Photoelectron Spectroscopy Study of the *X*-Ray-induced Decomposition of Some Gold(III) Dithiocarbamates

By **Paul M. Th. M. van Attekum** * and **Jan M. Trooster**,* Department of Physical Chemistry, University of Nijmegen, Toernooiveld, 6525 Ed Nijmegen, The Netherlands

The factors influencing the decomposition rate of two gold(III) complexes, [AuMe$_2$(S$_2$CNMe$_2$)] and [AuBr$_2$(S$_2$CNPr$^n{}_2$)], in an *X*-ray photoelectron spectroscopy experiment have been studied. It is shown that the decomposition rate can be slowed down by using graphite as substrate and by lowering the sample temperature. From the Au(4*f*) spectrum a direct measure has been made of the shift in the binding energy between Au^{III} and Au^{I} and this shift is shown to be dependent on the electronegativity of the ligands. The valence bands of the complexes show a narrow Au(5*d*) band with a spin–orbit splitting of *ca.* 1.6 eV.

X-RAY photoelectron spectroscopy (*X*-p.e.) studies of gold metal and gold alloys are numerous. On the other hand only a few *X*-p.e. investigations have been reported on solid samples of gold complexes.[1-3] A possible reason for this is that the study of inorganic or organic complexes is often hampered by decomposition of the compounds during measurement. As part of an extensive *X*-p.e. study of gold complexes we report here on the stability of two gold(III) compounds as a function of the sample-preparation technique, temperature, and *X*-ray intensity. Decomposition of the compounds enables us to measure directly the difference in Au(4*f*) kinetic energy between Au^{III} and Au^{I} without correcting for charging effects and to study changes in the valence-band structure with change in formal valence.

EXPERIMENTAL

The *X*-ray photoelectron spectra were measured with a Leybold-Heraeus LHS-10 spectrometer using Mg-K_α radiation. Lines due to *X*-ray satellites were removed from the experimentally measured spectra using a computer program described earlier.[4] The spectrometer was set for an instrumental resolution of 0.8 eV.† The compounds were prepared by Dr. J. G. M. van der Linden, University of Nijmegen, using published methods.[5] We have studied dimethylgold(III) dimethyldithiocarbamate, [AuMe$_2$(S$_2$CNMe$_2$)], and dibromogold(III) di-n-propyldithiocarbamate, [AuBr$_2$(S$_2$CNPr$^n{}_2$)]. The samples for the *X*-p.e. measurements were prepared either by sublimation in a preparation chamber at a pressure of *ca.* 10^{-5} Pa or by evaporation of a dilute solution. Sublimation was carried out on silver-plated stainless-steel platelets and has the advantage that very homogeneous thin layers can be made, which, in general, yield appreciably narrower lines than can be obtained when carrying out measurements on powders. Evaporation of solutions was done on graphite, on glassy carbon, and on the silver substrate. The porous surface of graphite induces rapid and even distribution of the liquid resulting in thin homogeneous samples. On the other hand, evaporation on the silver substrate or the glassy carbon often results in layers of uneven thickness and visible crystallites. The graphite and glassy carbon substrate have the advantage that the *X*-p.e. spectrum is simple with a very weak valence band.

Computer fits were carried out on an IBM 370/158 computer. The fitting program is a least-squares procedure described elsewhere.[6] Fitting the spectra to calculated lineshapes is difficult because the lines in general do not have a simple analytical lineshape and the background intensity is not a simple polynomial because of inelastically scattered electrons. If, however, a limited energy range is taken,

