minimized during the least-squares refinement was $\sum w(|F_o| - |F_c|)^2$; unit weights were chosen in the first cycles, and then the reflections were weighted according to the scheme $w = 1.1995/\sigma^2(F_o) + 0.005F_o^2)$ with $\sigma(F_o)$ based on counting statistics. The final R and R_w values were 6.6 and 7.0%, respectively (observed reflections only). The analytical scattering factors for neutral Ru, As, O, C, and H were used; both the real and imaginary components of anomalous dispersion were included for Ru and As atoms.[16] The final positional and thermal parameters for the nonhydrogen atoms are given in Tables III and IV respectively.

All calculations were performed on the Cyber 7600 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Bologna, with financial support from the University of Parma.

Acknowledgment. We gratefully acknowledge the support of the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We also thank Professor Fratielo and R. Perrigan for arranging use of NMR facilities at the California State University, Los Angeles.

Registry No. I, 57673-31-1; II, 76741-75-8.

Supplementary Material Available: Listings of calculated coordinates of the hydrogen atoms and observed and calculated structure factor amplitudes (14 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
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Thiocyanation, Selenocyanation, and Halogenation Reactions of Dithiocarbamate Complexes of Gold(I) and Silver(I). Generation of Gold(II) and Silver(II) Complexes[1]

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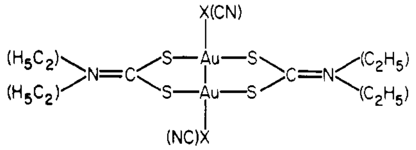
Received August 26, 1980

The reaction of (*N,N*-diethyldithiocarbamato)gold(I) (which exists as a dimer with eight-membered rings involving linear S–Au–S bonds) with Br_2, I_2, $(SCN)_2$, or $(SeCN)_2$ in CS_2 at −78 °C has permitted the isolation of what are believed to be dark green gold(II) complexes of the type shown, on the basis of the analytical and physical data obtained:



When allowed to warm to room temperature, the complexes undergo a rearrangement to form yellow salts of the type $[Au(detc)_2][Au(X(CN))_2]$ (detc = *N,N*-diethyldithiocarbamate), which have previously been reported by Beurskens et al. These salts are obtained as the initial reaction products when the reactions are carried out at room temperature in chloroform, with a dimer:(pseudo)halogen ratio of 1:1. If a ratio of 1:2 is employed under the latter conditions, complexes of the type $[Au(detc)(X(CN))_2]$ result, as previously noted by Blaauw et al., except for I_2, which continues to give only the $[Au(detc)_2][AuI_2]$ product. The isolation of the green gold(II) complexes casts considerable doubt on the interpretation given to the kinetic data obtained by Kita et al. for reactions of this type. The corresponding gold(II) di-*n*-butyldithiocarbamate thiocyanate derivative was found to be considerably more stable than its diethyl analogue, most probably due to the ponderable effects of the longer *n*-butyl groups. The hexameric Ag(I) homologue, $[Ag(detc)]_6$, proved to be more resistant to oxidation by $(SCN)_2$, yielding only a partially substituted $[Ag_6(detc)_5SCN]$ product at −78 °C. When the reaction was carried out at room temperature, partial oxidation to Ag(II) was observed, $[Ag_6(detc)_6(SCN)_4]$ being isolated. Even at room temperature, $(SeCN)_2$ failed to oxidize the hexamer, $[Ag_6(detc)_5SeCN]$ being formed.

Introduction

Chemists have long puzzled over the discontinuous common oxidation states exhibited by the group 1B metals. Whereas +2 is the dominant oxidation state for copper, it is virtually nonexistent for gold[2] and is relatively rare for silver. In a vintage example of chemical serendipity, we have discovered a way to generate gold(II) and silver(II) complexes by the oxidative addition of pseudohalogens and halogens to gold(I) and silver(I) dithiocarbamate complexes. We now wish to report the results of our studies in this area.

Experimental Section

Preparation of Compounds. The sodium salt of diethyldithiocarbamic acid, $Na[S_2CN(C_2H_5)_2]\cdot 2.5H_2O$, was purchased from Sigma Chemical Co. and was desiccated below 0 °C. The following compounds were prepared according to methods given in the literature: $(SCN)_2$[3] (CS_2 solution at −78 °C, used immediately after preparation), $(SeCN)_2$[4] (diethyl ether solution at −10 °C, used immediately after preparation), $Na[S_2CN(C_4H_9)_2]$,[5] $[Au(S_2CN(C_2H_5)_2)]_2$[6] and $[Au(S_2CN(C_4H_9)_2)]_2$.[6]

$[Au(S_2CN(C_2H_5)_2)SCN]_2$ and $[Au(S_2CN(C_2H_5)_2)_2][Au(SCN)_2]$. A 23-mL quantity of a −78 °C CS_2 solution containing 1.02 mmol of $(SCN)_2$ was slowly added to a slurry of 0.261 g (0.378 mmol) of $[Au(S_2CN(C_2H_5)_2)]_2$ in 20 mL of CS_2 at −78 °C. The addition

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[1] Abstracted, in part, from the M.S. thesis of D.C.C., University of Delaware, June 1978. Presented in parts at the 175th National Meeting of the American Chemical Society, Anaheim, CA, March 12–16, 1978 (Abstract INOR 23) and at the 14th Middle Atlantic Regional Meeting of the American Chemical Society, Valley Forge, PA, April 25, 1980 (Abstract UDGR 4).

