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Synthesis and Characterization of Dithiocyanato(N,N-di[(2-N,N-diethylamino)ethyl]dithiocarbamato)-*S,S'*)gold(III) and Isothiocyanato(N,N-di[(2-N,N-diethylamino)ethyl]dithiocarbamato-*N,N',N''*)gold(III) Thiocyanate: A Novel Example of Double Linkage Isomerism*

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Although the observation of linkage isomerism involving the thiocyanate ion is a relatively recent phenomenon [1], compared to that involving the nitrite ion [2], progress in the area has been both rapid and extensive [3, 4]. One measure of the validity of this statement is seen in the growth in the number of known thiocyanate linkage isomeric pairs (2 in 1963 [1], 14 in 1968 [5], 61 in 1976 [6]). The list of ambidentate ligands known to exhibit linkage isomerism has also grown spectacularly (6 in 1968 [5], 27 in 1976 [6]), and now includes ambidentate chelating ligands [5, 6] as well as several examples [3–6] of geminites [6] (complexes of ambidentate ligands wherein both bonding modes of the ambidentate ligand are found in a *single* complex). This variety notwithstanding, we now wish to report what we believe is a unique case of *double* linkage isomerism, resulting from the reaction of $[Au(SCN)_4]^-$ with sodium N,N-di[2-N,N-diethylamino)ethyl]dithiocarbamate in acetonitrile.

Experimental

Preparation of Compounds

Sodium N,N-di[2-N,N-diethylamino)ethyl]dithiocarbamate [7], $Na[S_2CN(CH_2CH_2N(C_2H_5)_2)_2]$ (abbreviated Na[Et_4dien-dtc]), and tetrachloroauric acid [8], $H[AuCl_4]\cdot 4H_2O$, were prepared according to methods given in the literature. 1,1,7,7-Tetraethyldiethylenetriamine was purchased from the Aldrich Chemical Co., Inc.

*Preparation of Dithiocyanato(N,N-di[2-N,N-diethylamino)ethyl]dithiocarbamato-*S,S'*)gold(III), $[Au(S_2CN(CH_2CH_2N(C_2H_5)_2)_2)(SCN)_2]$, and Isothiocyanato(N,N-di[(2-N,N-diethylamino)ethyl]dithiocarbamato-*N,N',N''*)gold(III) Thiocyanate, $[Au\{((C_2H_5)_2NCH_2CH_2)_2NCS_2\}NCS]SCN$*

To a cool CH_3CN solution (25 mL) containing 0.437 g (1.06 mmol) $HAuCl_4\cdot 4H_2O$ was slowly added 20 mL of cold CH_3CN containing 0.391 g (4.82 mmol) NaSCN, yielding a deep red solution with a large precipitate of NaCl. The slow addition of 0.295 g (1.15 mmol) of Na[Et_4dien-dtc] had no obvious effect. The NaCl was removed by filtration, and the deep red filtrate was allowed to stand at room temperature for 1.5 hr. Filtration yielded a small amount of an unidentified orange-brown precipitate. After storing the deep red filtrate in the freezer for two days, filtration again yielded a small amount of this unidentified solid. The filtrate was then evaporated to one-half of its original volume, yielding a copious amount of an orange precipitate, which was isolated by filtration, washed with cold H_2O and diethyl ether, and dried *in vacuo* for 2 days at 80°. The orange solid decomposes at 118–120 °C. *Anal.* Calcd. for $C_{15}H_{28}N_5S_4Au$: C, 29.84; H, 4.67; N, 11.60. Found: C, 29.64, H, 4.37, N, 11.87.

Physical Measurements

Infrared spectra were recorded using Nujol mulls on a Perkin-Elmer 180 grating spectrophotometer using 10X abscissa scale expansion from 2200 to 2000 cm^{-1} and 1650 to 1480 cm^{-1}. Melting points were measured using a Thomas–Hoover melting point apparatus, and are uncorrected. Molar conductances of 10^{-3} *M* solutions were measured at 25 °C with an Industrial Instruments, Inc., Model RC-16B2 conductivity bridge using platinum electrodes. A 10^{-3} *M* solution of tetra-n-butylammonium iodide was used as a reference. Elemental analyses were performed by Schwarzkopf Laboratories, Woodside, N.Y.