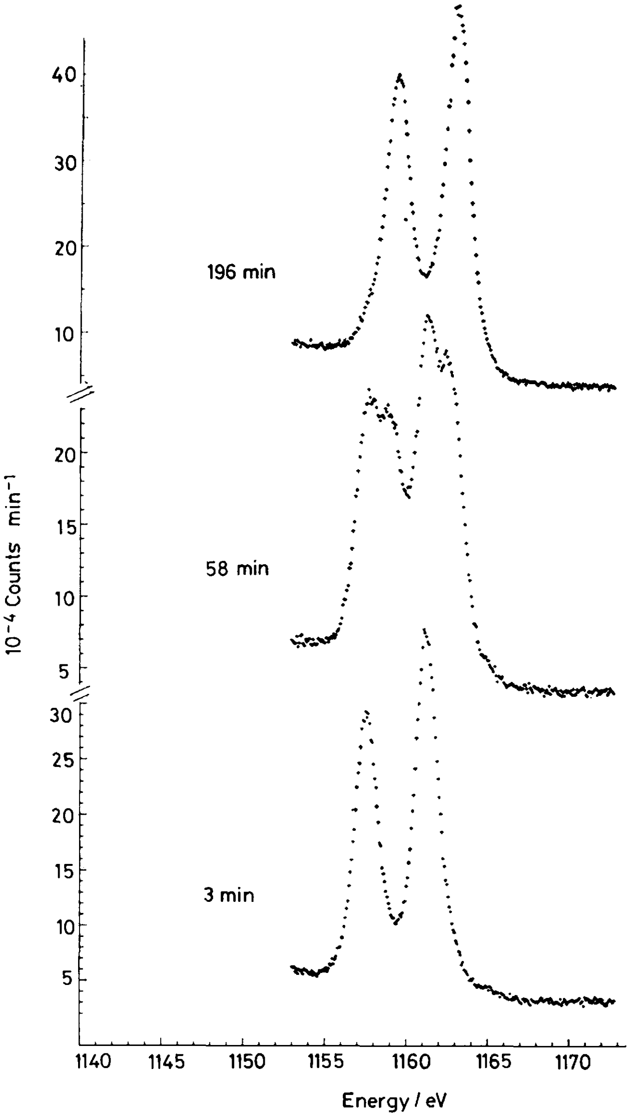

FIGURE 1 Au(4*f*) core lines of [AuMe$_2$(S$_2$CNMe$_2$)] sublimed on the silver substrate as function of the measuring time (245 K, 550 W). The kinetic energy scale is not corrected for charging

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† Throughout this paper: 1 eV ≈ 1.60 × 10^{-19} J.

the Au(4*f*) lines can be reasonably fitted with a sum of Lorentzians superposed on a sloping background.

RESULTS AND DISCUSSION

Decomposition Rate.—In Figures 1 and 2 the Au(4*f*) spectra of [$AuMe_2(S_2CNMe_2)$] and [$AuBr_2(S_2CNPr^n{}_2)$] measured on samples prepared by sublimation on the silver substrate are shown as a function of time. Clearly, both samples decompose in the spectrometer. The decomposition rate for sublimed samples was determined by fitting the experimental 4*f* spectra with two pairs of Lorentzians of equal linewidth, a separation of the lines within a pair of 3.70 eV, and an intensity ratio equal to 1.25 : 1 for the lines within a pair. (The value of 1.25 : 1 is the theoretical ratio given by Scofield.[7]) In Figure 3 the percentage of decomposition product, derived from the intensity ratio of the two pairs in the spectrum, is plotted for [$AuMe_2(S_2CNMe_2)$]. It is obvious that the decomposition rate depends strongly on the *X*-ray intensity and sample temperature. Similar results were found for [$AuBr_2(S_2CNPr^n{}_2)$] and for samples prepared by evaporation of a dilute solution on the silver substrate. With the *X*-ray tube switched off no decomposition occurred. The decomposition rate was independent of the thickness of the sample. However, for samples prepared by evaporation of a solution on graphite the decomposition rate is at least an order of magnitude slower. This cannot be due to the presence of carbon, since samples prepared by evaporation on glassy carbon decompose almost as fast as when evaporated on the silver substrate. A possible explanation of the stabilizing effect of graphite could be a binding of the compound with the delocalized π system of graphite (in glassy carbon this delocalization is much smaller). However, ^{197}Au Mössbauer spectra[8] of [$AuMe_2(S_2CNMe_2)$] pure and evaporated on graphite show no difference. Thus, the binding has to be weak and does not change the compound under study. Obviously, the substrate plays an important role in the decomposition as well as the *X*-ray irradiation.