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produced a very dark green, almost black, solution, which was left stirring at −78 °C for 40 min. Filtration through a precooled frit, followed by washing with cold CS_2, yielded a very dark green solid and a pale tan filtrate. The solid was stored in a freezer overnight and, by the following morning, had changed in color to bright yellow. The solid retains its initial dark green color indefinitely when kept at −78 °C. The dark green solid, when heated in the melting point apparatus, partially melted at 67–69 °C, the remainder being converted to a yellow component, which melted at 81–82 °C. Anal. Calcd for $C_{12}H_{20}N_4S_6Au_2$: C, 17.87; H, 2.50; N, 6.95; S, 23.85; Au, 48.84. Found: C, 17.60; H, 2.57; N, 6.67; S, 23.64; Au (by difference), 49.52. When the reaction was carried out at room temperature, mixing of the two reactant solutions produced an immediate darkening, which disappeared rapidly with stirring, and, eventually, a yellow colored solid (48% yield) whose properties matched those of the yellow final product of the low-temperature reaction described above.

$[Au(S_2CN(C_2H_5)_2)SeCN]_2$ and $[Au(S_2CN(C_2H_5)_2)_2][Au(SeCN)_2]$. A 15-mL quantity of a −10 °C diethyl ether solution containing 0.51 mmol of $(SeCN)_2$ was added to a slurry of 0.134 g (0.194 mmol) of $[Au(S_2CN(C_2H_5)_2)]_2$ in 20 mL of CS_2 in a dry ice/acetone bath. A bright green precipitate formed immediately. It was isolated by filtration and washed with cold ethanol and ether. When it was warmed to room temperature, the solid changed to yellow, albeit at a considerably slower rate than its thiocyanate analogue. The yellow solid decomposes at 113 °C. Anal. Calcd for $C_{12}H_{20}N_4S_4Se_2Au_2$: C, 16.01; H, 2.23; N, 6.22. Found: C, 16.30; H, 2.52; N, 6.10.

$[Au(S_2CN(C_2H_5)_2)Br]_2$ and $[Au(S_2CN(C_2H_5)_2)_2][AuBr_2]$. A solution of 10 mL of CS_2 containing 0.183 g (1.145 mmol) of Br_2 at −78 °C was slowly added to a slurry of 0.244 g (0.353 mmol) of $[Au(S_2CN(C_2H_5)_2)]_2$ in 30 mL of CS_2 at −78 °C. The addition caused an immediate darkening, yielding a dark green solution. Filtration and washing with CS_2 produced a bright green solid (88% yield) and a maroon filtrate. The solid was dried in vacuo and took on a yellow cast upon warming to room temperature. When heated, the bright green solid turned yellow between 84 and 108 °C and melted at 138–142 °C. Anal. Calcd for $C_{10}H_{20}N_2S_4Br_2Au_2$: C, 14.11; H, 2.37; N, 3.29. Found: C, 13.91; H, 2.29; N, 3.35.

$[Au(S_2CN(C_2H_5)_2)I]_2$ and $[Au(S_2CN(C_2H_5)_2)_2][AuI_2]$. A slurry of 0.1103 g (0.160 mmol) of $[Au(S_2CN(C_2H_5)_2)]_2$ in 25 mL of CS_2 at −78 °C was prepared. To this was added 15 mL of cold CS_2 (−78 °C) containing 0.0427 g (0.168 mmol) of I_2. Upon addition, the mixture went through a light green color, which darkened to finally give a deep dark green solution with complete addition. After being stirred at −78 °C for 20 min, the solution was filtered, yielding a very dark green solid and a dark green filtrate. After 15 min, the now purple filtrate was filtered and the solid thereby isolated was washed with CS_2, yielding a yellow solid, which melted at 118–120 °C. Anal. Calcd for $C_{10}H_{20}N_2S_4I_2Au_2$: C, 12.72; H, 2.13; N, 2.97; I, 26.88. Found: C, 13.10; H, 2.17; N, 2.83; I, 26.53.

$[Au(S_2CN(C_2H_5)_2)_2][Au(SCN)_2Br_2]$. To a slurry of 0.108 g (0.134 mmol) of $[Au(S_2CN(C_2H_5)_2)_2][Au(SCN)_2]$ in 15 mL of CS_2 was slowly added 5 mL of CS_2 containing 0.0323 g (0.202 mmol) of Br_2. Following the initial addition, a dark color appeared, which disappeared with stirring. With complete addition and stirring for 15 min, the initially yellow solution had turned orange. Filtration yielded an orange solid (68% yield), which decomposed at 84 °C. Anal. Calcd for $C_{12}H_{20}N_4S_6Br_2Au_2$: C, 14.91; H, 2.09; N, 5.80; S, 19.91. Found: C, 15.12; H, 2.34; N, 5.52; S, 20.88.

