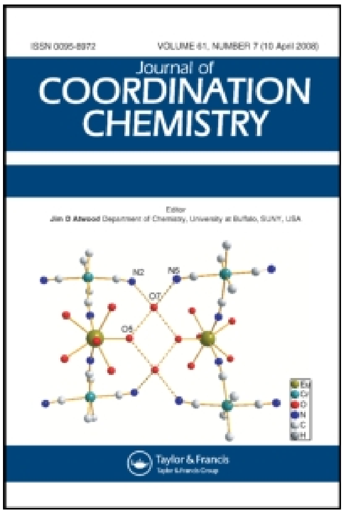

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SYNTHESIS OF NEW PYRIDINE SILVER(III) COMPLEXES

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SYNTHESIS OF NEW PYRIDINE SILVER(III) COMPLEXES

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New pyridine silver(III) complexes have been synthesized by the concurrent oxidation of silver(I) ion and ammonia in the reaction of pyridine and silver nitrate using ammonium peroxydisulfate in aqueous ammonia solution. At high pH values, *trans*-$[Ag(py)_2(N_2)_2](OH)_3$ was obtained, which was then converted to *trans*-$[Ag(py)_2(N_2)_2](ClO_4)_3$. However, at lower pH values $[Ag(py)_4](ClO_4)_2(NO_3)$ was isolated.

Keywords: Pyridine; Silver(III)

INTRODUCTION

The chemistry of silver(III) has been investigated in recent years and a few complexes of silver(III) have been reported in the literature [1–3]. Nitrogen donor heterocyclic ligands such as pyridine and its derivatives stabilize silver(II) in their complexes [4–7]. However, complexes of silver(III) with pyridines as ligand have not been reported. We attempted to prepare complexes of silver(III) with pyridine in an ammonia–ammonium ion solution. In this reaction not only silver(III) was formed by the oxidizing action of peroxydisulfate on silver(I) ion, but ammonia was oxidized to dinitrogen which appeared as a coordinated ligand. Coordination of dinitrogen to the metal ions and the oxidation of ammonia and ammonium ions with peroxydisulfate in aqueous solution have been reported in the literature [8–12]. In this paper we report the synthesis of new complexes of

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silver(III) with pyridine alone, and also with pyridine and dinitrogen, in which the source of the latter is the oxidation of ammonia.

EXPERIMENTAL

Reagents used were of analytical grade obtained from the Merck company. 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} using a Shimadzu FT-IR spectrophotometer. Electronic spectra were recorded for 0.1 M HCl solutions on a Shimadzu UV-265FW spectrophotometer. ^{1}H NMR were obtained using a Bruker AC80 spectrometer, in formic acid-d_2 or DMSO-d_6 using TMS as external standard. Magnetic susceptibilities were determined by the Faraday method, using a Cahan/Ventron instrument calibrated against Hg[Co(SCN)$_4$]. Microanalyses were performed using a C—H—N—O. Rapid Heraus Analyzer and silver was determined by atomic absorption spectrophotometry. Cyclic voltammetry was performed with a three-electrode Metrohm 746VA system. Pt wire was used as working and auxiliary electrode and Ag/AgCl (3 M KCl) as reference electrode.

Preparation of the Complexes

Tetrakis(pyridine)silver(III) Perchlorate Nitrate I

An aqueous solution of silver nitrate (0.17 g, 1 mmol) in 5 cm^3 of distilled water and ammonium peroxydisulfate (0.228 g, 1 mmol) in 5 cm^3 of water were added simultaneously with stirring to a solution of 20 cm^3 of pyridine. Upon oxidation of Ag(I), the solution immediately turned yellow and then brown. A precipitate was formed but quickly dissolved, upon addition of 1 M ammonia, to increase the pH of the solution to 7–8. The solution was filtered and then by addition of a saturated solution of $NaClO_4$ a precipitate was formed. This brown precipitate was filtered and washed with water and then diethylether and finally dried under vacuum over calcium chloride. Yield: 0.25 g, 36.5% based on $AgNO_3$; m.p. 122°C. *Anal.* Calc. for $C_{20}H_{20}N_5AgCl_2O_{11}$ (%); Ag, 15.75; C, 35.04; H, 2.92; N, 10.22. Found: Ag, 15.60; C, 34.90; H, 2.88; N, 10.51. IR (KBr): 3070m, 1788w, 1595s, 1483m, 1442s, 1392w, 1224w, 1097s, 1002w, 754m, 698s, 621s cm^{-1}. ^{1}H NMR (DMSO-d_6): δ7.43–7.59 ppm (*t*, H3, H5, 2H), δ7.82–7.93 ppm (*q*, H4, 1H), δ9.59 ppm (*q*, H1, H6, 2H). Electronic spectra showed absorption bands at 206, 260 nm and also in the region 580–340 nm. Cyclic voltammetry data were obtained from 1 M H_2SO_4 solution at a platinum electrode. Potentials were recorded *versus* a Ag/AgCl reference electrode. The formal potential, $E^{0'} = (E_{p.a} + E_{p.c})/2$, was 0.400 V for Ag(III)/Ag(I).