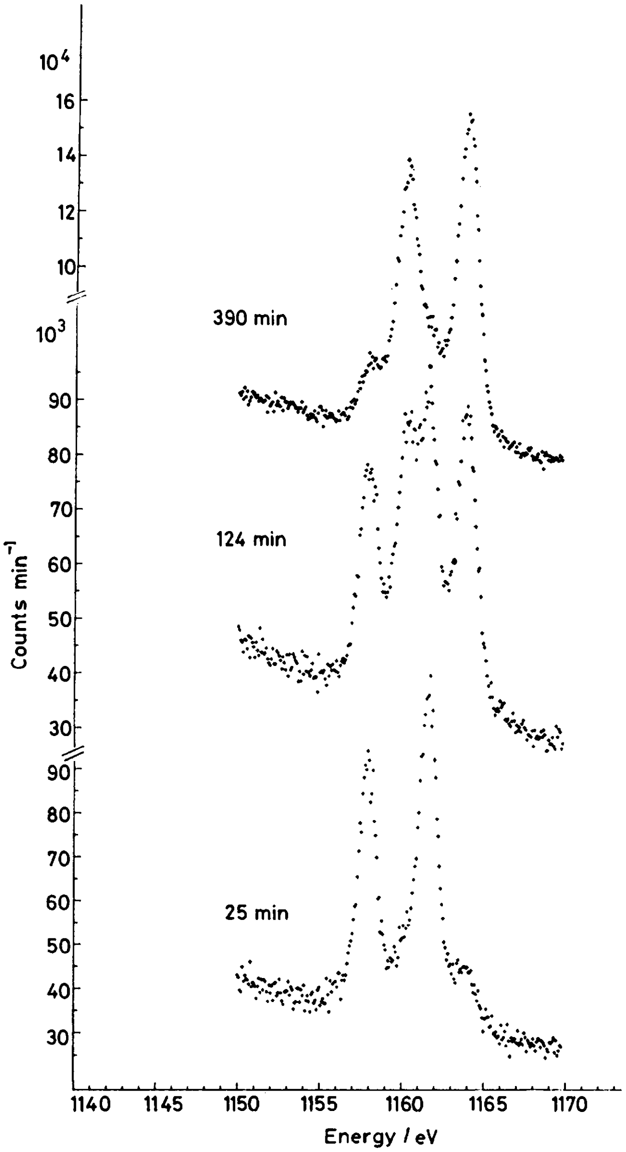

FIGURE 2 Au(4*f*) core lines of [$AuBr_2(S_2CNPr^n{}_2)$] sublimed on the silver substrate as function of the measuring time (245 K, 250 W). The kinetic energy scale is not corrected for charging

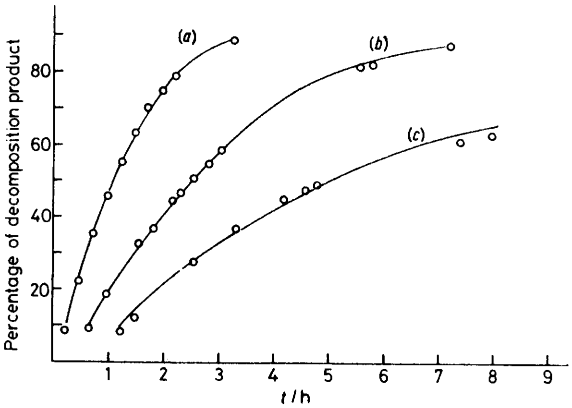

FIGURE 3 Increase of the percentage of the decomposition product of [$AuMe_2(S_2CNMe_2)$] as function of the sample temperature and *X*-ray intensity: (*a*) 245 K, 550 W; (*b*) 245 K, 250 W; and (*c*) 80 K, 250 W. The points were obtained by fitting the experimental spectra as shown in Figure 1 to two pairs of Lorentzians. The estimated error in the percentages is 10%