$[Au(S_2CN(C_4H_9)_2)SCN]_2$ and $[Au(S_2CN(C_4H_9)_2)_2][Au(SCN)_2]$. A 23-mL quantity of a −78 °C CS_2 solution containing 1.02 mmol of $(SCN)_2$ was slowly added to a solution of 0.303 g (0.378 mmol) of $[Au(S_2CN(C_4H_9)_2)]_2$ in 20 mL of CS_2 at −78 °C. The addition produced a very dark blue-green, almost black, solution. Filtration through a precooled frit yielded a very dark green solid and a blue-violet filtrate. The solid retains its initial dark green color indefinitely when kept at −78 °C. When stored at 0 °C, the solid slowly changes in color to bright yellow (after two months at 0 °C, the solid was still partly green). The dark green solid converts to yellow at 65–72 °C, finally melting at 208–210 °C; yield 77%. Anal. Calcd for $C_{20}H_{36}N_4S_6Au_2$: C, 26.14; H, 3.95; N, 6.10; S, 20.94; Au, 42.87. Found: C, 26.96; H, 3.89; N, 5.67; S, 20.55; Au (by difference), 43.93.

$[Ag(S_2CN(C_2H_5)_2)]_6$. Silver nitrate (2.5633 g, 15.09 mmol) was dissolved in 80 mL of H_2O and cooled to 0 °C. Sodium diethyldithiocarbamate (3.2961 g, 15.24 mmol) was dissolved in 200 mL of H_2O and cooled to 0 °C. The $Na[S_2CN(C_2H_5)_2]$ solution was added to the $AgNO_3$ solution at the rate of 5 mL/min, with constant stirring, resulting in the immediate formation of a light tan precipitate. Filtration yielded a bright yellow solid, which was washed with acetone until the filtrate changed from red to clear. The remaining solid, now light tan, was washed with diethyl ether and dried in vacuo for 1 h: yield 95%; mp 172–174 °C (same as literature[7] value); mol wt calcd 1537, found (by osmometry) 1629; % Ag calcd 42.1, found (by ignition) 43.3.

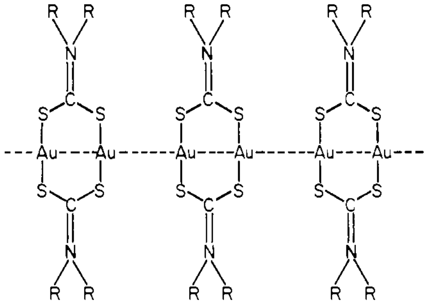
$[Ag_6(S_2CN(C_2H_5)_2)_5SCN]$. A 40-mL quantity of a −78 °C CS_2 solution containing 1.10 mmol of $(SCN)_2$ was added, with stirring, to 40 mL of a −78 °C CS_2 solution containing 0.4882 g (0.318 mmol) of $[Ag(S_2CN(C_2H_5)_2)]_6$. A yellow-orange color developed, which changed to dull yellow in ca. 5 min. The mixture was stirred at −78 °C for 30 min. Filtration yielded a light tan solid, which was washed with CS_2, acetone, ethanol, acetone, and diethyl ether, in that order, and dried in vacuo for 30 min: yield 94%; mp 145–151 °C. Anal. Calcd for $C_{26}H_{50}N_6S_{11}Ag_6$: C, 21.6; H, 3.5; N, 5.8; S, 24.4; Ag, 44.7. Found: C, 21.45; H, 3.39; N, 5.70; S, 24.93; Ag, 44.53 (by difference), 46.8 (by ignition). The compound's solubility in all suitable solvents was insufficient for a molecular weight determination.

$[Ag_6(S_2CN(C_2H_5)_2)_6(SCN)_4]$. The preparative method for this compound was exactly the same as that described for $[Ag_6(S_2CN(C_2H_5)_2)_5SCN]$, except that the reaction was carried out at room temperature: yield 90%; mp 135–140 °C. Anal. Calcd for $C_{34}H_{60}N_{10}S_{16}Ag_6$: C, 23.1; H, 3.4; N, 7.9; Ag, 36.6. Found: C, 22.80; H, 3.39; N, 7.70; Ag (by ignition), 38.0. The compound was not sufficiently soluble for a molecular weight determination.

Physical Measurements. Infrared spectra were recorded with use of Nujol and Fluorolube mulls on a Perkin-Elmer 180 grating spectrophotometer. Determination of thiocyanate and carbamate peaks used a 10× abscissa expansion from 2200 to 2000 cm^{-1} and 1650 to 1480 cm^{-1}. Proton NMR spectra were recorded on a Bruker WM-250 spectrometer. Electron spin resonance spectra were measured with a Varian E-109E ESR spectrometer. Melting points were measured with a Thomas-Hoover melting point apparatus and are uncorrected. Elemental analyses were performed by Schwarzkopf Laboratories, Woodside, NY.

Results and Discussion

Oxidative Addition Reactions with Gold(I) Complexes. The structurally interesting gold(I) dithiocarbamates[7,8] have been established as existing in discrete dimeric units which can stack up in the solid state to form linear gold chains (I). The



I

intradimer Au···Au distance generally falls in the 2.75–2.95-Å range, whereas the interdimer Au–Au distance is generally around 3.0–3.1 Å. These relatively short distances have been taken as an indication of a weak Au–Au interaction.