Results and Discussion

We initially became interested in the [Et_4dien-dtc]$^-$ ligand because of the fact that it has the potential to act as a chelating ambidentate ligand. Few examples of this type of ligand are known [6]. By using both of its chelating sites simultaneously, it also has the ability, at least theoretically, to bridge two metal centers:

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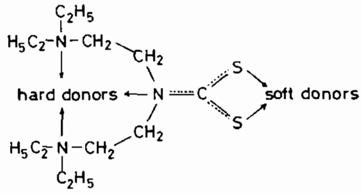
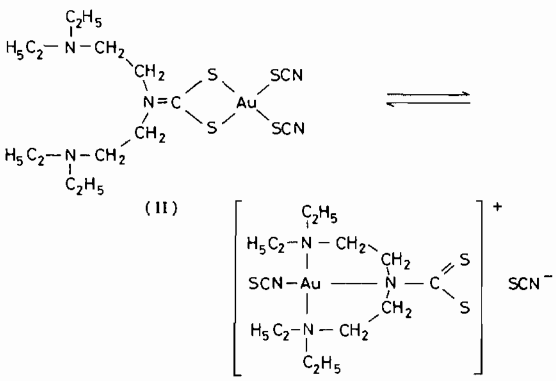


(I)

McCormick *et al.* [7] formed complexes of this ligand with Ni(II), Pd(II) and Co(III), and found no evidence for coordination of the tertiary nitrogens. The elemental analysis of our orange product clearly indicated the formation of a mononuclear species. The observation of four absorption bands in the thiocyanate ν_{CN} stretching region of the infrared spectrum (2136, 2131 cm^{-1} (doublet, s, sp) and 2054, 2024 cm^{-1} (doublet, s, br)) offers, we believe, convincing evidence for the existence of a mixture of the *doubly* linkage isomeric pair (II) and (III):



(II)

(III)

The strong, sharp thiocyanate ν_{CN} doublet observed at 2136 and 2131 cm^{-1} infers the expected *cis*-splitting, and falls well within the S-bound region [3] for a neutral square planar gold(III) complex (II), wherein the gold(III) is coordinated to the sulfur atoms of two *cis* thiocyanates, and is chelated by the sulfur donors of the Et_4dien-dtc$^-$ ligand. The strong, broad thiocyanate ν_{CN} doublet at 2054 and 2024 cm^{-1}, which did not diminish in intensity when washed with water, is apparently not due to an ionic NaSCN impurity. We have assigned the 2054 cm^{-1} peak to the SCN^- counterion (a typical [3] ν_{CN} value for ionic SCN^-), and the 2024 cm^{-1} peak to the N-bound thiocyanate of compound (III), in which the gold(III) is chelated to all three nitrogens of the Et_4dien-dtc$^-$ ligand, and is bound to the nitrogen atom of a thiocyanate in a square planar arrangement. Although gold(III) is normally considered to be a fairly soft coordination site, the existence of the N-bound thiocyanate in compound (III) would be expected, due to the large steric hindrance created by the four ethyl groups of the N,N′,N″-chelated Et_4dien-dtc$^-$ ligand. The same phenomenon has previously been observed [9] in the complex [Pd(Et_4dien)NCS]SCN. Although the 2024 cm^{-1} ν_{CN} peak is rather low in frequency for N-bound thiocyanate, even lower frequency N-bound ν_{CN} peaks have been observed [10].

The uncoordinated Et_4dien-dtc$^-$ ligand exhibits $\nu_{C=N}$ stretching bands at 1618 and 1615 cm^{-1}. The orange product gave a strong, broad $\nu_{C=N}$ peak at 1538 cm^{-1}, which would be due to the presence of compound (II). The existence of only one dithiocarbamate $\nu_{C=N}$ stretch is understandable if one realizes that the C–N bond in compound (III) has no double bond character at all, so that it would fall below the frequency region where the $\nu_{C=N}$ bands of dithiocarbamates are normally observed. Owing to the nebulous nature of this spectral region (1200–1000 cm^{-1}), the value of $\nu_{C=N}$ for compound (III) could not be assigned untimorously.

The existence of compound (III) was also indicated by the results of a series of electrical conductivity measurements carried out in acetone. The average λ_m value observed (73 ohm^{-1} cm^2 mol^{-1}) is indicative of the presence of a significant amount of the ionic compound (III), but is still below the range of λ_m values observed [11] for 10^{-3} *M* solutions of 1:1 electrolytes in acetone at 25 °C.

Efforts are currently underway to separate the two components (II and III).

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