Trans-bis(dinitrogen)bis(pyridine) Silver(III) Hydroxide, II

An aqueous solution of ammonium peroxydisulfate (2.28 g, 10 mmol) in 50 cm^3 of water was added at room temperature to a stirred solution of 0.170 g. (1.0 mmol) of silver nitrate in 50 cm^3 of water, 10 cm^3 of ammonia (25%) and 5 cm^3 of pyridine. The color of the solution immediately turned yellow and then brown. After 2 h at a pH of 9–10 a brown precipitate was formed, which was filtered and washed with water and acetone and finally dried in vacuum over calcium chloride. Yield, 0.20 g, 53% based on $AgNO_3$; decomposed at 220°C. *Anal.* Calc. for $C_{10}H_{13}AgN_6O_3$(%): Ag, 28.92; C, 32.17; H, 3.48; N, 22.52. Found: Ag, 28.88; C, 32.51; H, 3.60; N, 22.57. IR (KBr), 3390s, 3116s, 3055m, 2156m, 1623s, 1591s, 1502m, 1477m, 1336w, 1141m, 769m, 675w cm^{-1}. Electronic absorption bands were observed at 208, 253 nm and also in the region 345–560 nm. ^{1}H NMR peaks in formic acid-d_2 were at δ7.18 to 9.22 ppm (multiplet). Cyclic voltammetry data were obtained from 1 M H_2SO_4 solution at a platinum electrode. Potentials were recorded *versus* an Ag/AgCl reference electrode. The formal electrode potential, $E^{0'} = (E_{p.a} + E_{p.c})/2$, was 0.330 V for Ag(III)/Ag(I).

Trans-bis(dinitrogen)bis(pyridine) Silver(III) Perchlorate, III

A sample 0.2 g of the *trans*-$[Ag(py)_2(N_2)_2](OH)_3$ was dissolved in 10 cm^3 of concentrated $HClO_4$ and then 200 cm^3 of water was added to the solution, which was left to stand for 2 h. A brown precipitate was formed, which was filtered and then washed with water and acetone and finally dried in vacuum over calcium chloride. Yield, 0.15 g, 24%; decomposed at 235°C. *Anal.* Calc. for $C_{10}H_{10}AgCl_3N_6O_{12}$(%): Ag, 17.39; C, 19.34; H, 1.61; N, 13.54. Found: Ag, 17.25; C, 19.54; H, 1.7; N, 13.83. IR (KBr): 3064m, 2158m, 1627s, 1556s, 1437s, 1271m, 1087s, 767m, 624m cm^{-1}. Electronic absorption bands were observed at 206, 250 nm and also in the region 350–580 nm. ^{1}H NMR peaks in DMSO-d_6 were at δ7.00–8.80 ppm (multiplet). The complex is diamagnetic. Cyclic voltammetry data were obtained from 1 M H_2SO_4 solution at a platinum electrode. Potentials were recorded *versus* an Ag/AgCl reference electrode. The formal electrode potential, $E^{0'} = (E_{p.a} + E_{p.c})/2$, was 0.340 V for Ag(III)/Ag(I).

RESULTS AND DISCUSSION

It is reported in the literature that silver(I) in oxidation reactions by peroxydisulfate ion acts as a catalyst and is first oxidized to silver(III) [12]. However, in the presence of aromatic heterocyclic amines this ion is converted to complexes of silver(II). It is also reported that at $pH > 6.5$ silver(III) complexes are formed and they are predominantly square planar [3]. However, until now, silver(III) complexes of pyridine and its derivatives have not been reported. It seems that a suitable ligand such as pyridine would be capable of stabilizing silver(III) in its complexes. The appropriate reaction occurs in an alkaline buffer solution (ammonia–ammonium ion) to stabilize silver(III) ions. At higher concentration of ammonia, in addition to the oxidation of ammonium ion to nitrate, oxidation of ammonia to dinitrogen also occurs. However, in alkaline solution the predominant reaction is the oxidation of ammonia to dinitrogen.