Our interest in exploring the propensity of the gold(I) diethyldithiocarbamate dimer, $[Au(detc)]_2$, to undergo oxidative addition reactions was a natural outgrowth of our earlier work involving the oxidative addition reactions of the pseudohalogens thiocyanogen, $(SCN)_2$,[3,9,10] and selenocyanogen, $(SeCN)_2$,[4] with a variety of (d^8)[9] and (d^{10})[3,4,9,10] substrates. These reactions were found to follow two different pathways: oxidation

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with an increase in coordination number (square-planar Rh(I)[9] and Ir(I)[9] → octahedral Rh(III) and Ir(III); linear Au(I)[3,9,10] → square-planar Au(III)) and oxidation with constant coordination number (tetrahedral Pt(0)[4] → square-planar Pt(II)). What we had anticipated to be a straightforward reaction, wherein the linear coordination environment of the Au(I) in the $[Au(detc)]_2$ dimer would be converted into a square-planar $[Au(detc)(SCN)_2]$ complex by an oxidative reaction with $(SCN)_2$, turned out to produce results that were far more interesting and important.

When 1 mmol of thiocyanogen was added to 0.378 mmol of (diethyldithiocarbamato)gold(I) dimer in CS_2 at −78 °C (thiocyanogen in excess), an immediate color change occurred from bright yellow to a very deep, dark green (almost black). Filtration yielded a dark green solid, which, over a period of several hours at 0 °C, turned to a yellow-orange color. An initial infrared spectrum of the dark green substance revealed thiocyanate ν_{CN} peaks at 2119 (sh) and 2113 cm^{-1} (s, sp), as well as dithiocarbamate $\nu_{C=N}$ bands at 1548 (s, br) and 1522 cm^{-1} (s, sp). As the color lightened to yellow over a period of 30 h, the thiocyanate region coalesced to one strong ν_{CN} peak at 2119 cm^{-1} and the dithiocarbamate $\nu_{C=N}$ 1522-cm^{-1} peak slowly diminished in intensity to a shoulder, concomitant with a growth in intensity on the part of the 1548-cm^{-1} peak. The reactions with $(SeCN)_2$, Br_2, and I_2, under the same conditions, produced similar results, i.e., isolation of a green solid, which, upon warming, became yellow in color. In each case, a dithiocarbamate $\nu_{C=N}$ band at ca. 1520 cm^{-1} diminished in intensity as the color change progressed, coincident with the growth of a dithiocarbamate $\nu_{C=N}$ band at ca. 1550 cm^{-1}. The green selenocyanate- and bromide-containing products proved to be more resistant to the color change. In the case of the selenocyanate complex, the green solid exhibited a selenocyanate ν_{CN} stretching band at 2116 cm^{-1}; transformation to the yellow final product resulted in the appearance of a new selenocyanate ν_{CN} peak at 2126 cm^{-1}.

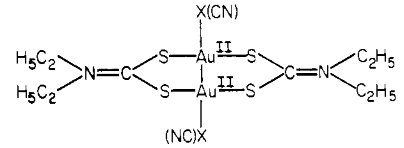
Analysis of the products revealed a gold:dithiocarbamate:(pseudo)halide ratio of 1:1:1, formally implying the presence of gold(II). Although, as we will now demonstrate, the yellow solids are, in point of fact, mixed-valence square-planar gold(III)/linear gold(I) salts, similar to those isolated by previous investigators, their green precursors are bona fide Au(II) complexes.

The products of previous studies of reactions of this type have exhibited a dependence of the amount of oxidant added. Blaauw et al.[6] observed that the addition of 2 mol of Cl_2 or Br_2 to 1 mol of a (dithiocarbamato)gold(I) dimer in chloroform at room temperature gave 2 mol of a dihalo(dithiocarbamato)gold(III), $[Au(dtc)X_2]$, product. These reaction mixtures underwent a brief intemediate color change to dark red for Cl_2, and dark violet for Br_2, before giving the final yellow and red products, respectively. When half as much halogen was used in these reactions, a product, which analyzed for $[Au(dtc)X]$, seemingly involving gold(II), was obtained. In the case of I_2, the $[Au(dtc)I]$ product was obtained regardless of how much I_2 was added.

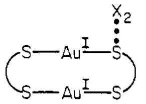
The crystal structure and properties of the $[Au(dtc)X]$ species where X = Cl^-, Br^-, I^- and CN^- were studied by Beurskens et al.,[11,12] in order to determine the actual oxidation state of gold in these compounds. In a very definitive investigation using X-ray, ESR, magnetic susceptibility, electric conductivity, electronic spectra, infrared spectra, and molecular weight measurements, they unquestionably established the nature of these apparent Au(II) compounds as actually consisting of a mixed-oxidation-state, Au(III)–Au(I) ionic configuration, $[Au(dtc)_2]^+[AuX_2]^-$. Using the same preparative method as Blaauw, they also observed a short-lived dark intermediate, which was postulated as being due to an unstable Au(II) intermediate, which quickly disproportionated to equal amounts of Au(I) and Au(III).

The results of our oxidative addition reactions with the (diethyldithiocarbamato)gold(I) dimer appear to correlate well with the findings of both Blaauw and Beurskens. The significance of our work is that, by using different reaction conditions, we have been able to stabilize the intermediate Au(II) dimers long enough to enable us to isolate and characterize green solids, which undergo slow color changes.

