# THE BIDENTATE CHELATING AGENT, 8-DIMETHYLARSINOQUINOLINE–II

## COMPLEXES OF COPPER, SILVER AND GOLD

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**Abstract** – Mono- and bis-chelates of univalent copper and gold, and bis-chelated complexes of monovalent silver, have been isolated using the bidentate chelating agent 8-dimethylarsinoquinoline (As-N, Fig. 1). Physico-chemical measurements of the mono-chelated copper(I) complexes Cu(As-N)X indicate the presence of both a salt-like species  $[Cu(As-N)_2][CuX_2]$  and a non-conducting form Cu(As-N)X in solution, while similar measurements on the analogous gold(I) compounds, Au(As-N)X, preclude the salt-like structure. The isolation of the apparently five co-ordinate copper (II) complex  $[Cu(As-N)_2(NO_3)]NO_3$  is also reported.

THE PREPARATION of the chelating agent 8-dimethylarsinoquinoline and its reactions with a variety of metal salts have been reported [1, 2]. In all instances the compound behaves as a bidentate, co-ordinating through its tertiary ring nitrogen and arsenic atoms. Thus, the co-ordination centres in this ligand are a tertiary ring nitrogen atom as in  $2,2^1$ -dipyridyl and 1,10 phenanthroline and a tertiary alpha-arsenic atom as in the di-tertiary arsine *o*-phenylenebisdimethylarsine.

Although attempts to prepare copper, silver and gold complexes of 8dimethylarsinoquinoline proved to be difficult in many cases, some complexes of each metal have been isolated and their properties investigated. In every instance, complexes of the lower oxidation states were more readily prepared than those of high oxidation states, as the addition of 8-dimethylarsinoquinoline to solutions of the metal salts immediately reduced the metal ion to its lowest oxidation state.

Copper(I) complexes of 8-dimethylarsinoquinoline were isolated as both the mono- and bis-chelated species. The mono-chelates,  $Cu(As-N)X \{X = Br, I\}$ , can possibly exist as (a) the dimeric molecule  $[Cu_2(As-N)_2X_2]$  of structure,



(b) the salt-like form  $[Cu(As-N)_2][CuX_2]$  or (c) the three covalent monomer [Cu(As-N)X]. The existence of three covalent copper(I) has been confirmed

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- 1. Part I. G. A. Barclay, M. A. Collard, C. M. Harris and J. V. Kingston, J. chem. Soc. (A), 830 (1969).
- 2. G. A. Barclay, C. M. Harris and J. V. Kingston, Chem. Ind. 1965, 227.



Fig. 1. 8-Dimethylarsinoquinoline.

by X-ray structural analysis in the compound  $KCu(CN)_2[3]$  while compounds of the type Cu(chel)X (chel = 1, 10 phenanthroline, or 2,2<sup>1</sup>-dipyridyl) have been shown to exist in nitrobenzene solution partly in the form of the salt  $[Cu(chel)_2]$  $[CuX_2]$ , and partly in the form of a non-electrolyte[4]. The existence of both forms in solution has been interpreted as being possibly due to the equilibria (1) and (2).

$$[\operatorname{Cu}_2(\operatorname{chel})_2 X_2] \rightleftharpoons [\operatorname{Cu}(\operatorname{chel})_2]^+ + [\operatorname{Cu} X_2]^- \tag{1}$$

$$2\mathrm{Cu(chel)}X \rightleftharpoons [\mathrm{Cu(chel)}_2]^+ + [\mathrm{Cu}X_2]^-.$$
(2)

As conductivity measurements of the mono-chelated complexes of empirical formula Cu(As-N)X indicate an incomplete ionisation in nitrobenzene and nitromethane solutions (Table 1), attempts were made to examine by spectro-photometric methods the nature of the equilibria present.

Table I				
Complex	Colour	Conductivity at 25°C $\Lambda_M(\Omega^{-1} \text{ cm}^2 \text{mole}^{-1})$	Solvent 10 <sup>-3</sup> M	
[Cu(As-N) <sub>2</sub> ]ClO <sub>4</sub>	pale-yellow	30.1	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	
. –		93-2	CH <sub>3</sub> NO <sub>2</sub>	
Cu(As-N)I	orange	7.1	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	
		19.8	CH <sub>3</sub> NO <sub>2</sub>	
Cu(As-N)Br	yellow	12.3	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	
$[Cu(As-N)_2(NO)_3]NO_3$	green	26	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	
[Ag(As-N) <sub>2</sub> ]ClO <sub>4</sub>	colourless	30	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	
		88	CH <sub>3</sub> NO <sub>2</sub>	
$[Ag(As-N)_{2}]PF_{6}$	colourless	26	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	
$[Ag(As-N)_2]B_4$	colourless	16	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	
$[Au(As-N)_2]ClO_4$	colourless	29	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	
Au(As-N)Cl	colourless			
Au(As-N)Br	colourless	< 0.1	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	
Au(As-N)I	cream	< 0.1	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	

