added to ionic melts. A plot of E *vs.* ln $\{[MoO_4^{2-}]^2/[Mo_2O_7^{2-}]\}$ should yield a straight line having a slope of $RT/2F$. Several titrations were carried out at various temperatures and concentration ranges. In all cases we obtained a straight line whose slope is in good agreement with the theoretical slope, Figure 3.

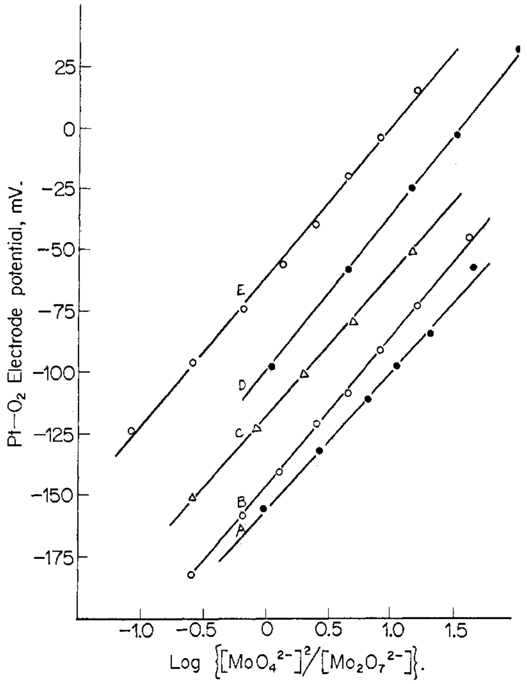

Figure 3.—Nernst plots of a representative sampling of the titrations studied. The points are experimental and the lines are theoretical: A, 2 mmol of $Na_2Mo_2O_7$ in a $NaNO_3$–KNO_3 eutectic melt at 294°; B, 5 mmol of MoO_4^{2-} in a $NaNO_3$–KNO_3 eutectic melt at 338°; C, 2.5 mmol of MoO_4^{2-} in a $NaNO_3$–KNO_3 eutectic melt at 310°; D, the acidic reaction product of 4.5 mmol of MoO_3 eutectic melt at 354°; E, 5.0 mmol of MoO_4^{2-} in KNO_3 at 348°.

There is the possiblility that higher polymers may exist in the nitrate melt; therefore, we continued our titrations of MoO_4^{2-} with MoO_3 beyond the first equivalence point to see if a second equivalence point could be obtained. The potential did not change much and NO_2 was slowly produced as more MoO_3 was added to the melt. When MoO_3 is added to pure nitrate melts it is quite evident that MoO_3 is not very soluble and goes into solution as the reaction $2MoO_3 + 2NO_3^{2-} \rightarrow 2NO_2 + 0.5O_2 + Mo_2O_7^{2-}$ proceeds. However, MoO_3 dissolves rapidly if MoO_4^{2-} is present in the melt, even beyond the first equivalence point. This observation indicates that MoO_3 is pulled into solution first by MoO_4^{2-} to form the dimer and then by $Mo_2O_7^{2-}$ to form the trimer. If the trimer is formed it is too acidic to be stable since NO_2 is generated after the first equivalence point is reached.

To gain further evidence for the dimer, we titrated $Na_2Mo_2O_7$ which we had prepared and found that an equimolar amount of base was required to titrate the $Na_2Mo_2O_7$, Figure 1. A Nernst plot similar to the previous ones gave a straight line within 1% of the theoretical slope, Figure 3.

