the dichloride (4) confirms this and indicates that the chloride is bridging two gold atoms; the band at  $275\text{ cm}^{-1}$  may in fact be assigned to the metal-chloride stretching in the Au-Cl-Au group.<sup>5</sup>

The same band is observed in the perchlorate (8), the fluorophosphate (9), and the tetraphenylborate (10), which therefore must contain the cation  $[\text{Au}_6(\text{DPE})_2\text{Cl}]^+$  which is present also in the dichloride (4). This cation may be considered as formed by two clusters of three gold atoms bonded by two DPE and one chloride bridges.

The intermetallic bond should, in this case, involve three gold atoms, as in the ethyldiphenylphosphine derivatives,<sup>2</sup> instead of the five, found in the triphenylphosphine compound  $[\text{Au}_5\text{P}_4]\text{Cl}$ .<sup>1</sup>

The fact that in this case the average oxidation number of gold is higher (1/3) than in the triphenylphosphine compounds (1/5) can be considered a consequence of the stronger basicity of the ligands.

The bromide (5) and the iodide (6) should be strictly analogous to the chloride (4); only, in the former compounds the presence of bridging halogen atoms could not be shown because the metal-halogen IR bands were beyond the range of our instrument.

(4) R. S. Nyholm, *Nature*, 168, 705 (1951).

(5) D. M. Adams, J. Chatt, J. M. Davidson and J. Garrett, *J. Chem. Soc.*, 2189 (1963).

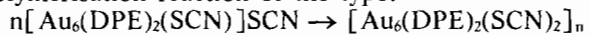
Table II.

		$10^{-3}$ mol $\Lambda$	IR Frequencies ( $\text{cm}^{-1}$ ) in Nujol
(1)	$\text{Au}_2(\text{DPE})\text{Cl}_2$	—	330 vs $\nu(\text{Au-Cl})$
(2)	$[\text{Au}(\text{DPE})_2]\text{Cl}$	25.4 *	
(3)	$[\text{Au}(\text{DPE})_2]\text{BPh}_4$	23.0 *	
(4)	$[\text{Au}_6(\text{DPE})_2\text{Cl}]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$	100 +	275 m $\nu(\text{Au-Cl-Au})$
(4a)	$[\text{Au}_6(\text{DPE})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}]$	—	280 m $\nu(\text{Au-Cl-Au})$
(5)	$[\text{Au}_6(\text{DPE})_2\text{Br}]\text{Br} \cdot \text{H}_2\text{O}$	70 +	
(6)	$[\text{Au}_6(\text{DPE})_2\text{I}]\text{I} \cdot \text{H}_2\text{O}$	68 +	
(7)	$[\text{Au}_6(\text{DPE})_2\text{SCN}]\text{SCN} \cdot \text{H}_2\text{O}$	67 +	2105 vs $\nu(\text{CN})$ ; 2054 vs $\nu(\text{CN})$
(7a)	$[\text{Au}_6(\text{DPE})_2(\text{SCN})_2 \cdot \text{H}_2\text{O}]$	—	2105 vs $\nu(\text{CN})$
(8)	$[\text{Au}_6(\text{DPE})_2\text{Cl}]\text{ClO}_4$	23.4 *	1105 vs $\nu_{\text{as}}(\text{ClO}_4)$ ; 280 m $\nu(\text{Au-Cl-Au})$
(9)	$[\text{Au}_6(\text{DPE})_2\text{Cl}]\text{PF}_6$	26.0 *	850 vs $\nu_{\text{as}}(\text{PF}_6)$ ; 280 m $\nu(\text{Au-Cl-Au})$
(10)	$[\text{Au}_6(\text{DPE})_2\text{Cl}]\text{BPh}_4$	18.5 *	275 m $\nu(\text{Au-Cl-Au})$
(11)	$[\text{Au}_6(\text{DPE})_2\text{SCN}]\text{ClO}_4$	22.4 *	1090 vs $\nu_{\text{as}}(\text{ClO}_4)$ ; 2105 vs $\nu(\text{CN})$
(12)	$[\text{Au}_6(\text{DPE})_3]\text{Cl}_2 \cdot \text{H}_2\text{O}$	41 *	
(13)	$[\text{Au}_6(\text{DPE})_3]\text{Br}_2 \cdot \text{H}_2\text{O}$	38 *	
(14)	$[\text{Au}_6(\text{DPE})_3]\text{I}_2 \cdot \text{H}_2\text{O}$	36 *	
(15)	$[\text{Au}_6(\text{DPE})_3](\text{SCN})_2 \cdot 2\text{H}_2\text{O}$	44.3 *	2054 vs $\nu(\text{CN})$
(16)	$[\text{Au}_6(\text{DPE})_3](\text{ClO}_4)_2$	43 *	1090 vs $\nu_{\text{as}}(\text{ClO}_4)$
(17)	$[\text{Au}_6(\text{DPE})_3](\text{BPh}_4)_2$	31 *	