3. J. Cramer, J. phys. Chem. 611, 1388 (1957).

4. N. T. Barker and C. M. Harris, Private communication.

The absorption curves of the bis-chelated copper(I) ion and the monochelated copper(I) iodide were measured in the solvents nitrobenzene (Fig. 2) and nitromethane and a similarity was noted in the shapes of the spectra. However, the reflectance spectra of the solid complexes were found to differ (Fig. 3) as small shoulders appeared on the curve of the reflectance spectra at approximately 440 m $\mu$  for the mono-chelated bromide complex and at approximately 475 m $\mu$  for the mono-chelated iodide complex.

Conductivity measurements (Table 1) indicate that an equilibrium has been established. Values of the equilibrium constant estimated from the conductivity data are listed in Table 2. They are of approximately the same order as those calculated for the analogous mono-chelated 1,10 phenanthroline system  $(k = 3.4 \times 10^{-1})^4$ .



Fig. 2. Absorption spectra of copper(I) complexes in nitrobenzene solutions.



Fig. 3. Reflectance spectra of some copper(I) complexes.

Complex	Salt* %)	k	Solvent
Cu(As-N)I	42.5	1·4 × 10 <sup>-1</sup>	CH <sub>3</sub> NO <sub>2</sub>
	<b>47</b> ·1	$1.0 \times 10^{-1}$	φNO <sub>2</sub>
Cu(As-N)Br	<b>81·7</b>	2.1	$\phi NO_2$

 Table 2. Equilibrium constants estimated from conductivity data

\*%salt is expressed in terms of the dimeric molecular weight.

The optical density of solutions of varying concentrations of the 8-dimethylarsinoquinoline complexes were measured at 380 mµ in nitromethane solutions and 430 m $\mu$  in nitrobenzene solutions. These results show that the solutions obey the Beer-Lambert law, thus indicating that the equilibrium may be obtained spectrophotometrically by measuring the absorption of the fully ionised bis(8dimethylarsinoquinoline)copper(I) perchlorate at different concentrations and expressing the absorption of  $[Cu(As-N)_2]^+$  ions in the equilibrium mixture as a fraction of the absorption of the same ion in the fully ionised salt only if it is assumed that the absorption of any other species in the equilibrium mixture is negligible. This assumption unfortunately is not true since the spectrophotometric results (Table 3) show that the optical density of the mono-chelated complex (when the concentration is expressed in terms of the complex salt) is greater than the value expected if all the compound exists in the salt form. The conductivity measurements indicate the presence of less than 50 per cent of [Cu(As-N)<sub>2</sub>][CuX<sub>2</sub>] in 10<sup>-3</sup> M nitrobenzene solution, hence the absorption of the nonconducting species in the equilibrium is very considerable. Thus, equilibrium constants could not be calculated from the spectrophotometric results as the

Table 3				
Concentration expressed as the complex salt [Cu(As-N) <sub>2</sub> ] [CuX <sub>2</sub> ] in g.moles/l. 10 <sup>-4</sup>	Solvent $X =$	Optical density	Optical density of [Cu(As-N) <sub>2</sub> ] <sup>4</sup>	
5.05	CH <sub>3</sub> NO <sub>2</sub> I	0.621	0.580	
4.04	CH <sub>3</sub> NO <sub>2</sub> I	0.497	0.469	
3.03	CH <sub>3</sub> NO <sub>2</sub> I	0.381	0.360	
2.02	CH <sub>3</sub> NO <sub>2</sub> I	0.237	0.244	
0.50	CH <sub>3</sub> NO <sub>2</sub> I	0.062	0.059	
4.75	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> I	0.305	0.230	
3.80	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> I	0.235	0.185	
1.90	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> I	0.117	0.094	
0.95	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> I	0.023	0.048	
0.20	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> I	0.023	0.022	
5.15	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> Br	0.243	0.250	
4.10	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> Br	0.192	0.200	
3.10	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> Br	0.147	0.121	
2.05	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> Br	0.096	0.101	
1.05	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> Br	0.047	0.021	

extinction coefficient of the monomeric species is not accurately known. Using the conductivity measurements in nitrobenzene and nitromethane solutions (Table 1) approximate extinction coefficients at 430 and 380 m $\mu$  of the monomeric species were estimated (Table 4) and are of the same order of magnitude as those of [Cu(As-N)<sub>2</sub>]ClO<sub>4</sub>. The postulate of equilibrium (1) is supported however by spectrophotometric measurements over a concentration range since the Beer-Lambert law is obeyed.

