TABLE I

L	Wt of $B_{10}H_{12}L_2$, g	Reactor	Temp, °C	Time, hr	HCCH flow, cm³/min	Yield, %[a]
Et_2S	1.0	B	100	6	250	Trace
Et_2S	3.0	B	70	3	250	Trace
$(C_6H_5)_3P$	2.0	B	150	17	50	0.0
$(C_6H_5)_3P$	3.0	B	195	3	50	Trace[b]
CH_3CN	5.0	B	100	5	100	20.4
CH_3CN	3.0	B	96	144	96	33.1
CH_3CH_2CN	3.0	B	96	46	50	41.5
CH_3CH_2CN	3.0	B	96	58	50	45.2
CH_3CH_2CN	3.0	B	96	82	50	45.7
CH_3CH_2CN	10.0	A	92	7	25	20.7
CH_3CH_2CN	10.0	A	92	72	25	44.0
CH_3CH_2CN	10.0	A	93	120	50	52.7
$CH_3CH(CH_3)CN$	3.0	B	92	21	50	2.4

[a] Yield based on $B_{10}H_{12}L_2$. [b] Product contaminated with $(C_6H_5)_3P$.

Results and Discussion

A displacement series for Lewis bases, L, in $B_{10}H_{12}L_2$ has been established by Hawthorne[5] and expanded by Zakharkin.[6] The solution preparation of *o*-carborane is most successful when L in eq 1 is one of the bases which is most easily displaced. The low yield for the nonsolution preparation of *o*-carborane when L = $(C_6H_5)_3P$ is in agreement with this generalization. When $B_{10}H_{12}(Et_2S)_2$ was allowed to react in the nonsolution system, softening of the reactant was observed even below its normal melting point and the low yield of product may be due to inefficient contact between this melt and the acetylene. The difference in yield of *o*-carborane for the various nitriles tested is not easily explained.

Higher yields might be realized by changes in the apparatus design. In particular, the use of a fluidized bed of $B_{10}H_{12}L_2$ has been suggested.[7] However, the apparatus described above is easy to assemble and provides a satisfactory yield.

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Gold(III)-Gold(II) and Silver(II)-Silver(III) Equilibria with the *N,N*-Di-*n*-butyldithiocarbamate Ligand

BY TIMOTHY J. BERGENDAHL* AND ESTERINA M. BERGENDAHL

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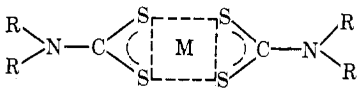
In 1959 Vänngard and Åkerström[1] reported that they had observed electron spin resonance spectra when gold(I) and silver(I) complexes containing the *N,N*-diethyldithiocarbamate ligand were allowed to react with tetraethylthiuram disulfide in benzene solution. The electron spin resonance spectra were presumably due to divalent complexes having structure I (R = C_2H_5, M = Au, Ag). These workers also reported the observation of an electron spin resonance



I

spectrum when tris(*N,N*-diethyldithiocarbamato)gold(III) was dissolved in benzene. The origin of the signal was attributed to equilibrium reaction 1 (R = C_2H_5, M = Au).

$$[R_2NCS_2]_3M \rightleftharpoons [R_2NCS_2]_2M + 0.5[R_2NCS_2]_2 \qquad (1)$$

It was of interest to investigate the possibility of generating an equilibrium reaction similar to (1) with silver as the metal. If such an equilibrium could be identified, it would be in support of a complex of silver(III) containing a sulfur-donor ligand. The *N,N*-di-*n*-butyldithiocarbamate ligand was chosen for the study.

Experimental Section

General Information.—Tetrahydrofuran was distilled from lithium aluminum hydride and collected under nitrogen. Electron spin resonance spectra were obtained on a Varian V-4502-13 instrument. The standard for esr measurements was 1,1-diphenylpicrylhydrazyl.

Preparation of Reactants.—Tetra-*n*-butylammonium tetrabromoaurate(III)[2] and silver(I) *N,N*-di-*n*-butyldithiocarbamate[3] were prepared according to the published methods.

Stock solutions containing the *N,N*-di-*n*-butyldithiocarbamate ligand and tetra-*n*-butylthiuram disulfide were prepared by methods similar to those reported in the literature.[3] Lithium methoxide was used as the base and tetrahydrofuran was the solvent.

Gold Reactions.—For all reactions involving gold 20 ml of a ligand stock solution containing 0.0039 mol of lithium *N,N*-di-*n*-butyldithiocarbamate and where appropriate tetra-*n*-butylthiuram disulfide was allowed to react with a solution consisting of 0.0013 mol of tetra-*n*-butylammonium tetrabromoaurate(III) in 30 ml of tetrahydrofuran.

Electron spin resonance spectra were obtained under identical conditions for all gold experiments.

Silver Reactions.—For all reactions involving silver 0.0004 mol of silver(I) *N,N*-di-*n*-butyldithiocarbamate in 5 ml of tetrahydrofuran was allowed to react with 10 ml of a stock solution containing the appropriate amount of tetra-*n*-butylthiuram disulfide.

Electron spin resonance spectra were obtained under identical conditions for all silver experiments.

Apparatus.—All vacuum-line experiments were conducted in an apparatus consisting of two reactant vessels, one of which contained an esr tube.

The gold- or silver-containing reactant was placed in one reactant vessel and the ligand stock solution or the disulfide stock solution was placed in the other along with a small stirring bar. Both solutions were degassed three times before they were mixed. The pressure in the apparatus was maintained at 1 μ.

After the reactants were mixed, the reaction solution was stirred for 5 min. The esr tube was filled and sealed with a propane torch. All esr spectra were recorded 21 min after the reactants were allowed to mix.

