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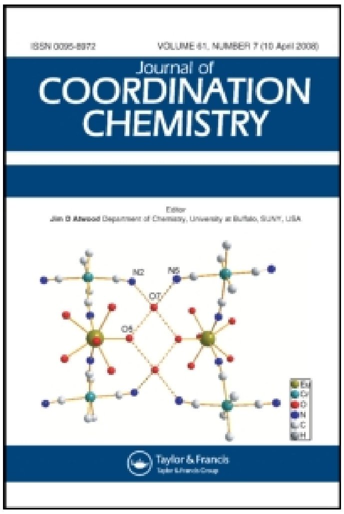

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A COBALT(II) COMPLEX CONTAINING A NOVEL CATIONIC AMINO ACID LIGAND

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A COBALT(II) COMPLEX CONTAINING A NOVEL CATIONIC AMINO ACID LIGAND

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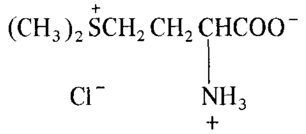
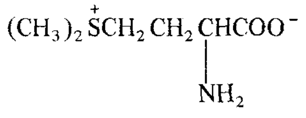
INTRODUCTION

For a large number of years inorganic chemists have investigated the type of complex formed between metal ions and amino acids – the study of such simple systems being a first step to an understanding of the much more complicated interaction of metal ions with proteins. We have been especially interested in transition metal derivatives of the sulphur-containing amino acids methionine[1], S-methylcysteine[2], penicillamine[3], and cysteine[4]. Methionine biosynthesis from methylcobalamin and homocysteine is well documented[5,6], and because transmethylation and methionine biosynthesis[6] is so important biologically, we decided to examine the donor properties of a sulfur-containing amino acid with a cationic sulfur center. We choose to study the reactions of DL-methylsulfoniummethionine chloride (LHCl) with transition metal salts. Although this species can react with metal ions eliminating HCl to form complexes of the neutral zwitterion, L,[7] we have also discovered that it can coordinate to cobalt(II) as a cationic species, LH^+, which contains two positive centers, $(CH_3)_2S^+-$ and $-{}^+NH_3$, and a negative center, $-COO^-$. Such a ligand with formal charge separation of such a degree has hitherto not been encountered in the literature. The cationic nature of this ligand represents the first type of overall cationic carboxylate donor, other cationic ligands having N, P, As, or S donor atoms.[8]



$$Cl^-\quad (CH_3)_2\overset{+}{S}CH_2CH_2\underset{\underset{\underset{+}{NH_3}}{|}}{C}HCOO^-$$

(LHCl)



$$(CH_3)_2\overset{+}{S}CH_2CH_2\underset{\underset{NH_2}{|}}{C}HCOO^-$$

(L)

EXPERIMENTAL

DL-methylsulfoniummethionine chloride was obtained from Sigma Chemical Company and used without further purification.

$[Co(LH)Cl_3]$ was prepared by refluxing anhydrous cobalt(II) chloride (1.3 g; 0.01 mole) with methylsulfoniummethionine chloride, LHCl, (2.0 g; 0.01 mole) in absolute ethanol for 8 hr. The bright blue product was filtered while hot, washed with hot absolute ethanol (150 ml) and dried *in vacuo*. Analyses: Calc. for $[Co(C_6H_{14}O_2SN)Cl_3]$ Co, 17.9; Cl, 32.3; C, 21.9; H, 4.3%. Found Co, 17.7; Cl, 31.9; C, 22.2; H, 4.5%. Yield 93%.

Refluxing for a shorter period of time, or using different ratio of reagents produced the same complex contaminated with uncoordinated ligand hydrochloride. The complex could be separated from ligand hydrochloride by abstraction of the latter into refluxing absolute ethanol in which it is slightly soluble.

Physical measurements were obtained as previously described.[9]

RESULTS AND DISCUSSION

We have discovered that the products of the reactions of methylsulfoniummethionine chloride, LHCl, with transition metal salts in absolute ethanol are metal ion dependent. Thus iron(III), nickel(II), and copper(II) salts readily react with LHCl with the elimination of HCl and the formation of complexes containing the neutral L[7,10] e.g. FeL_2Cl_3, $NiLCl_2$, and $CuLCl_2$. However, under identical conditions cobalt(II) chloride and LHCl react to produce a blue complex of empirical formulation $Co(LH)Cl_3$.

The magnetic moment of this complex in the solid state, $\mu_{eff} = 4.51$ B.M., and the visible reflectance spectrum (which exhibits absorptions at 680, 635 (br), 537, 518, 493, 455, 440 mμ) is indicative of a pseudotetrahedral structure, exactly analogous to the C_{3v} type complexes, $[CoL^+Cl_3]$, formed by a wide variety of cationic ligands investigated by Quagliano[8] and Meek[8]. The possibility that this species is some sort of chloro-bridged $Co_2Cl_6{}^{2-}$ entity stabilized by LH^+ counter-cations may be discounted for, although the electronic spectrum is indicative of tetrahedral stereochemistry, it differs quite significantly from spectra reported for tetrachlorocobaltate(II) species.[11]

We assign coordination of the cationic ligand as through the negative (presumably monodentate) carboxylate end of the molecule. The solid-state infrared spectrum exhibits bands characteristic of the ammonium moeity, at 3200–3,000 cm^{-1}, and to the carboxylato group, at 1610 and 1500 cm^{-1}. (Had the cationic ligand coordinated through and amino group then the carboxylic acid group would have appeared clearly in the infrared spectrum.) Moreover, the near-infrared reflectance spectrum exhibits a quite drastic splitting of the $4A_2 \rightarrow 4T_1(F)$ absorption (distinct peaks are observable at 1380, 1640, and 1930 mμ). In a pseudo-tetrahedral species with one 0 and 3Cl donors the splitting of this band should be noticeable.[12]

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