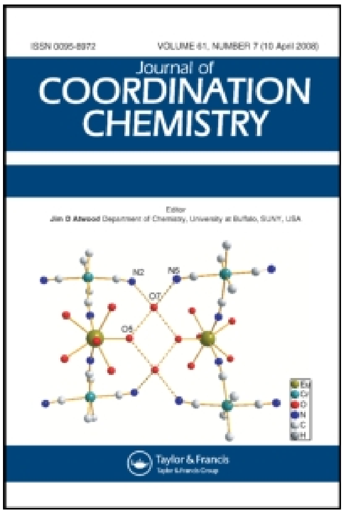

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SYNTHESIS OF A SILVER(III) DIETHYLDITHIOCARBAMATO COMPLEX

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Note

SYNTHESIS OF A SILVER(III) DIETHYLDITHIOCARBAMATO COMPLEX

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Diethyldithiocarbamate reacts with silver(I) in the presence of hydrogen peroxide to give $[Ag_2(Et_2NCS_2)_2(OH)_2]^{2+}$ in solution. The complex ion was precipitated as $[Ag_2(Et_2NCS_2)_2(OH)_2](ClO_4)_2$.

Keywords: Sodium diethyldithiocarbamate; silver(III)

INTRODUCTION

The chemistry of silver(III) is more limited than that of gold(III) and copper(III).[1] In view of the fact that stable dialkyldithiocarbamato complexes of gold(III) and copper(III) are known, it seems that these ligands are capable of stabilizing high oxidation states of the transition metals in their complexes.[2–5] A special feature of dialkyldithiocarbamato ligands is strong electron donation promoting the stability of compounds with a metal in a high oxidation state.[6] To date, however, only univalent silver dithiocarbamato complexes have been isolated and the existence of the Ag(III) dithiocarbamato complex is reported only in solution. Attempts to oxidize Ag(I) dithiocarbamato complexes with halogens to the respective silver(III) complexes failed.[7,8] In this work we report the first synthesis of a diethyldithiocarbamato complex of silver(III).

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EXPERIMENTAL

General

Reagents used were of analytical grade obtained from Merck. All preparations were carried out in air and solvents were of technical grade, used after distillation.

Instrumentation

Infrared spectra were obtained using KBr pellets in the range 4000–500 cm^{-1} with a Shimadzu FT-IR spectrometer. Electronic spectra were recorded in methanol solution on a Shimadzu UV-265FW spectrophotometer. ^{1}H NMR were obtained using a Bruker AC 80 spectrometer (acetone-d_6) and TMS was used as internal standard. Magnetic susceptibilities were determined by the Faraday method, calibrated against Hg[Co(SCN)$_4$]. Silver was determined by atomic absorption and iodometry. In the reaction of the complex with KI, 2 mols of I_2 were liberated per mol of complex. This reaction could be used to confirm the oxidation state of silver in the complex. Cyclic voltammetry was performed with a three-electrode system with a Metrohm 746 VA Trace Analyzer, with Pt wires as working and auxiliary electrodes and Ag/AgCl (3M KCl) as reference electrode. Conductometric measurements were carried out in acetone solution with a Metrohm 660 instrument.

μ-Dihydroxo-bis-[N,N-diethyldithiocarbamatosilver(III)] perchlorate

An aqueous solution of 0.170 g (1.0 mmol) of $AgNO_3$ in 20 cm^3 of water and 2 cm^3 of 30% w/w hydrogen peroxide in 20 cm^3 of water were added at room temperature to a stirred solution of sodium *N,N*-diethyldithiocarbamate trihydrate 0.450 g (2 mmol) in 20 cm^3 of water. The colour of the solution immediately turned yellow and then orange. A precipitate formed but quickly redissolved, a process which was accompanied by effervescence and heat evolution. After 20 min the colour of the mixture changed to dark brown. The solution was filtered and then, by addition of a saturated solution of $NaClO_4$, the Ag(III) complex precipitated. This dark brown precipitate was filtered and washed with water then diethylether and then dried under vacuum over calcium chloride. Yield: 0.30 g; m.p. 75°C. *Anal.* calc. for $C_{10}H_{22}N_2S_4Ag_2Cl_2O_{10}$ (%): Ag, 28.89; C, 16.12; H, 2.98; N, 3.76. Found: Ag, 28.82; C, 15.81; H, 3.00; N, 4.14. IR (KBr): 3415m, 2970m, 2870w, 1656w, 1539m, 1490s, 1452sh, 1432s, 1377sh, 1350m, 1296sh, 1267s, 1179m, 1143m, 1083vs, 1062m, 970m, 900m, 833w, 779sh, 628m, 557sh cm^{-1}. ^{1}H NMR (CD_3COCD_3): 0.80–1.39 ppm (nine peaks), 3.71–4.46 ppm (twelve peaks) and 4.32 ppm (singlet). Cyclic voltammetry data were obtained from acetone solution (0.1 M $NaClO_4$) at a platinum electrode. Potentials were recorded *versus* a Ag/AgCl reference electrode. The formal potentials, $E^{0'} = (E_{p.a} + E_{p.c})/2$, of complex ions were observed at 0.300 V for Ag(III)/Ag(II) and 0.255 V for Ag(II)/Ag(I). Conductometry in acetone solution at 25°C gave a value of 240 Ω^{-1} cm^2 M^{-1}.

RESULTS AND DISCUSSION

The diethyldithiocarbamato ligand, the hydroxo group and the perchlorate anion were characterized by infrared frequencies. The band at 1540 cm^{-1} is attributed to the C=N stretch (thiureide band) when the NCS_2 the group bonds to a metal ion in a high oxidation state.[4,6] The diamagnetic nature of the complex is indicative of Ag(III). Absorption bands at 1083 and 620 cm^{-1} are characteristic of uncoordinated perchlorate anion. Bands at 3415 and 1062 cm^{-1} show the presence of the hydroxo group in the complex. Electronic spectra of this complex show absorption bands in methanol at 203 and 268 nm for the ligand and an intense ligand-to-metal charge transfer band in the region 625–350 nm, characteristic of Ag(III). Observation of the absorption band at 268 nm in the spectrum of the new complex confirms the bidentate nature of the ligand in this complex.[9]

Chemical shift values in ppm at 80 MHz from TMS for diethyldithiocarbamato and hyroxo groups in the complex were observed (a total of nine peaks) in the range 0.80–1.39 ppm for the methyl protons and (a total of twelve peaks) in the range 3.25–4.46 ppm for the methylene protons. A singlet at 4.32 ppm is due to the hydroxyl groups. It is noted that the appearance of additional peaks for the methyl and methylene protons is due to hindered rotation about the C–N bond, indicating the formation of different conformers.[10,11]

Reduction in this complex occurs reversibly in two steps, Ag(III) → Ag(II) and Ag(II) → Ag(I). The reversibility of these processes was evaluated on the basis of cyclic voltammetry.[12] Electron transfer steps are rapid although cyclic voltammetry reveals that the complex has a rather short life time in acetone solution. However, the reduction peaks and reverse scan oxidation peaks disappear when KI is added to the acetone solution of the complex. Conductometric measurements correspond with three ions in acetone solution which agrees with the proposed formulation of the complex.

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