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A Reaction between Cobalt(II) Chloride and Methyl Thiocyanate

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Early efforts to prepare methyl thiocyanate complexes of cobalt(II) met with failure in this laboratory [1]. Such attempts consisted in mixing acetone solutions of anhydrous $CoCl_2$ and CH_3SCN followed by either evaporation of the solvent or prolonged refluxing of the reaction mixture. In either instance, the original components were obtained. Recently, however, we were able to isolate a cobalt-containing substance obtained from refluxing a solution of anhydrous $CoCl_2$ dissolved in CH_3SCN. The blue cobalt product was not any of the expected substances (*i.e.*, $[Co(MeSCN)_4Cl_2]$, $[Co(MeSCN)_6]Cl_2$, $[Co(MeSCN)_4]Cl_2$, and $[Co(MeSCN)_2Cl_2]$) but was, instead, trimethylsulfonium tetrathiocyanatocobalt (II), $(Me_3S)_2Co(NCS)_4$. A second product, CH_3Cl, was also obtained. The cobalt product was formulated on the basis of its chemical and physical properties. Other cobalt-containing products were evident, but the opportunity to isolate and characterise them was not available. Consequently, only the preparation of $(Me_3S)_2Co(NCS)_4$ and its proof of composition are described here.

Experimental

Infrared spectra were obtained from a Perkin–Elmer 621 grating spectrophotometer, and a Cary 14 spectrophotometer was used to obtain electronic absorption spectra. Mass spectra of solids were run on a Nuclide 12-90-G mass spectrometer operating at an accelerating voltage of 6 kV, inlet temperature 200 °C, and probe temperature 93 °C; spectra were recorded at 70 eV. Proton magnetic resonance spectra were recorded on a Varian T-60 nmr spectrometer.

Magnetic susceptibility measurements were taken at 21 °C with a Gouy balance which was calibrated with $CoHg(SCN)_4$. The calibration was checked using $Ni(en)_3S_2O_3$ [2] Diamagnetic corrections were calculated using Pascal's constants [3].

A Wheatstone bridge and a conventional conductance cell, which was calibrated with 0.02 *M* aqueous KCl, afforded molar conductivities in CH_3NO_2 solutions.

Elemental analyses were performed by PCR, Inc., Gainsville, Florida.

Preparation of $[(CH_3)_3S]_2Co(NCS)_4$

A typical preparation is described as follows. Anhydrous $CoCl_2$ (4.0 g) was dissolved in 50 ml of distilled CH_3SCN in a 100-ml round-bottom flask fitted with a 30-cm water-cooled condenser. The resulting deep-blue solution was refluxed for 16 hours, during which 2.8 ml of CH_3Cl was condensed in a dry ice–acetone trap that was connected to the condenser. Methyl chloride was identified by its ir spectrum using a gas cell (10-cm path; pressure = 38 torr). Excess CH_3SCN was evaporated from the reaction mixture at 100 °C for about four hours. A dark-grey product (25 g) was obtained. Absolute C_2H_5OH was added to the product and the mixture was boiled until a deep-blue solution was obtained. The ethanolic extract was decanted, and the extraction was repeated until a dark solid remained. The extracts were combined and evaporated yielding 7.7 g of a blue–green solid. Methylene chloride (75 ml) was added to the blue–green solid and a deep-green solution was formed, leaving deep-blue crystals. These crystals were collected in a Buechner funnel, washed with CH_2Cl_2 and suction dried. The blue crystals were purified by recrystallization from C_2H_5OH. Yield 4.0 g (29%), mp 150–152 °C. Analysis expected: 26,96% C, 4.07% H, 12.57% N, 43,17% S, 13,22% Co. Analysis found: 26.94% C, 4.79% H, 12.11% N, 43,02% S, 13.30% Co.

Results and Discussion

It is probable that the deeply colored solution initially formed on dissolving $CoCl_2$ in CH_3SCN is due to the formation of a tetrahedral complex, *e.g.*, $Co(MeSCN)_2Cl_2$. Similar tetrahedral complexes have been proposed when $CoCl_2$ is dissolved in acetone and in pyridine [4, 5]. An octahedral cobalt complex is expected to be less intensely colored. Furthermore, the reaction condition of prolonged refluxing can be reasonably expected to labilise the methyl group in the coordinated CH_3SCN and liberate thiocyanate ion. This expectation is supported by the observed presence of $(CH_3)_3S^+$ and $Co(NCS)_4^{-2}$ ions and the absence of chlorine in the blue crystals and the release of CH_3Cl attending the reaction. The formulation of the blue product as $[(CH_3)_3S]_2$-$Co(NCS)_4$ is based on elemental analysis (above) and on the product's static and dynamic properties which are discussed as follows.

Static Properties

The ir spectrum contains the same key bands as those reported for $(Et_4N)_2Co(NCS)_4$ [6]. Absorptions (in cm^{-1}) were found for our blue product at 2800–3000 (CH stretch, 2065 and 2095 (CN stretch), 836 (CS stretch), 485 (SCN bend), and 297 (CoN stretch). The electronic absorption spectrum of an acetone solution of the blue compound shows bands at 7713 cm^{-1} ($^4A_2 \rightarrow {}^4T_1(F)$) and 16061 cm^{-1} ($^4A_2 \rightarrow {}^4T_1(P)$) agreeing with the reported spectrum of the closely related $(Me_4N)_2Co(NCS)_4$ [7]. The magnetic moment equals 4.3 B.M., which agrees with the reported value of 4.4 B.M. for $(Me_4N)_2Co(NCS)_4$ [7].

Dynamic Properties

The blue product dissolves in water giving a light-pink solution, which turns to a dark-red color on addition of aqueous ferric sulfate. These manifestations are interpreted as the formation of pink $Co(H_2O)_6^{+2}$, the released thiocyanate ion reacting with the added ferric ion to form red ferric thiocyanate complexes. Evaporation of an aqueous solution of the blue product yields again the blue compound, indicating the re-association of Co^{+2} and SCN^- ions. No organic substances can be extracted from aqueous solutions of the blue compound with ether, CH_2Cl_2, *etc.* this observation is consistent with the presence of $(CH_3)_3S^+$ ions in the product. Gravimetric analysis for the thiocyanate ion as AgSCN shows that the SCN/Co molar ratio equals four. A 0.0947 *M* solution of the blue product in CH_3NO_2 at 23.5 °C has a conductance of 189 cm^2 ohm^{-1} mol^{-1}, which is in the range reported for 2:1 electrolytes [8].

When the blue compound is dissolved in a concentrated solution of sodium iodide in acetone, a white solid (mp 212 °C) is obtained which is soluble in water, gives positive tests for sulfur and iodine after alkaline fusion, and gives a negative test for nitrogen. The mass spectrum of the white solid shows peaks at m/e 142 (CH_3I), 127 (I), 62 ($(CH_3)_2S$), 47 (CH_3S) and 15 (CH_3) a.m.u. The nmr and ir spectra of the white solid are identical to those reported for $(CH_3)_3SI$ [9, 10]. Presumably, NaI and $(Me_3S)_2Co(NCS)_4$ react in acetone solution precipitating $(CH_3)_3SI$.

Finally, the mass spectrum of the blue product shows peaks at m/e 73 (CH_3SCN), 62 ($(CH_3)_2S$), 47 (CH_3S), and 15 (CH_3) a.m.u. The compound appears to decompose in the mass spectrometer according to the equation

$$[(CH_3)_3S]_2Co(NCS)_4 \rightarrow 2(CH_3)_2S + 2CH_3SCN + Co(NCS)_2$$

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