Line Positions.—The Table lists the experimentally measured kinetic energies of the core lines for the initial and decomposition products of [$AuMe_2(S_2CNMe_2)$] and [$AuBr_2(S_2CNPr^n{}_2)$]. Since the compounds are electrical insulators, charging of the sample can occur, resulting in lower measured kinetic energies. However, charging of samples is smaller the thinner the sample and from a series of measurements on very thin samples of [$AuMe_2(S_2CNMe_2)$] we derive a maximum value of 1 163.0 eV for the kinetic energy of the Au($4f_{\frac{7}{2}}$) line. This is to be compared with a kinetic energy of 1 165.2 eV for Au($4f_{\frac{7}{2}}$) in Au metal. The C(1*s*) kinetic energy in this case is 964.4 eV compared to 964.7 eV in graphite. In the Table we have used this value of C(1*s*) as an internal standard for all compounds measured, to account for the effects of charging.

Kinetic energy (±0.2 eV), corrected for charging (see text), of the relevant core levels of the compounds studied

	[$AuMe_2(S_2CNMe_2)$]		[$AuBr_2(S_2CNPr^n{}_2)$]			
Peak	Initial product	Decomposition product	Initial product	Decomposition product	Au[$S_2CNBu^n{}_2$]	Au[$S_2CNPr^n{}_2$]
C(1*s*)	964.4	964.4	964.4	964.4	964.4	964.4
Au($4f_2$)	1 163.0	1 164.5	1 162.2	1 164.6	1 164.6	1 164.8
S(2*p*)	1 085.9	1 086.0	1 085.7	1 086.1	1 086.4	1 086.6
N(1*s*)	848.8	848.7	848.8	848.8	849.2	849.3

From the shift in kinetic energy of the Au($4f_2$) line during the decomposition it is clear that the Au is reduced in both cases. The reduced product is probably a gold(I) dithiocarbamate complex, since the values of the kinetic energies of the core levels of C, Au, S, and N in the decomposition product closely resemble those of two gold(I) dithiocarbamate complexes which were measured separately and did not show any decomposition. The kinetic energy of the Au(4*f*) lines of the initial and decomposition products differs by 2.4 ± 0.1 eV for [$AuBr_2(S_2CNPr^n{}_2)$] and 1.5 ± 0.1 eV for [$AuMe_2(S_2CNMe_2)$]. If we assume that the end product in both cases is a gold(I) dithiocarbamate, the difference in shift of the Au(4*f*) lines must be attributed to the difference in electronegativity of Br and CH_3. According to Gelius *et al.*[9] the group electronegativities of Br and CH_3 as derived from a series of *X*-p.e. spectra are 3.3 and 2.0, respectively. The larger electronegativity of Br results in a larger positive charge on Au in [$AuBr_2(S_2CNPr^n{}_2)$]. This is also in agreement with Mössbauer measurements on these compounds.[6] The complex [$AuMe_2(S_2CNMe_2)$] has a larger isomer shift and quadrupole splitting than the dibromide indicating a more covalent bonding in the methyl complex. It is unlikely that the decomposition product is metallic gold since the kinetic energy of the 4*f* electrons of the end product is 0.6 eV lower than for Au metal. Van de Vondel *et al.*[1] found an energy difference of 2.0 eV between formal gold(III) and gold(I) compounds. The present results show, however, that the range of Au(4*f*) binding energies in gold(III) complexes is at least 1.0 eV.