\* In  $\text{C}_6\text{H}_5\text{NO}_2$ ; + in  $\text{CH}_3\text{NO}_2$ .

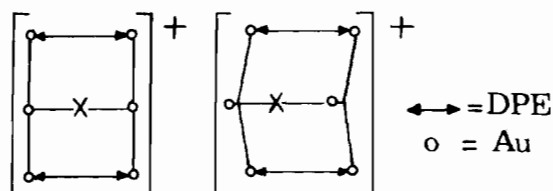
A strong spectroscopic evidence was however obtained for the thiocyanate (7) which showed in the IR a strong band at  $2054 \text{ cm}^{-1}$  assigned to the CN stretching of the ionic  $\text{SCN}^-$ , and a band at  $2105 \text{ cm}^{-1}$  characteristic for the CN stretching in bridging  $\text{SCN}^-$ .

The polymerisation of the thiocyanato compound (7) analogous to that of the chloro, bromo and iodo compounds (4), (5) and (6), could also be interpreted by the IR spectrum; in fact, it could be followed by the slow gradual disappearance of the band of the ionic  $\text{SCN}^-$  accompanied by the increasing intensity of the band of the bridging thiocyanato group. This and the insolubility of the compound (7a) seem to indicate a polymerisation reaction of the type:



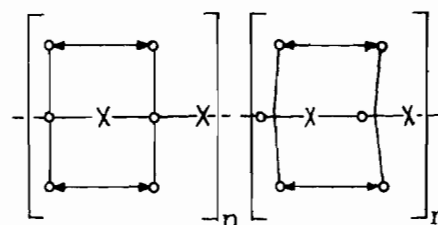
The compounds (4a), (5a) and (6a) which form under similar conditions, are considered also polymeric, although in these cases no spectroscopic evidence could be obtained. The weak coordinative unsaturation of compounds (4), (5), (6), (7), which brings about their polymerisation to (4a), (5a), (6a) and (7a) is confirmed by the reaction of these compounds with DPE in dichloromethane to give the green compounds (12), (13), (14), (15) which behave as uni-bivalent electrolytes in solution, and by the IR spectrum of the compound (15) which shows only one band assignable to ionic  $\text{SCN}^-$  group.

It is surprising that these green compounds cannot be obtained directly from the ionic red-brown compounds. Although there are not yet any direct data on the configuration of the clusters of gold atoms in these compounds, we propose the following hypothetical structures according whether the triangular or linear disposition of gold atoms is assumed. These structures are in accordance with the conductivities and solubilities and with the infrared evidence: Type A, cationic ( $1+$ ) hexanuclear:



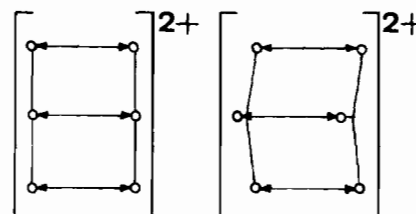
Compounds (4), (5), (6), (7), (8), (9), (10), (11) belong to this type.

Type B, neutral polymer



Compounds (4a), (5a), (6a) and (7a) belong to this type.

Type C, cationic ( $2+$ ) hexanuclear



Compounds (12), (13), (14), (15), (16) and (17) belong to this type.

These structures could explain how compounds of type A may polymerize to type B and how the polymeric compounds of type B may depolymerize to type C.

The stable forms appear in both cases to be the most symmetric, probably having less internal strain. As for the water which is present in many of these compounds, as inferred both from the analyses (oxygen determination) and the IR evidence, we have no precise idea whether it should be considered as lattice water or as bound through hydrogen bonds to the anionic groups.

*Acknowledgment.* This work was supported with a Grant of C.N.R. (Italian Research Council).