Finally we duplicated Shams El Din's experiments. That is, we allowed MoO_3 to react with the melt and then titrated the melt with Na_2O_2. We had suspected that the reason our results did not agree with those of Shams El Din was that we had used CO_3^{2-} as a base and he had used O_2^{2-} as a base. When CO_3^{2-} was used as the base, 0.5 mol was required to neutralize the melt for every mole of MoO_3 added. This observation indicated the dimer as the species being formed, eq 1 and 3. When we used O_2^{2-} as our base, we obtained inflection points greater than 0.5 mol but less than 0.66 mol of Na_2O_2 added. Two-thirds of a mole would indicate trimer formation, the reaction of MoO_3 with melt being $3MoO_3 + 2NO_3^- \rightarrow Mo_3O_{10}^{2-} + 2NO_2 + 0.5O_2$ followed by titration with peroxide, $Mo_3O_{10}^{2-} + 2O_2^{2-} \rightarrow 3MoO_4^{2-} + O_2$. Indeed, Shams El Din, who used O_2^{2-} exclusively as his base, reported always requiring 0.66 mol of O_2^{2-} per mole of MoO_3. We noticed after each titration, however, quantities of unreacted Na_2O_2 in the melt which appeared to be greater than the amount by which we had exceeded the equivalence point. Apparently Na_2O_2 is not very soluble in the melt and is "pulled in" by an acid present in the melt; however, near the equivalence point as the acid concentration becomes more dilute the peroxide will not dissolve readily. Thus, consistently high results are obtained unless one waits long enough for the Na_2O_2 to dissolve and react before taking readings. We found that when we waited sufficiently long on our readings near the equivalence point, very close to 0.5 mol of peroxide was required, thus agreeing with our other data.

There are other properties of peroxide ion which make it an undesirable base titrant. One such property is the tendency for Na_2O_2 to pick up water; therefore appropriate techniques for weighing and transferring accurate quantities are required. Another property, which causes a much more serious problem, is the reaction of peroxide ion with glass in nitrate melts leaving the glass visibly etched. Presumably this effect is more prevalent near the equivalence point of the titration when the acid concentration of the melt is low. Both of these effects will give high results when titrating an acidic species with peroxide ion in nitrate melts.

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A Reinvestigation of the Supposed Linkage Isomerism Exhibited by the *trans*-Dicyanodithiocyanatoaurate(III) Ion

BY JOHN B. MELPOLDER AND JOHN L. BURMEISTER*

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Negoiu and Baloiu recently claimed[1] to have synthesized S- and N-bonded thiocyanate linkage isomers of the title ion, *trans*-$[Au(CN)_2(SCN)_2]^-$, as both the potassium and tetraethylammonium salts. If correct, this would represent the first example of electronic

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(1) D. Negoiu and L. M. Baloiu, *Z. Anorg. Allg. Chem.*, **382**, 92 (1971).

ligand control of the bonding mode of the thiocyanate ion in a gold(III) complex; *i.e.*, all gold(III) thiocyanate complexes previously reported have involved Au–SCN bonding,[2] *e.g.*, $[Au(SCN)_4]^-$. The sensitivity of the bonding mode of the thiocyanate group to the electronic character of other ligands present in the coordination sphere has been observed[3] for square-planar complexes of Pd(II), Pt(II), Rh(I), and Ir(I). We now wish to report the results of studies previously carried out in our laboratory which, we believe, indicate that the conclusions reached by Negoiu and Baloiu[1] are incorrect. We also wish to report the synthesis of the analogous selenocyanate complex.

Experimental Section

Preparation of *trans*-$[(CH_3)_4N][Au(CN)_2(SCN)_2]$.—To a 0° solution of 0.099 g of potassium thiocyanate, dissolved in 15 ml of Spectrograde acetone, was added 0.20 g of *trans*-$[(CH_3)_4N]$-$[Au(CN)_2Cl_2]$, prepared according to the method of Mason.[4] After stirring the mixture for 5 min, the potassium chloride which precipitated was removed by filtration, the yellow filtrate being allowed to pass directly into 150 ml of anhydrous diethyl ether. The yellow solid which precipitated was isolated by filtration, washed with anhydrous diethyl ether, and dried *in vacuo*. It was stored at 0° to prevent it from decomposing; yield, 92%. *Anal.* Calcd for $AuC_8H_{12}N_5S_2$: Au, 44.84; C, 21.87; H, 2.75; N, 15.94; S, 14.60. Found: Au, 44.83; C, 22.04; H, 2.75; N, 16.08; S (by difference), 14.30.

Preparation of *trans*-$[(CH_3)_4N[]Au(CN)_2(SeCN)_2]$.—This yellow complex was prepared by the same method, using stoichiometric amounts of potassium selenocyanate and *trans*-$[(CH_3)_4N]$-$[Au(CN)_2Cl_2]$; yield, 43%. *Anal.* Calcd for $AuC_8H_{12}N_5Se_2$: Au, 36.85; C, 17.97; H, 2.26; N, 13.17; Se, 29.75. Found: Au, 37.29; C, 18.04; H, 2.27; N, 13.31; Se (by difference), 29.09.