Table 4				
(a) Estimated extinction coefficients at 430 m $\mu$ in nitrobenzene soln.				
Complex	Σ			
Cu(As-N) <sub>2</sub> ClO <sub>4</sub>	497			
Cu(As-N)I	367			
Cu(As-N)Br	141			
(b) Estimated extinction coefficients	at 380 m $\mu$ in nitromethane soln.			
Complex	Σ			
Cu(As-N) <sub>2</sub> ClO <sub>4</sub>	1140			
Cu(As-N)I	669			

A further investigation of the bis-chelated copper(I) perchlorate by means of conductometric titrations with halide ions in nitrobenzene solution gave an end-point in the case of the iodide titration at a copper:iodide ratio of 1:1. This is undoubtedly due to the equilibrium reaction

$$2[Cu(As-N)_2]^+ + 2I^- \rightleftharpoons 2Cu(As-N)I + 2As-N \rightleftharpoons [Cu(As-N)_2]^+ + [CuI_2]^- + 2As-N$$

producing the non-conducting Cu(As-N)I species to an appreciable extent. Titration with chloride and bromide ions produced no well defined end-points although the curves obtained are indicative of a similar reaction occurring, but to a much lesser extent.

Complexes of copper(II) with the ligand 8-dimethylarsinoquinoline were particularly difficult to prepare owing to the reduction of the copper(II) ion to copper(I) in the presence of most anions with the exception of the nitrate ion. The apparently five co-ordinated nitrato bis(8-dimethylarsinoquinoline)copper(II) nitrate was prepared by reacting two moles of ligand with one mole of copper(II) nitrate in ethanolic solution. The assignment of a five co-ordinate structure has been verified by conductivity and i.r. measurements. The molecular conductivity of a  $0.38 \times 10^{-3}$  nitrobenzene solution was found to be  $26 \Omega^{-1} \text{ cm}^2 \text{mole}^{-1}$  indicating the presence of a uni-univalent electrolyte, while from the i.r. spectrum, bands have been assigned to one ionic nitrate group (1390 cm<sup>-1</sup>) and one monodentate co-ordinated nitrate group (1465, 1290 and 1015 cm<sup>-1</sup>).

The complex which has a magnetic moment of 1.8 B.M. at 295°K ( $\chi'_M = 1341$ ), is unstable in solution as the copper(II) ion is partially reduced to the copper(I) ion. In nitromethane solution the reduction is complete but in nitro-

benzene solution the absorption is similar to that of the solid reflectance spectra with a very broad diffuse band centred at  $800 \text{ m}\mu$ . The green colour is due to this absorption coupled with what appears to be a charge-transfer band at  $450 \text{ m}\mu$ , (Fig. 4). Owing to the sparing solubility of the compound accurate solution spectra could not be obtained.



Fig. 4. Absorption and reflectance spectra of nitratobis(quinoline-8-dimethylarsine) copper(11) nitrate.

The colourless bis-chelated silver(I) cation has been isolated by the addition of large anions, such as perchlorate, hexafluorophosphate and tetraphenylborate to give complexes which are uni-univalent electrolytes in solution. The perchlorate was investigated conductometrically both in nitrobenzene and nitromethane solutions by titration with halide ions, and well defined end-points were obtained at silver: halide ratios of 1:1. Fine precipitates of the silver halides formed in the solution. Attempts to prepare silver halide complexes of the ligand were however unsuccessful.

8-Dimethylarsinoquinoline, reacts with gold(III) chloride to yield mono- and bis-chelated complexes of gold(I). The colourless mono-chelated chloride and bromide complexes are non-electrolytes in nitrobenzene solution, which eliminates the salt like structure  $[Au(As-N)_2][AuX_2]$ . Possible structures for these complexes are conceivably a three covalent monomer or a dimeric non-electrolyte of the following structure



Unfortunately the sparing solubility of this compound prevented a determination of its molecular weight.