Infrared spectra of the complexes showed absorption bands expected of the corresponding ligands. Bands assigned to pyridine ring vibrations in the complexes were shifted to lower frequencies, a good indication of coordination of the heterocyclic nitrogen atom to silver(III). The shift of the ring vibration bands to lower wave numbers relative to the free ligand results from a decrease in the π-bond character owing to coordination. In complex I, absorption bands at 1091 and 621 cm^{-1} are characteristic of uncoordinated ClO_4^- ion. Absorption bands at 1392, 1002, 698 cm^{-1} and the combination band at 1788 cm^{-1} are characteristic of the NO_3^- ion. Complexes II and III showed the end-on absorption bands of N_2 at 2156 and 2158 cm^{-1}, respectively, and here the shift of the absorption band of dinitrogen to higher frequency was a good indication of the high oxidation state of the metal ion in these complexes, because with the increase of the positive charge in a complex the stretching of the coordinated $N{\equiv}N$ shifts to higher frequency [13]. In these complexes only the asymmetric stretching vibration of $N{\equiv}N$ was observed, which is compatible with the formation of the *trans* isomer of these complexes. In $[Ag(py)_2(N_2)_2](OH)_3$ the absorption band at 3390 cm^{-1} is characteristic of OH^- ions in this complex. In $[Ag(py)_2(N_2)_2](ClO_4)_3$ absorption bands at 1087 and 624 cm^{-1} are characteristic of ClO_4^- ions in the complex.

Interpretation of the electronic spectra of Ag(III) complexes has been reported in the literature [14, 15]. The $d-d$ transition in silver(III) complexes is difficult to observe because of proximity to ligand-metal charge transfer bands. The spectra of the Ag(III) complexes in a 0.1 M HCl solution exhibit three absorption bands. The positions of the UV bands are almost identical to the absorption bands of pyridine and are assigned to $\pi \rightarrow \pi*$ transitions. Absorptions in the visible range can be assigned to ligand-metal charge transfer by the analogy to other silver(III) complexes.

In the characterization of complexes of *N*-heterocyclic ligands coordinated to a metal centre, ^{1}H NMR spectroscopy is a very important technique [16]. The ^{1}H NMR spectrum of complex **I** showed the aromatic ring protons as a quartet for the α protons at δ9.59 ppm, a quartet in the region δ7.82–7.93 ppm for the γ proton and a triplet in the region δ7.45–7.59 ppm for the β protons. ^{1}H NMR of **I** compared to the free ligand showed a downfield shift of the aromatic protons, which is due to the coordination of pyridine to the metal centre. The ^{1}H NMR of **II** showed a multiplet in the region δ7.18–9.22 ppm for the aromatic ring protons. The ^{1}H NMR of **III** appeared as a multiplet in the region δ7.00–8.80 ppm for the aromatic ring protons. The downfield shifts of the aromatic ring protons is due to the coordination of the ligand to the metal centre.

Chemical and electrochemical reductions of silver(III) complexes are usually a two-electron process [17, 18]. In these complexes the reduction $Ag(III) + 2e \rightarrow Ag(I)$ is *quasi*-reversible. The *quasi*-reversibility of this process was evaluated on the basis of the peak separation in excess of 28 mV. Cyclic voltammograms of $[Ag(py)_4](ClO_4)_2(NO_3)$ showed an $E_{p.c}$ of 0.340 V and an $E_{p.a}$ of 0.460 V yielding a ΔE_p of 120 mV. The ΔE_p of 120 mV is larger than expected for a reversible process. In cyclic voltammetry of this complex in 1 M HCl the reverse oxidation peak disappeared. These observations and the diamagnetic nature of the complex are indicative of the presence of silver(III) in this complex. Cyclic voltammograms of $[Ag(py)_2(N_2)_2](OH)_3$ showed an $E_{p.c}$ of 0.210 V and an $E_{p.a}$ of 0.450 V, yielding a ΔE_p of 240 mV. The ΔE_p of 240 mV is also much larger than expected for a reversible process. Cyclic voltammograms of $[Ag(py)_2(N_2)_2](ClO_4)_3$ showed an $E_{p.c}$ of 0.220 V and an $E_{p.a}$ of 0.460 V yielding ΔE_p of 240 mV.

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