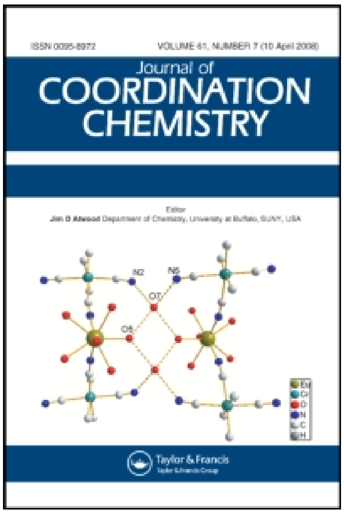

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Synthesis and Characterization of Tris[*P,P,P',P'*-Tetramethylimidobis (Phosphine Sulfido)*S,S'*] Bismuth(III)

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NOTE

SYNTHESIS AND CHARACTERIZATION OF TRIS[*P,P,P′, P′*-TETRAMETHYLIMIDOBIS (PHOSPHINE SULFIDO)*S,S′*] BISMUTH(III)

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INTRODUCTION

Complexes of tetramethylimidodithiodiphosphinate, $[(CH_3)_2P(S)N(S)P(CH_3)_2]^-$, are relatively rare in the literature. The bis-complexes of Co(II), Ni(II), and Fe(II) as well as a few other divalent cations have been reported,[1,2] and the crystal structure of the Fe(II) and Ni(II) complexes have been determined.[3,4] A bis-complex of Pb(II) has also been reported.[5] The tetraphenylimidodithiodiphosphinate ligand has gained a great deal more attention with several bis- and tris-complexes having been reported for both main group and transition elements.[1,2,6] A crystal structure of the free protonated ligand has been determined as well.[7]

In studies investigating the hard-soft acid-base (HSAB) nature of ligands and acceptors in AX_6E systems (A = central atom, X = ligand, E = nonbonded electron pair) as first proposed by Wynne,[8] we reported the crystal and molecular structure of $[(C_6H_5)_2P(S)N(S)P(C_6H_5)_2]_3Bi$.[6d] Site symmetry about the Bi atom was a slightly distorted octahedron with no apparent evidence of a lone pair. There was, however, strong evidence for steric crowding brought on possibly by the phenyl groups forcing octahedral symmetry. To assess this degree of crowding, we recently synthesized and characterized the tetramethyl analogue. To our knowledge, this is the first reported example of a tris-complex with this particular ligand.

EXPERIMENTAL

$H[(CH_3)_2P(S)N(S)P(CH_3)_2]$ was synthesized according to previously reported methods.[9] The potassium salt was prepared by stirring stoichiometric quantities of potassium *t*-butoxide (Aldrich) and the protonated ligand in tetrahydrofuran for 24 hrs under a dry N_2 atmosphere in a glovebag. The potassium salt was isolated by filtration, washed with diethyl ether, and allowed to air dry. All other chemicals were used as obtained without further purification. Elemental analyses were performed by Atlantic Microlabs. Melting point (uncorrected) was determined on a Fisher-Johns stage-type melting point apparatus. The proton NMR spectrum was determined in $CDCl_3$

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(Aldrich) with Me_4Si internal standard on a Varian EM360A spectrometer. Shift data are reported in ppm (±0.01) relative to Me_4Si.

$[(CH_3)_2P(S)N(S)P(CH_3)_2]_3Bi$.

Addition of 0.43 g (0.88 mmols) of $Bi(NO_3)_3 \cdot 5H_2O$ (Baker) in 15 cm^3 CH_3OH to 0.60 g of the potassium salt of the ligand (2.6 mmols) in 35 cm^3 CH_3OH yielded a bright yellow precipitate. Approximately half of the solvent was boiled off on a steam bath, and the solution was cooled in ice. Isolation by filtration and washing with cold CH_3OH yielded 0.33 g (47%) of fine lustrous yellow-green needles of $[(CH_3)_2P(S)Ni(S)P(CH_3)_2]_3Bi$. The substance yielded flat hexagonal plates upon recrystallization in $CH_2Cl_2/EtOH$. Mp. 185–190°C(d). Elemental Analyses: Calc: C, 17.80; H, 4.48; N, 5.19; S, 23.76%. Found: C, 17.92; H, 4.50; N, 5.12; S, 23.85%. ^1H NMR data: δ 2.04 (d, J_{PCH} = 11.4 Hz, CH_3).

RESULTS AND DISCUSSION

An air-stable lustrous yellow-green solid with the chemical composition reported above was isolated after stoichiometric addition of $Bi(NO_3)_3 \cdot 5H_2O$ to potassium tetramethylimidodithiodiphosphinate in CH_3OH. The solid was slightly soluble in acetone, CH_2Cl_2, $CHCl_3$ and CCl_4, but virtually insoluble in benzene, alkanes, and low molecular weight alcohols. Furthermore, solutions appeared to be unstable and deposited a black, metallic precipitate upon standing for several hours. The identity of the precipitate was not determined. A wide variety of solvents and solvent pairs failed to produce crystals of X-ray quality, thus we have abandoned further characterization of this complex with regard to crystallographic studies for comparison to the tetraphenyl analogue.

A sharp, well-defined doublet was observed in the proton NMR spectrum at δ 2.04 and indicates a uniform magnetic environment for the methyl protons. The chemical shift is further downfield than in the free anionic ligand (*cf.* for Na salt in CH_2Cl_2: δ 1.38, d, J = 12.5 Hz) and therefore demonstrates coordination. Unfortunately, due to solution instability and low solubility, we were unable to carry out temperature-variable proton or ^{31}P NMR studies, and thus the data is inconclusive with regard to fluxional behavior. The compound may indeed provide another example of an octahedral AX_6E complex with nonstereoactive lone pairs since a pentagonal pyramidal structure such as that observed[10] for $[(C_6H_5)_2PS_2]Sb$ or a monocapped octahedron as seen[11] for $(C_2H_5OCS_2)_3Sb$ would give rise to definite inequivalent magnetic environments for the methyl protons barring fluxionality, but a single crystal X-ray study or temperature-variable NMR studies would give more support to this thesis.

Very few complexes of this particular ligand are reported in the literature as stated above, and this compound is the only *tris*-complex to have been synthesized and reported to date. Synthesis of other *tris* complexes with this ligand are currently being pursued to isolate X-ray-quality crystals for comparative studies with the tetraphenyl analogue.

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