The bis-chelated gold(I) ion which is isolated as the perchlorate was titrated conductometrically, with halide ions, in nitrobenzene and nitromethane solutions. An end-point was obtained in every instance at a gold:halide ratio of 1:1, which indicated attack on the bis-chelated gold(I) cation with the resultant formation of the mono-chelated halides

$$[\operatorname{Au}(\operatorname{As-N})_2]^+ + X^- \to \operatorname{Au}(\operatorname{As-N})X + \operatorname{As-N}.$$

The mono-chelated halides are prepared by reacting one mole of gold(III) chloride with two moles of ligand, in ethanol solution. A study of the i.r. spectrum of bis(8-dimethylarsinoquinoline)gold(I) perchlorate indicated the presence of an ionic perchlorate (1088 and  $622 \text{ cm}^{-1}$ )[4], while molecular conductivity measurements in nitrobenzene solution (Table 1) support the presence of a univalent electrolyte.

The ability of the chelating agent, 8-dimethylarsinoquinoline to stabilise monovalent copper, silver and gold complexes parallels the behaviour of 1,10 phenanthroline [5] and o-phenylenebisdimethylarsine [6]. However, a large number of copper(II) complexes can be prepared using the nitrogeneous ligands 1,10 phenanthroline and 2,2'-dipyridy [7], while with 8-dimethylarsinoquinoline it was possible to prepare only one, and none have been described with o-phenylenebisdimethylarsine.

### **EXPERIMENTAL**

Analysis. Carbon, hydrogen and nitrogen were by Dr. E. Challen of the Microanalytical Laboratory, University of N.S.W. Arsenic and copper analyses were carried out on solutions of the decomposed sample by Atomic absorption spectroscopy using an air hydrogen flame  $\lambda = 1937$ Å, lamp current I = 10 mA and slit width of  $300 \mu$ , (Arsenic), and an air coal gas flame  $\lambda = 2438$  Å, I = 10 mA and slit width of  $25 \mu$  (Copper). Infrared spectra were taken in mulls (nujol and hexachlorobutadiene) on a Perkin-Elmer infracord model 337, while absorption and reflectance spectra were obtained on a Zeiss PMQ11 spectrophotometer. Electrical conductivities were measured at 25°C using a Philips Philoscope in conjunction with a Philips immersion cell with platinised electrodes. Solvents (nitromethane, nitrobenzene and tetrahydrofuran) were distilled after standing for 24 hr over molecular sieves and used immediately.

### 8-Dimethylarsinoquinoline

The chelating agent was prepared as described previously[1]. Found: C, 56·7; H, 5·1; N, 6·2; M(chloroform)224.  $C_{11}H_{12}AsN$  requires C, 56·1; H, 5·2; N, 6·0%. Mol. Wt. 233.

### 8-Dimethylarsinoquinolinecopper(I)iodide monohydrate

A solution of 8-dimethylarsinoquinoline (0.3 g) in acetone (5 ml) was added to an aqueous solution (10 ml) of copper(11) chloride dihydrate (0.1 g) followed by an aqueous solution (10 ml) of sodium iodide (3 g). The orange precipitate was filtered and washed with water and ether. Yield 0.3 g. Found: C, 30.1; H, 3.2; N, 3.3; Cu, 14.3; Calculated for C<sub>11</sub>H<sub>14</sub>AsCuNO: C, 29.9; H, 3.2, N, 3.2; Cu, 14.4%.

#### 8-Dimethylarsinoquinolinecopper(I)bromide

The yellow complex was prepared in a similar manner to that described for the iodide complex except for the addition of potassium bromide instead of sodium iodide. Found: C, 34.9; H, 3.0; N, 4.1; Cu, 15.8; C<sub>11</sub>H<sub>12</sub>AsBrCuN requires C, 35.1; H, 3.2; N, 3.7; Cu, 16.1%.

- 5. W. W. Brandt, F. P. Dwyer and E. C. Gyarfas, Chem. Rev. 54, 959 (1954).
- A. Kabesh and R. S. Nyholm, J. chem. Soc. 38, 1951: J. Lewis, R. S. Nyholm and D. J. Phillips, J. chem. Soc. 2177, 1962; C. M. Harris and R. S. Nyholm, J. chem. Soc. 63, 1957.
- 7. C. M. Harris, T. N. Lockyer and H. Watermann, Nature 192, 424 (1961).