As Blaauw noted,[6] the gold(I) and dihalogold(III) dithiocarbamates are soluble in carbon disulfide, while the "monohalogold dithiocarbamate" is very sparingly soluble. By using carbon disulfide as our solvent, we were able to carry out our reactions at low temperature (−78 °C) and, consequently, isolate the gold(II) dithiocarbamate dimers, which previous investigators had seen only fleetingly at room temperature in chloroform or carbon tetrachloride. Once isolated as a solid, their rate of disproportionation to $[Au(detc)_2]$-$[Au(X(CN))_2]$ is much slower than in solution. Our conclusion that an Au^{II}–Au^{II} bond exists in the $[Au(detc)(X(CN))]_2$ dimers (II) is supported by the results of an earlier study by Kita et al.,[13] who studied the kinetics and mechanism of the oxidation of bis(μ-(dibutyldithiocarbamato-*S*,*S*′)-digold(I) by Br_2, I_2, and IBr in dichloromethane at −50 °C. Using ESR measurements, they found that the dark green 1:1 $I_2/[Au(n\text{-}Bu_2dtc)]_2$ complex formed at −50 °C was *diamagnetic*. They concluded that this was due to the formation of a charge-transfer complex of the type III. They had no independent means of assessing whether or not the X–X bonds had cleaved, resulting in oxidation to diamagnetic Au(II) complexes of the type shown above (II). In our case, however, the dramatic decreases in the thiocyanate and selenocyanate ν_{CN} stretching frequencies from those exhibited[14] by the parent pseudohalogens ($(SCN)_2$, 2160 cm^{-1}; $(SeCN)_2$, 2157 cm^{-1}) leave no doubt[15] that the thiocyanate and selenocyanate ions are, respectively, S and Se coordinated in the green Au(II) dimers. Their presence formally requires that the gold atoms be in the +2 oxidation state, and the diamagnetic nature of the dimers further suggests that an Au–Au bond is present.



II, X = Br, I, S(CN), Se(CN)



III

There is, however, an alternative mixed-valence structure, IV, whose properties would also be consistent with the experimental data presented thus far. Low-temperature proton NMR measurements offered the possibility of distinguishing between structures II and IV. All of the alkyl groups would be in identical environments in II, whereas IV should contain nonequivalent alkyl groups at temperatures where rotation

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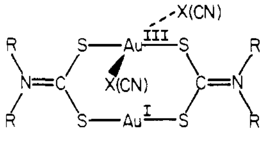


IV

about the C=N bonds is restricted.

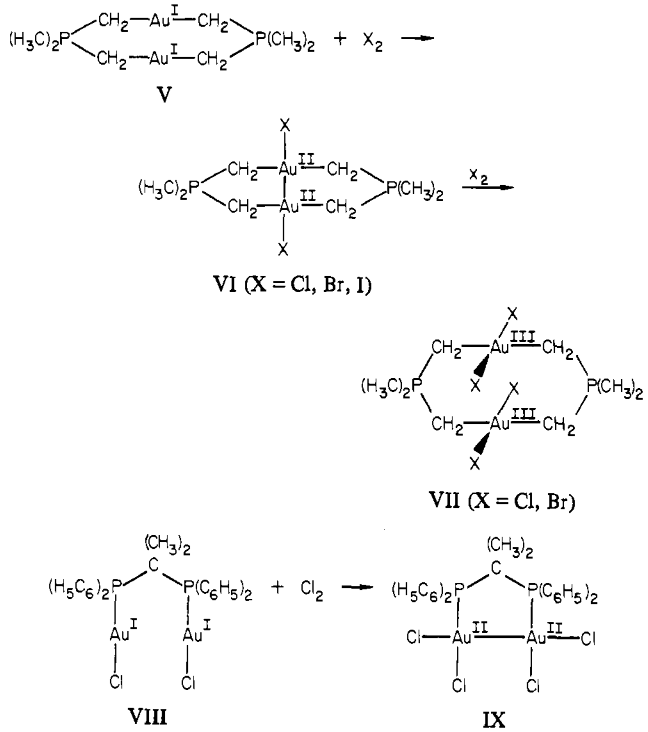
In order to investigate this possibility, it was necessary to synthesize and utilize the corresponding di-*n*-butyldithiocarbamate derivative, since the low solubility of the diethyl derivative precluded its being used for the proton NMR measurements. The infrared behavior of the di-*n*-butyl derivative was comparable to that of the diethyl derivative, described previously. The dark green solid initially isolated exhibited a thiocyanate ν_{CN} stretching band at 2119 cm^{-1} and a dithiocarbamate $\nu_{C=N}$ band at 1520 cm^{-1}. When heated, the compound became yellow, and the bands shifted to 2135 and 1555 cm^{-1}, respectively.

As is shown in Table I, the low-temperature (down to −80 °C) proton NMR spectrum of the dark green solid gave no indication of more than one environment for the *n*-butyl groups. At about 0 °C, however, a second triplet due to the methylene group closest to the nitrogen atom appeared at δ 3.64. As the solution continued to warm up, the intensity of this triplet increased, coincident with a diminution in intensity of the original triplet at δ 3.79. At the same time, the three remaining signals increased in complexity. When the conversion to the yellow $[Au(S_2CN(C_4H_9)_2)_2][Au(SCN)_2]$ salt was complete, the original triplet at δ 3.79 had completely disappeared, the new triplet at δ 3.68 had grown to an equivalent intensity, and the three remaining signals had regained their original patterns, albeit slightly shifted. All of these observations are in accord with the conversion of structure II (dark green) into $[Au(S_2CN(C_4H_9)_2)_2][Au(SCN)_2]$ and tend to negate the possibility of the dark green compound having structure IV.