Characterization of Complexes.—Microanalyses were performed by the Alfred Bernhardt Microanalytical Laboratory, Elbach über Engelskirchen, West Germany. Infrared spectra, both of Nujol mulls and solutions, were measured on a Perkin-Elmer 180 spectrophotometer, using a fivefold wave number scale expansion for the precise assignment of band frequencies. Matched 1.0-mm sodium chloride cells were employed for the solution measurements. The infrared absorption bands exhibited by the thiocyanate and selenocyanate complexes, as Nujol mulls, in the 4000–400-cm^{-1} range, are shown in Table I. The band assignments were made, in part, by comparing the infrared spectra of the pseudohalide complexes with the spectra of the *trans*-$[Au(CN)_2X_2]^-$ complexes (X = Cl, Br, I) reported in the literature.[5]

TABLE I

INFRARED SPECTRA[a] (CM^{-1}) OF *trans*-$[(CH_3)_4N][Au(CN)_2(XCN)_2]$ COMPLEXES

Assignment	X = S	X = Se	Assignment	X = S	X = Se
$\nu_{AuC\equiv N}$	2176 w	2176 w	δ_{AuSCN}	466 w	. . .
$\nu_{AuXC\equiv N}$	2131 vs	2139 vs	δ_{AuCN}	448 m	451 m
$2\delta_{AuSCN}{}^{b}$	828 m	. . .	ν_{Au-CN}	427 m	435 m
ν_{AuX-CN}	694 m	533 m	δ_{AuSCN}	411 w	. . .

[a] Abbreviations: vs, very strong; m, medium; w, weak. Nujol mulls, 4000–400 cm^{-1}; a KBr disk spectrum of the thiocyanate complex indicated the occurrence of a slight amount of Br^- substitution for the SCN^- ion. [b] See discussion concerning this band by A. Sabatini and I. Bertini, *Inorg. Chem.*, **4**, 1665 (1965).

Dissolution of the thiocyanate complex in nitrobenzene results in a small amount of dissociation of the thiocyanate groups, as indicated by the appearance of a weak band at 2053 cm^{-1} (the same CN stretching frequency as that exhibited by tetra-*n*-butylammonium thiocyanate in this solvent). The thiocyanate groups which remain coordinated do not change their bonding mode, as evidenced by the negligible change in their CN stretching frequency (2138 cm^{-1}), relative to that exhibited in the solid state (2131 cm^{-1}). The integrated absorption intensity[6] of this band, corrected for the slight dissociation which occurs in nitrobenzene solution, is 0.84×10^4 M^{-1} cm^{-2} per mole of coordinated thiocyanate. This is to be compared with an integrated absorption intensity of 7.0×10^4 M^{-1} cm^{-2} for tetra-*n*-butylammonium thiocyanate in the same solvent.

Dissolution of the selenocyanate complex in nitromethane also results in some dissociation of the selenocyanate groups (an ionic selenocyanate CN stretching band appears at 2062 cm^{-1}), but in addition to a CN stretching band at 2143 cm^{-1}, which corresponds to the 2139-cm^{-1} band exhibited by the coordinated selenocyanate groups in the solid state, a third selenocyanate CN stretching band appears at 2117 cm^{-1}.

Discussion

Negoiu and Baloiu claimed[1] to have prepared *trans*-$K[Au(CN)_2(NCS)_2]$ by mixing aqueous solutions of *trans*-$K[Au(CN)_2Cl_2]$ and KNCS, whereupon the N-bonded isomer separated as a yellow precipitate. Dissolution of the yellow compound in methyl alcohol, followed by evaporation of the solvent, yielded a mixture of red and yellow crystals, AuCN, and metallic gold. The red crystals, which they claimed to be *trans*-$K[Au(CN)_2(SCN)_2]$, were separated mechanically in very small yield. Conversion to the tetraethylammonium salts was effected by treating an aqueous solution of the potassium salt of either isomer with aqueous $(C_2H_5)_4NI$, the N isomer precipitating as orange-red crystals and the S isomer precipitating slowly from the filtrate as dark red crystals. No analytical data were given for either S-isomer salt and that given for the N-isomer salts was fragmentary and, in the case of the potassium salt, very poor. Bonding mode assignments were made on the basis of the infrared spectra of the potassium salts, as KBr disks.

