Novel arsenic-containing ligands for the stabilisation of Au^{II}

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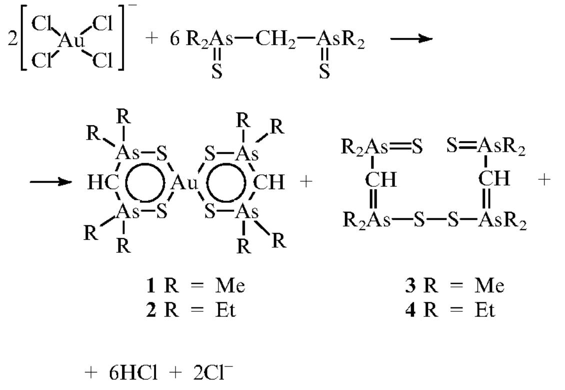
Stable bis-chelate Au^{II} complexes containing two arsenic atoms in the chelate rings have been prepared.

Gold(II) complexes are known to be usually unstable, and their synthesis is a difficult task. Nevertheless, during the last 20–25 years, various authors, especially Fackler, Schroder and Schmidbauer, have managed to prepare a fairly large number of mono- and binuclear coordination compounds of Au^{II}. Numerous studies devoted to the stabilisation of Au^{II} by complex formation have been published. Some of them are mentioned in monographs[1,2] to which the reader is referred for more details. However, it is noteworthy that the stabilisation of Au^{II} has been carried out using mostly sulfur-containing ligands (dithiocarbamates and dithiolates)[3–13] and only in one study has a nitrogen-containing ligand (phthalocyanine) been used.[14] There are no published papers in which any other heteroorganic ligands (in particular, arsenic containing ones) have been used for this purpose.

We now report the synthesis of the previously unknown and fairly stable chelates of Au^{II} with bidentate ligands of the $R_2As(S)–CH_2–As(S)R_2$ type, namely with bis(dimethylarsinothiono)methane (R = Me) and bis(diethylarsinothiono)methane (R = Et), which are of interest, if only because they contain two arsenic atoms in their metal-containing chelate rings. We found that when tetrachloroauric(III) acid reacts with a ~1.5-fold molar excess of bis(dimethylarsino-thiono)methane or bis(diethylarsinothiono)methane in a methanolic solution at 0 °C or below, dark-brown solutions are initially formed from which dark-green compounds precipitate over a period of 2–3 min. If these precipitates are quickly isolated from the mother liquors, washed with methanol and ethanol and dried under an inert atmosphere, their initial dark-green colour remains unchanged at least for 5 days at temperatures below −15 °C. If ethanol is used instead of methanol as the solvent, the yields of the target products (*i.e.* dark-green substances) decrease. If the synthesis is conducted in any other solvent, no dark-green precipitates are formed. Both precipitates are readily soluble in toluene, benzene and tetrachloromethane. However, in all these cases the intial dark-green solutions are decolourised over a period of 1–2 min. As these compounds are heated to 240 °C, they lose 74.0 and 77.2% of their weight, respectively, which corresponds to the elimination of two ligand molecules in both cases. The elemental analysis data of the dark-green compounds permit the empirical formulae $AuC_{10}As_4S_4H_{26}$ (**1**) and $AuC_{18}As_4S_4H_{42}$ (**2**) to be attributed to them.[†] This corresponds to the stoichiometric composition AuL_2 (L^- is the deprotonated form of the ligand). The yields of the products were 82.5% and 83.0%, respectively. Both compounds are paramagnetic (μ_{eff} = 1.82–1.86 B.M.) and they exhibit sharp EPR signals at 77 K. The values of the *g*-factors of these compounds as well as their μ_{eff} values indicate, in conformity with the data reported previously,[3–14] that the dark-green compounds incorporate Au^{II} with a coordination number equal to 4. The X-ray photoelectron spectra of the compounds AuL_2 also support this conclusion: they exhibit sharp $Au4f_{7/2}$ lines at 86.0 eV corresponding exactly to Au^{II} (according to numerous data, Au^{I} is responsible for the $Au4f_{7/2}$ line at 84.0–85.0 eV, whereas in the presence of Au^{III}, this line appears at 87.0–88.3 eV[15–17]). After evaporation of the solvent (methanol or ethanol), compounds that have, according to chemical analysis data, the empirical formulae $C_5As_2S_2H_{13}$ and $C_9As_2S_2H_{21}$, respectively, can be isolated from the mother liquor.[‡] In addition, the molecular weights of these compounds found by the cryoscopic method both in methanol and ethanol were 580 and 690, respectively. Therefore, the doubled empirical formulae presented above, *i.e.* $C_{10}As_4S_4H_{26}$ (**3**) and $C_{18}As_4S_4H_{42}$ (**4**), can be attributed to them. Possible structures for **3** and **4** are suggested in Scheme 1. The IR spectra of the products exhibit ν(As–S) bands (at 390 and 395 cm^{-1}, respectively) and ν(As = C) bands (at 705 and 710 cm^{-1}, respectively); these bands are missing from the spectra of the initial ligands. The IR spectra of both compounds under consideration also contain ν(As = S) bands at 485 and 490 cm^{-1}, respectively, and ν(As–S) bands at 570 and 575 cm^{-1}, respectively; these bands are also recorded in the spectra of both ligands studied (480 and 570 cm^{-1}; 490 and 575 cm^{-1}). Since in all Au^{II} complexes with dithio-ligands, which are able to form five- and six-membered metal-containing chelate rings, the gold atoms coordinate to two sulfur atoms, the formation of the chelates AuL_2 with the ligands under consideration can be represented by Scheme 1.