One unexpected beneficial side effect was realized in switching to the di-*n*-butyl derivative—a remarkable increase in stability. Whereas the diethyl derivative undergoes a complete green → yellow conversion in 12 h at 0 °C in the solid state, some of a sample of the di-*n*-butyl derivative is still green after 2 months at 0 °C. This is most certainly due to a steric effect. Conversion of II to $[Au(S_2CN(C_4H_9)_2)_2][Au(SCN)_2]$ would require rearrangement of the dithiocarbamate groups. The ponderable effects of the longer *n*-butyl groups would be expected to retard the rate of the rearrangement, although the magnitude of the retardation was found to greatly exceed our expectations.

The thiocyanation reaction was repeated at room temperature with 0.5 mmol of $(SCN)_2$/0.5 mmol of (diethyldithiocarbamato)gold(I) dimer. This time the dark green species was observed only briefly, and with complete addition, a yellow-brown solid resulted. The infrared spectrum exhibited peaks at 2119 (s, sp), 2068 (w), and 1546 cm^{-1} (s, br), a very weak shoulder at 1523 cm^{-1}, which vanished in several hours, and a weak, broad peak at 1493 cm^{-1}, which corresponds to unreacted starting material (1495 cm^{-1}). The 1546-cm^{-1} peak is assigned to the dithiocarbamate $\nu_{C=N}$ stretch of $[Au(detc)_2]^+[Au(SCN)_2]^-$ and compares favorably with the 1550-cm^{-1} $\nu_{C=N}$ peak exhibited by the corresponding di-*n*-butyldithiocarbamate halide analogues.[11] The intense 2119-cm^{-1} ν_{CN} peak is assigned as being due to the S-bound thiocyanates of $[Au(detc)_2]^+[Au(SCN)_2]^-$, in good agreement with the ν_{CN} frequency reported[16] for $K[Au(SCN)_2]$. The transitory 2113- and 1522-cm^{-1} peaks observed in the infrared spectrum of the low-temperature product would then be due to the ν_{CN} and $\nu_{C=N}$ bands, respectively, of the short-lived, green Au(II) dimer.

Scheme I



V

VI (X = Cl, Br, I)

VII (X = Cl, Br)

VIII

IX

The addition of another 0.05 mmol of $(SCN)_2$ at room temperature in CS_2 to 0.05 mmol of the product of the preceding reaction yielded a product that was browner in color and exhibited ν_{CN} peaks at 2124 (sh) and 2114 cm^{-1} (m, sp) and a $\nu_{C=N}$ peak at 1547 cm^{-1} (s, br). The appearance of the 2124-cm^{-1} shoulder is indicative of the formation of some $[Au(detc)_2]^+[Au(SCN)_4]^-$. If the product had rearranged to form $[Au(detc)(SCN)_2]$, a higher $\nu_{C=N}$ frequency should have been observed for the dithiocarbamate moiety. As reported by Beurskens et al.,[11] the $\nu_{C=N}$ frequencies of the $[Au(dtc)X_2]$ complexes are 1570, 1565, and 1561 cm^{-1}, respectively, for the chloro, bromo, and iodo di-*n*-butyldithiocarbamates. It should be noted that there is a smooth increase in the $\nu_{C=N}$ frequency of the dithiocarbamato ligand as the oxidation state of gold increases, i.e., $[Au^I(detc)]_2$, 1495 cm^{-1} < $[Au^{II}(detc)SCN]_2$, 1523 cm^{-1} < $[Au^{III}(detc)_2][Au(SCN)_2]$, 1548 cm^{-1}.

When 0.2 mmol of Br_2 was added to 0.134 mmol of the $[Au(detc)_2]^+[Au(SCN)_2]^-$ salt (Br_2 in excess), a light orange solid resulted with ν_{CN} peaks at 2130 and 2125 cm^{-1} (m, sp) and a $\nu_{C=N}$ peak at 1547 cm^{-1} (m, br). We have assigned the ν_{CN} doublet as resulting from a cis splitting of the thiocyanates in the anion of $[Au(detc)_2]^+[\textit{cis}\text{-}Au(SCN)_2Br_2]^-$.

The only previously reported dimeric gold(II) complexes (VI, IX), shown in Scheme I, have emanated from the work of Schmidbaur and his colleagues.[17-21] They, too, were able to add either 1 or 2 mol of Cl_2 or Br_2 to 1 mol of the phosphonium ylide dimer V, whereas only 1 mol of I_2 could be added. To explain these results, they proposed that 2 mol of halogen added to give a Au(III)–Au(III) dimer, VII (the trans structure being supported by the observation of a single Au–X stretching band), while, when only 1 mol of halogen added,

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Table I. Proton NMR Data

compd	solvent	temp, °C	chemical shift, δ -N-CH_2-	-CH_2-*CH_2*-CH_2-	-*CH_2*-CH_3	-CH_3
$Na[S_2CN(C_4H_9)_2]$	$DCCl_3$	20	3.93 (t)	1.66 (m)	1.29 (hex)	0.926 (t)
$[Au(S_2CN(C_4H_9)_2)]_2$	CS_2	20	3.74 (t)	1.76 (m)	1.33 (hex)	0.992 (t)
$[Au(S_2CN(C_4H_9)_2)SCN]_2$[a]	CS_2	−50	3.80 (t)	1.81 (m)	1.45 (hex)	1.06 (t)
green/yellow mixture	CS_2	12	3.79 (t) 3.64 (t)	1.78 (m)	1.43 (m)	1.04 (m)
$[Au(S_2CN(C_4H_9)_2)_2][Au(SCN)_2]$[b]	CS_2	20	3.68 (t)	1.76 (m)	1.47 (hex)	1.00 (t)

[a] Green, compound II. [b] Yellow.

a rare Au(II)–Au(II) dimer, VI, resulted. The results of a single-crystal diffraction study of VI (X = Cl) confirmed the existence of the proposed structure. Schmidbaur explained the inability to form compound VII when X = I as being due to the unfavorable steric interaction of the bulky I^- ligands in compound VII, where the X groups are arranged in an eclipsed configuration.