At the outset of our work, we observed that the potassium salt could not be dried *in vacuo* without some decomposition occurring, but the tetramethylammonium salt could be dried and stored for an indefinite period of time at a low temperature without decomposing. Since the solid-state infrared spectra of both the potassium and tetramethylammonium salts were virtually identical (*vide infra*), except for the absorption bands attributable to the latter cation, prior to the decomposition of the potassium salt, all of the ensuing studies were carried out using the latter salt.

Based[7] on its decreased ν_{AuS-CN} frequency, its decreased δ_{SCN} frequencies, and its decreased $\nu_{AuSC\equiv N}$ integrated absorption intensity, all relative to the corresponding free-ion values,[7] it is quite certain that the yellow complex $[(CH_3)_4N][Au(CN)_2(SCN)_2]$ contains S-bonded thiocyanate groups, both in the solid state and in solution, as does the yellow potassium salt. The very weak $\nu_{AuC\equiv N}$ band is comparable, in both frequency and intensity, to that exhibited by the *trans*-$[Au(CN)_2Cl_2]^-$ complex and is caused by the trans arrangement of the π-acid CN^- groups. The reduction in intensity of the $\nu_{C\equiv N}$ band caused by the presence of electron-withdrawing groups has been discussed by Brown.[8]

As would be expected[3] in a thiocyanate complex of a class b or soft metal in a relatively high oxidation state, the π-withdrawal by the cyanides is therefore

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[2] H.-H. Schmidtke, *Ber. Bunsenges. Phys. Chem.*, **71**, 1138 (1967).

[3] See, for example, J. L. Burmeister and F. Basolo, *Inorg. Chem.*, **3**, 1587 (1964); N. J. DeStefano and J. L. Burmeister, *ibid.*, **10**, 998 (1971).

[4] W. R. Mason, *ibid.*, **9**, 2688 (1970).

[5] L. H. Jones, *ibid.*, **3**, 1581 (1964); **4**, 1472 (1965).

[6] D. A. Ramsay, *J. Amer. Chem. Soc.*, **74**, 72 (1952).

[7] J. L. Burmeister, *Coord. Chem. Rev.*, **1**, 205 (1966); **3**, 225 (1968).

[8] T. L. Brown, *Chem. Rev.*, **58**, 581 (1958).

insufficient to convert the gold(III) to a class a or hard coordination center. Likewise, neither counterion[9] nor solvent[10] control of the thiocyanate's bonding mode is operative in this case. As originally prepared, the potassium salt exhibits an additional thiocyanate CN stretching band at 2060 cm^{-1}, along with strong water absorption bands at 3640, 3560, and 1620 cm^{-1}. As the water absorption bands diminish in intensity when the salt is dried *in vacuo*, the thiocyanate band at 2060 cm^{-1} also diminishes in intensity, suggesting that it is due to an aquo complex impurity which contains an ionic thiocyanate, *e.g.*, $[Au(CN)_2(H_2O)_2]SCN$, the thiocyanate entering the coordination sphere as the water is removed. The 2060-cm^{-1} band also disappears when the potassium salt is washed thoroughly with water, leaving a compound whose spectrum is virtually identical with that of the tetramethylammonium salt, except for water absorption bands and the bands due to the latter cation. As mentioned earlier, drying this compound results in its beginning to decompose. We have also observed that the tetramethylammonium salt immediately turns red when placed on a cesium iodide plate, indicating the ease with which the thiocyanate groups can be replaced by iodide ions.

Both the potassium and tetramethylammonium salts of the thiocyanate complex develop red colors as they decompose in ethanolic solution. We were unable, after repeated attempts, to isolate an analytically characterizable sample of the red substance. However, it is now clear that it is *not* a linkage isomeric form of the yellow complex.

Although the infrared data indicate[7] that the selenocyanate complex contains Se-bonded groups in the solid state (the $\nu_{\text{AuSe}-\text{CN}}$ frequency is lowered relative to the free-ion value[7]), the appearance of the third selenocyanate CN stretching band at 2117 cm^{-1} indicates that a solvent-induced[10,11] partial Se→N-bonded isomerization takes place in nitromethane solution.

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[9] D. F. Gutterman and H. B. Gray, *J. Amer. Chem. Soc.*, **91**, 3105 (1969).