1 R = Me
2 R = Et
3 R = Me
4 R = Et

+ 6HCl + 2Cl⁻

Scheme 1

It is notable that when the Au^{II} chelates synthesised are stored at 20 °C, even under an inert atmosphere, the intensity of the EPR signal corresponding to Au^{II} starts to decrease fairly rapidly, within 0.5–1.0 h, and over a period of 3–4 days this signal disappears entirely. As this takes place, the dark-green compounds are decolourised. Moreover, during storage of both Au^{II} complexes two additional bands at 84.7 and 85.7 eV appear in their X-ray photoelectron spectra, apart from the $Au4f_{7/2}$ line corresponding to Au^{II}. According to published data,[15–17] these lines can be assigned to $Au4f_{7/2}$ from Au^{I} and Au^{III}, respectively. The intensities of these two lines increase with time, whereas that of the line at 86.0 eV

[†] For $AuC_{10}As_4S_4H_{26}$ (**1**), calculated: Au, 25.55; C, 15.58; As, 38.85; S, 16.65; H, 3.37%; found Au, 26.0; C, 15.3; As, 38.7; S, 16.4; H, 3.6%. The overall yield 82.5% of the theoretically possible quantity. For $AuC_{18}As_4S_4H_{42}$ (**2**), calculated: Au, 22.31; C, 24.46; As, 33.93; S, 14.54; H, 4.76%; found Au, 22.8; C, 24.9; As, 33.1; S, 14.9; H, 4.3%. The overall yield 83.0% of the theoretically possible quantity.

[‡] For $C_5As_2S_2H_{13}$, calculated: C, 20.91; As, 52.20; S, 22.36; H, 4.53; found: C, 21.1; As, 52.3; S, 22.2; H, 4.4%; for compound $C_9As_2S_2H_{21}$, calculated: C, 31.49; As, 43.67; S, 18.72; H, 6.12, found: C, 31.3; As, 43.8; S, 19.0; H, 5.9%.

decreases gradually and, finally, disappears entirely . It is noteworthy that the instant this line disappears coincides with the instant at which the EPR signal corresponding to $\mathrm{Au^{II}}$ disappears and with the instant when both complexes are completely decolourised. At the same time, the chemical analysis data indicate that the elemental analysis remains unchanged during decolouration. The molecular weights of the resulting colourless products in benzene solutions are 1540 and 1770, respectively; these values are two times greater than the molecular weights of the initial chelates $\mathrm{AuL_2}$. The coordination number 4 is known to be the most typical of $\mathrm{Au^{I}}$, $\mathrm{Au^{II}}$ and $\mathrm{Au^{III}}$. Thus, the observed transformations may be due to the formation of 'heterovalence' complexes as shown in Scheme 2.

Attention is drawn to the fact that the attempts to obtain

$$2\mathrm{Au^{II}L_2} \longrightarrow [\mathrm{Au^{III}L_2}]^+[\mathrm{Au^{I}L_2}]^-$$

Scheme 2

analogous $\mathrm{Au^{II}}$ complexes with other ligands of the $\mathrm{R_2As(S)–CH_2–As(S)R_2}$ type, where R is propyl, isopropyl, butyl and isobutyl, were unsuccessful. This can be accounted for by the fact that the replacement of Me or Et groups in the molecules of the ligands by other alkyl or aryl groups decreases, on the one hand, the electron-donating ability of the sulfur atoms and, on the other hand, the tendency of the ligands to thiolisation and, as a consequence, the probability of the formation of uncharged $\mathrm{Au^{II}}$ complexes.

Unfortunately, we could not carry out an X-ray diffraction study of the chelates $\mathrm{AuL_2}$ we synthesised. Firstly, these compounds do not form sufficiently large single crystals under the conditions of their synthesis described above and, secondly, they are both destroyed fairly readily when exposed to X rays. Therefore, the spatial structure of the compounds in question remains unknown.

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