Results and Discussion

When tetra-*n*-butylammonium tetrabromoaurate(III) was allowed to react with 3 molar equiv of lithium *N,N*-di-*n*-butyldithiocarbamate, in tetrahydrofuran,

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[2] W. R. Mason, III, and H. B. Gray, *Inorg. Chem.*, **7**, 55 (1968).

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and under atmospheric conditions, an electron spin resonance spectrum consisting of four lines was observed. The intensity of the spectrum was arbitrarily assigned a value of 1.00.

When the same reaction was repeated in carefully degassed solvent in a vacuum apparatus a four-line electron spin resonance spectrum of relative intensity 1.79 was obtained. The origin of the paramagnetic gold(II) complex may be attributed to (1) (R = n-C_4H_9, M = Au).

The forementioned experiments demonstrate that the gold(II) *N,N*-di-*n*-butyldithiocarbamate complex is air sensitive. The values of g and $\langle a\rangle$ for this complex are displayed in Table I.

TABLE I
ESR PARAMETERS FOR SOME GOLD(II) AND SILVER(II) DITHIOCARBAMATE COMPLEXES

Complex	g	$\langle a\rangle$, G	Ref
$[(C_2H_5)_2NCS_2]_2Au$	2.040	29.4	1
$[(n\text{-}C_4H_9)_2NCS_2]_2Au$	2.039	27.5	This work
$[(C_2H_5)_2NCS_2]_2Ag$	2.019	28.2	1
$[(n\text{-}C_4H_9)_2NCS_2]_2Ag$	2.022	29.0	This work

When tetra-*n*-butylthiuram disulfide was added to a solution containing a mixture of gold(III) and gold(II) *N,N*-di-*n*-butyldithiocarbamate complexes, the intensity of the electron spin resonance spectrum decreased. This behavior supports equilibrium reaction 1 (R = n-C_4H_9, M = Au).

Silver(I) *N,N*-di-*n*-butyldithiocarbamate was allowed to react with 0.5 molar equiv of tetra-*n*-butylthiuram disulfide under atmospheric conditions. A blue solution formed immediately. The solution contained a paramagnetic complex which produced a two-line electron spin resonance spectrum. The intensity of the spectrum was arbitrarily assigned a value of 1.00.

The same experiment was repeated in carefully degassed solvent. The relative intensity of the resulting electron spin resonance spectrum was 1.86. The origin of the paramagnetic silver(II) complex may be attributed to (2).

$$(n\text{-}C_4H_9)_2NCS_2Ag + 0.5[(n\text{-}C_4H_9)_2NCS_2]_2 \longrightarrow [(n\text{-}C_4H_9)_2NCS_2]_2Ag \qquad (2)$$

The previous behavior suggests that under atmospheric conditions some of the silver(II) *N,N*-di-*n*-butyldithiocarbamate complex formed by (2) is air oxidized to a silver(III) *N,N*-di-*n*-butyldithiocarbamate species. It is possible that the silver(III) complex formed by air oxidation is a bis species of the type $[(n\text{-}C_4H_9)_2NCS_2]_2Ag^+$. This type of structure is proposed because there is not enough ligand present to form a neutral tris silver(III) complex.

When the vacuum line experiment was repeated with the same amount of silver(I) *N,N*-di-*n*-butyldithiocarbamate and 1 molar equiv of tetra-*n*-butylthiuram disulfide, a dark red color immediately appeared. The red color faded after 10 min and was replaced with a blue solution. The relative intensity of the electron spin resonance spectrum was 1.71.

The decrease in the intensity of the electron spin resonance spectrum when 1 molar equiv of tetra-*n*-butylthiuram disulfide was added can be explained as follows. If the electron spin resonance spectra obtained for the two vacuum-line silver reactions were equal, it would indicate that the silver(I) complex is oxidized only to a silver(II) species, probably *via* (2). In the case of the silver(I) reaction with 1 molar equiv of thiuram disulfide, however, excess thiuram disulfide would remain. If this excess thiuram disulfide further oxidized the silver(II) complex to a tris silver(III) species, there should be a decrease in the intensity of the electron spin resonance spectrum. This decrease is observed experimentally.

The color change from red to blue can be explained by assuming the formation of a red tris silver(III) complex. By considering (1) (R = n-C_4H_9, M = Ag) the silver(III) complex could participate in an equilibrium with the blue silver(II) species and 0.5 molar equiv of thiuram disulfide. This behavior would be analogous to the gold(III)–gold(II) equilibrium reactions discussed earlier.

The values of g and $\langle a\rangle$ for the silver(II) complex are displayed in Table I. It was not possible to resolve the hyperfine structure due to the silver-107 and -109 isotopes.

The g values for *N,N*-diethyldithiocarbamate and *N,N*-di-*n*-butyldithiocarbamate complexes containing the same metal are nearly identical. This likely means that in solution the structures of the complexes are the same. It would be expected that the paramagnetic silver and gold complexes are square planar.

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A New Synthesis of Potassium *cis*- and *trans*-Bis(oxalato)diaquorhodate(III)

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The potassium salts of *cis*- and *trans*-bis(oxalato)-diaquorhodate(III) are reported to have been prepared in crystalline form by Gillard and Wilkinson.[1] Other workers have obtained these isomers in solution from the aquation of tris(oxalato)rhodate(III) ion[2,3] and of *cis*- and *trans*-dichlorobis(oxalato)rhodate(III) ions.[4]

In connection with our continued interest in reactions of rhodium oxalato complexes[3,5] it became desirable to prepare pure solid salts of the *cis*- and *trans*-bis(oxalato)diaquorhodate(III) ions. In spite of several attempts, we have not been successful in repeating the synthesis as described by Gillard and Wilkinson.[1]

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