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### Bis(8-dimethylarsinoquinoline)copper(I) perchlorate

A solution of copper(11) perchlorate hexahydrate (0.3 g 1 mole) in ethanol (5 ml) was added to a solution of 8-dimethylarsinoquinoline (0.5 g 2 mole) in warm ethanol (10 ml) to give a yellow solution. Yellow crystals formed on standing which were filtered, and washed with ethanol. Yield 0.3 g. Found: C, 42.0; H, 3.8; N, 4.7; C<sub>22</sub>H<sub>24</sub>As<sub>2</sub>ClCuN<sub>2</sub>O<sub>4</sub> requires C, 42.0; H, 3.8; N, 4.4%.

## Nitratobis(quinoline-8-dimethylarsine)copper(11) nitrate monohydrate

A solution of 8-dimethylarsinoquinoline (0.2 g 2 mole)dissolved in ethanol (10 ml) was added to an ethanol solution (10 ml) of copper(II) nitrate hexahydrate (0.15 g 1 mole). The solution was heated on a steam bath and the green crystals that separated from the solution on standing, were filtered off and washed with ethanol. Yield 0.2 g. Found: C, 38.9; H, 3.5; N, 8.5; As, 22.3; C<sub>22</sub>H<sub>26</sub> As<sub>2</sub>CuN<sub>4</sub>O<sub>7</sub> requires C, 39.3; H, 3.9; N, 8.3; As 22.3%.

### Bis(8-dimethylarsinoquinoline)silver(1) perchlorate

Silver perchlorate (0.1 g) in ethanol (5 ml) was added to a solution of 8-dimethylarsinoquinoline (0.3 g) in ethanol (5 ml). A white precipitate formed on standing. This precipitate was filtered and washed with ethanol. Found: C, 38.9; H, 3.7; N, 4.4;  $C_{22}H_{24}AgAs_2ClN_2O_4$  requires C, 39.2; H, 3.6; N, 4.2%.

### Bis(8-dimethylarsinoquinoline)silver(I) hexafluorophosphate

A solution of silver nitrate (0.1 g) in ethanol (5 m) was added to an ethanol solution (5 m) of 8-dimethylarsinoquinoline (0.3 g). To this clear solution was added a solution of potassium hexafluorophosphate (0.5 g) in aqueous ethanol (10 ml, 50%) and a white precipitate formed on standing. The precipitate was filtered and washed with ethanol. Yield 0.2 g. Found: C, 36.5; H, 3.3; N, 4.1;  $C_{22}H_{24}AgAs_2F_6N_2P$  requires C, 36.7; H, 3.4; N, 3.9%.

### Bis(8-dimethylarsinoquinoline)silver(1) tetraphenylborate

This complex was prepared in a similar manner to that described above for the hexafluorophosphate complex except for the addition of sodium tetraphenylborate instead of potassium hexafluorophosphate. Found: C,  $62 \cdot 2$ ; H,  $5 \cdot 2$ ; N,  $3 \cdot 2$ ;  $C_{22}H_{24}AgAs_2BN$  requires C,  $61 \cdot 8$ ; H,  $5 \cdot 0$ ; N,  $3 \cdot 1\%$ .

### Bis(8-dimethylarsinoquinoline)gold(1) perchlorate

A yellow ethanol solution (5 ml) of sodium tetrachloroaurate(III) (0.1 g) was added to a solution of 8-dimethylarsinoquinoline (0.4 g) in ethanol (10 ml). The colourless solution was heated and filtered and solid sodium perchlorate was added to the filtrate. A while precipitate formed and this washed with water, ethanol and ether. Yield 0.2 g. Found: C, 35.0; H, 3.5; N, 3.9; C<sub>22</sub>H<sub>24</sub>As<sub>2</sub>AuClN<sub>2</sub> O<sub>4</sub> requires C, 34.6; H, 3.2; N, 3.7%.

### 8-Dimethylarsinoquinolinegold(I) chloride

8-Dimethylarsinoquinoline (0.4 g) dissolved in ethanol (5 ml) was added to an ethanol solution (5 ml) of sodium tetrachloroaurate(III) (0.1 g). On standing, colourless crystals formed and these were filtered off and washed with ethanol. Yield 0.1 g. Found: C, 28.4; H, 2.6; N, 3.4; C<sub>11</sub>H<sub>12</sub>AsAuClN requires C, 28.4; H, 2.6; N, 3.0%.

#### 8-Dimethylarsinoquinolinegold(1) bromide

This complex was prepared in a similar manner to that described for the chloride except for the addition of lithium bromide to the solution before precipitation occurred. Yield 0.1 g. Found: C, 26.3; H, 2.4; N, 3.0;  $C_{11}H_{12}AsAuBrN$  requires C, 25.9; H, 2.4; N, 2.8%.

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