Since only 1 mol of I_2 can be added to either of the two Au(I) dimers I and V, they are probably going through a similar pathway. Schmidbaur's steric explanation, as well as his preparation of stable Au(II) dimers, suggests that the common intermediate is the initial formation of an Au(II) dimer analogous to compounds II and VI. In the case of the dithiocarbamate system, the unstable Au(II) dimer resulting from the addition of Cl_2 or Br_2 either disproportionates to $[Au(dtc)_2]^+[AuX_2]^-$ in the absence of any more halogen or oxidizes further in the presence of excess halogen to an Au(III) dimer, as in compound VII, which ultimately undergoes ring cleavage to give 2 mol of $[Au(dtc)X_2]$. When I_2 is added, only disproportionation occurs, since the formation of the Au(III) dimer is sterically unfavorable. Alternatively, the phosphonium ylide Au(I) dimers can add all three halogens to give stable Au(II) dimers, as well as 2 mol of Cl_2 or Br_2 to form stable Au(III) dimeric products. Apparently, the eight-membered phosphonium ylide Au(II) and Au(III) rings are more stable than analogous dithiocarbamate rings. Schmidbaur has ascribed this unexpected stabilization of a normally labile M–C moiety to the presence of onium centers adjacent to the four Au–C σ bonds.[19]

Oxidative Addition Reactions with Silver(I) Dithiocarbamate Hexamer. Although we have not investigated these reactions as extensively, the results that we have obtained thus far indicate that the oxidative addition reaction chemistry of the Ag(I) dithiocarbamate hexamer differs significantly from that described above for its Au(I) homologue. The first, most obvious difference involves the more complicated structure of the hexameric substrate. The crystal and molecular structures of both the (diethyldithiocarbamato)- and (di-*n*-propyldithiocarbamato)silver(I) hexamers have been described by Hesse.[22,23] The silver atoms (see Figure 1) are situated in the central part of the molecule and form a somewhat distorted octahedron with six comparatively short and six longer edges. The long edges form two centrosymmetrically related triangles in the silver octahedron. Outside each of the other six faces of the octahedron, one dithiocarbamate ligand is situated, linked to the silver atoms of the face by silver–sulfur coordination. One of the sulfur atoms is linked to one and the other to two silver atoms.

Attempts to oxidize the $[Ag(detc)]_6$ hexamer at −78 °C by reaction with $(SCN)_2$ resulted only in partial substitution to form $[Ag_6(detc)_5SCN]$. [Presumably, the $(SCN)_2$ oxidized the missing dithiocarbamate to give thiuram disulfide, although this was not confirmed by its isolation and characterization. This type of oxidation has been previously observed in the reactions between iodine and $[Sn(CH_3)_2(detc)_2]$[24] and $[Zn(dbtc)_2]$[25] in cyclohexane.] The $\nu_{C=N}$ bands exhibited by both the hexameric substrate and the partially thiocyanate-substituted product were found at essentially the same frequency (1495 cm^{-1}). The latter, in addition, exhibited an S-bonded thiocyanate ν_{CN} stretching band at 2101 cm^{-1}. Both the substrate and the product did not exhibit an ESR signal.

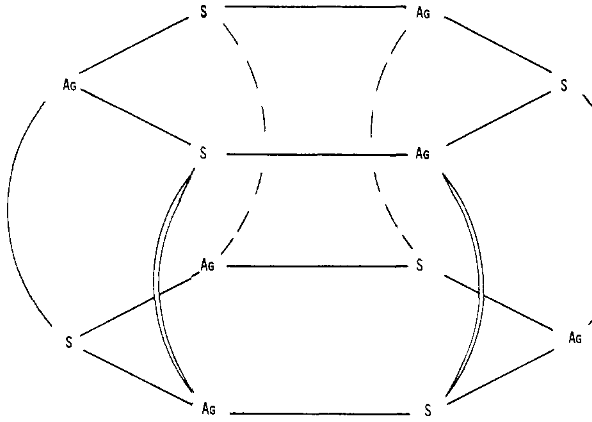

Figure 1. Structure of silver(I) dithiocarbamate hexamers.[22,23] (Curved lines represent the remaining skeletons of the dithiocarbamate moieties.)

However, when the reaction was carried out at room temperature, partial oxidation of the Ag(I) to Ag(II) finally occurred, yielding $[Ag_6(detc)_6(SCN)_4]$ as the final product. This conclusion is supported by the appearance of an additional higher frequency dithiocarbamate $\nu_{C=N}$ stretching band at 1530 cm^{-1} in the product's infrared spectrum and a broad (2000-G) singlet at 3000 G ($g \sim 2.3$) in its ESR spectrum, which remained constant with time. The thiocyanate ν_{CN} stretching frequency remained at 2101 cm^{-1}.