Valence Bands.—In Figure 4 the valence bands of [$AuMe_2(S_2CNMe_2)$] and its decomposition product are compared with the valence band of gold metal. To our knowledge this is the first *X*-p.e. measurement of the Au(5*d*) level in a molecular complex. The spectrum of the complex is a sum of several measurements each requiring 1 h at 80 K and 250 W of *X*-ray power, and the amount of decomposition product during this time is less than 5%. The broadening of the 5*d* band in gold metal due to overlap of Au(5*d*) bands is reduced in the complexes. In the valence-band spectrum of [$AuMe_2(S_2CNMe_2)$] the two peaks are attributed to the Au(5*d*) level with a spin–orbit splitting of 1.6 ± 0.1 eV. The free-atom spin–orbit splitting is 1.5 eV.[10] The shoulder on the high kinetic energy side of the spectrum is ascribed to the bonding molecular orbitals. The Au(5*d*) levels in the decomposition product, gold(I) dimethyldithiocarbamate, are shifted by *ca.* 1.6 eV with respect to the parent in good agreement with the shift of the Au(4*f*) lines. The shoulder is reduced in intensity, presumably reflecting the removal of CH_3.

Conclusions.—The results of this investigation lead to the following conclusions. In *X*-p.e. measurements of gold(III) complexes, and possibly of other compounds as well, the decomposition rate can be reduced considerably by using graphite as substrate and by lowering the sample temperature. The gold(III) dithiocarbamate complexes studied are reduced to a gold(I) dithiocarbamate. The binding energy of the 4*f* core levels of the gold(III) complexes is strongly dependent on the ligand-group electronegativity. The shift in binding energy of the 4*f* core levels on reduction is also found for the Au(5*d*)

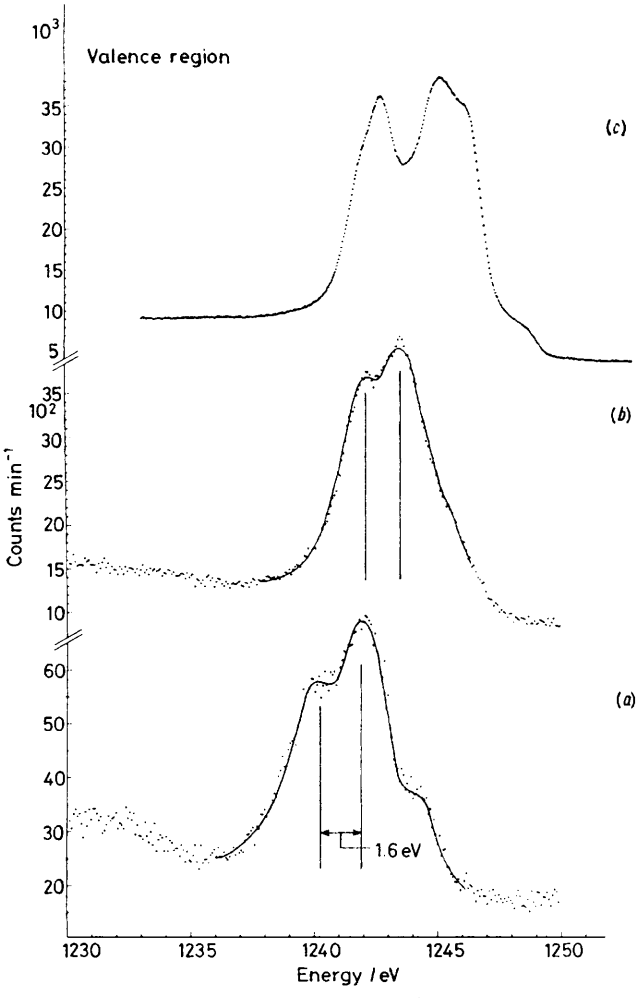

FIGURE 4 Valence bands of [$AuMe_2(S_2CNMe_2)$] (*a*), its decomposition product (*b*), and gold metal (*c*). The kinetic energy scale of the gold compounds is adapted such that the Au(4*f*) core lines lie at the positions as quoted in the Table

level, which shows narrow atomic-like lines with a spin–orbit splitting of 1.6 eV.

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