[10] J. L. Burmeister, R. L. Hassel, and R. J. Phelan, *Chem. Commun.*, 679 (1970).

[11] J. L. Burmeister, R. L. Hassel, and R. J. Phelan, *Inorg. Chem.*, **10**, 2032 (1971).

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Silicon-Fluorine Chemistry. VI. The Reaction of Silicon Difluoride with Butadiene

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A number of recent studies have been concerned with the reactions between silicon difluoride and unsaturated compounds.[1-6] This report describes the reaction between 1,3-butadiene and silicon difluoride. The system was of interest in comparison with the reactions with benzene,[2] which apparently acts as a 1,3-diene in its addition to silicon difluoride, and some of the other olefinic or acetylenic species[4-6] where not only do addition reactions occur but also specific hydrogen migrations are observed forming rearranged products.

Experimental Section

Silicon difluoride was prepared as previously described[7] by the reaction of silicon tetrafluoride with silicon at 1150°. Commercially available 1,3-butadiene (Matheson) was used without further purification. An approximately 2:1 molar excess of butadiene (based on 50% conversion of SiF_4 to SiF_2) was used, since this ratio appeared to give the best yields of volatile products, which were, however, only about 2% based on olefin used.

Volatile compounds were manipulated in a conventional greaseless vacuum system and studied by mass spectrometry (Bendix 14-107 Time-of-Flight instrument), by infrared spectrometry (Beckman IR-20), and by nmr spectroscopy (Varian A-56/60 and HA-100 instruments).

$C_4H_6Si_2F_4$ was separated at room temperature on a 6 ft × $^3/_8$ in. column containing 10% Kel-F-10 oil on Chromosorb W, using helium as carrier gas.

A sample of 1-vinyl-2,2,3,3-tetrafluorocyclobutane was kindly donated by Dr. J. J. Drysdale of Du Pont (Jackson Laboratory). This was passed at low pressures through a Vycor tube heated to 700°, and from the volatile products samples of the tetrafluorocyclohexenes IV and V were obtained by gas chromatographic separation.[8] They were identified by their mass and nmr spectra (see below).

Results

At −196° the cocondensed reaction mixture of SiF_4, SiF_2, and butadiene was olive green, while on warming to room temperature a pale yellow involatile solid remained and volatile products were given off. The solid residue was not spontaneously inflammable but burned readily with a smoky flame on ignition. It dissolved fairly readily in dilute alkali but was attacked very slowly by dilute HF solution, without liberation of spontaneously inflammable silicon hydrides.

The volatile products, after separation of excess SiF_4 and butadiene, were found to consist of colorless crystals and a rather oily liquid; this mixture proved to be inseparable by vacuum distillation. However an apparently pure crystalline solid (mp 29.5°) was obtained by gas chromatographic separation at room temperature; none of the liquid emerged from the column at this temperature and the use of higher temperatures apparently caused rapid decomposition since there was continuous evolution of SiF_4 from the column above 40°.

The mass spectrum of the crystalline solid, Table I, showed the heaviest ion at m/e 186, corresponding to a formula of $C_4H_6Si_2F_4$ (I). Gas-phase molecular weight determinations were hampered by the low vapor pressure of the compound at room temperature (∼22 mm);

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[1] J. C. Thompson, P. L. Timms, and J. L. Margrave, *Chem. Commun.*, 566 (1966).

[2] P. L. Timms, D. D. Stump, R. A. Kent, and J. L. Margrave, *J. Amer. Chem. Soc.*, **88**, 940 (1966).

[3] C. S. Liu and J. C. Thompson, *Inorg. Chem.*, **10**, 1100 (1971).

[4] C. S. Liu, J. L. Margrave, J. C. Thompson, and P. L. Timms, *Can. J. Chem.* in press.

[5] C. S. Liu, J. L. Margrave, and J. C. Thompson, *ibid.*, in press.

[6] C. S. Liu and J. C. Thompson, *J. Organometal. Chem.*, in press.

[7] P. L. Timms, R. A. Kent, T. C. Ehlert, and J. L. Margrave, *J. Amer. Chem. Soc.*, **87**, 824 (1965).

[8] J. J. Drysdale, U. S. Patent 2,831,025, assigned to E. I. du Pont de Nemours and Co., Wilmington, Del., Nov 1958.