Preliminary results indicate that the silver(I) dithiocarbamate hexamer is even more resistant to oxidation by $(SeCN)_2$. Even when the reaction was carried out at room temperature, only a partially substituted, nonoxidized $[Ag_6(detc)_5SeCN]$ product was isolated.

We intend to explore the chemistry of Au(II) in compounds of type II more fully, with an eye toward finding combinations that will stabilize the +2 oxidation state. This will involve (1) varying the nature of the R groups in the dithiocarbamate moiety, from electron donating to electron withdrawing, including cationic[26] dithiocarbamates and (2) varying the bridging ligand, e.g., diselenocarbamates[27] and dialkyl dithiophosphates.[28] A particularly intriguing possible substrate

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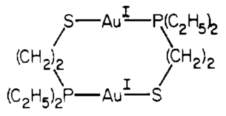
in the last category is found in the gold(I) dimer X.[29] Compound X has been investigated[30] in terms of its being used in arthritis therapy.



X

A logical future extension of this research will involve an exploration of the oxidative addition reactions between thallium(I) dialkyldithiocarbamates and pseudohalogens. The structure of (dipropyldithiocarbamato)thallium(I) dimer has been shown[31] to be different than that of its gold(I) analogue I. It consists of a unique zigzag chain structure in which the distorted $[(C_3H_7)_2NCS_2Tl]_2$ dimers are connected by interdimer Tl–S linkages such that one Tl(I) is six-coordinate while the other is five-coordinate. Instead of an eight-membered ring, it exists as a distorted bipyramid with Tl(I) atoms at the apices.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

Registry No. $[Au(S_2CN(C_2H_5)_2)SCN]_2$, 79255-13-3; $[Au(S_2CN(C_2H_5)_2)_2][Au(SCN)_2]$, 79255-14-4; $[Au(S_2CN(C_2H_5)_2)SeCN]_2$, 79255-15-5; $[Au(S_2CN(C_2H_5)_2)_2][Au(SeCN)_2]$, 79255-17-7; $[Au(S_2CN(C_2H_5)_2)Br]_2$, 79255-18-8; $[Au(S_2CN(C_2H_5)_2)_2][AuBr_2]$, 33916-73-3; $[Au(S_2CN(C_2H_5)_2)I]_2$, 79255-19-9; $[Au(S_2CN(C_2H_5)_2)_2][AuI_2]$, 79255-20-2; $[Au(S_2CN(C_2H_5)_2)_2][Au(SCN)_2Br_2]$, 79255-22-4; $[Au(S_2CN(C_4H_9)_2)SCN]_2$, 79255-23-5; $[Au(S_2CN(C_4H_9)_2)_2][Au(SCN)_2]$, 79255-24-6; $[Ag(S_2CN(C_2H_5)_2)]_6$, 59859-16-4; $[Au(S_2CN(C_2H_5)_2)]_2$, 66712-10-5; $[Au(S_2CN(C_4H_9)_2)]_2$, 59306-90-0; $(SCN)_2$, 505-14-6; $(SeCN)_2$, 27151-67-3; Br_2, 7726-95-6; I_2, 7553-56-2.

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Preparation and Characterization of Novel Six-Membered Cyclopalladated Complexes of 2-Benzylpyridine

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Received March 4, 1981

The novel six-membered cyclopalladated complex bis(μ-acetato)-bis[2-(2-picolyl)phenyl-C^1,N]dipalladium(II) {$[Pd(OAc)(piph)]_2$} has been synthesized by the reaction between palladium(II) acetate and 2-benzylpyridine. Its di-μ-chloro analogue, {$[PdCl(piph)]_2$}, yielded by the metathetical reaction with lithium chloride, undergoes bridge-splitting reactions with 3,5-lutidine and thallium(I) acetylacetonate to afford the corresponding mononuclear cyclopalladated complexes. All the cyclopalladated complexes are characterized by means of elemental analysis and mass, IR, and NMR spectroscopy. The cyclopalladated structure of the piph moiety is also confirmed by the formation of 2-(2-vinylated benzyl)pyridines, which were obtained by the reactions of {$[PdCl(piph)]_2$} with styrene and methyl vinyl ketone.

Introduction

In recent years considerable interest has developed concerning the utilization of cyclometalated complexes for organic syntheses.[1,2] Many articles have already been published concerning five-membered cyclometalated complexes having nitrogen, phosphorus, oxygen or sulfur donor atoms.[3-5] However, six-membered cyclometalated complexes are less popular, and only five reports have appeared about six-membered cyclometalation of 2,2′-bis(diphenylphosphino)dibenzyl,[6] *trans*-2,2′-bis(diarylphosphino)stilbene,[7] (*o*-alkoxyphenyl)diorganophosphine,[8] *N*-arylamides,[9,10] and *N*,*N*′-diarylamidines.[9] Moreover, it has been reported that hydrometalation of diphenyl(*o*-styryl)phosphine,[11] oxymetalation of (but-3-enyl)diphenylphosphine,[12] diphenyl(*o*-styryl)phosphine,[13] and dimethyl(*o*-styryl)arsine,[13] and bromometalation of (*o*-allylphenyl)diphenylphosphine[14] also resulted in the formation of six-membered C,P- or C,As-chelating complexes.

In the course of investigation about new cyclopalladation reactions,[15-17] we have found that 2-benzylpyridine (Hpiph) easily reacted with palladium(II) acetate to yield a novel six-membered cyclopalladated complex {$[Pd(OAc)(piph)]_2$}

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