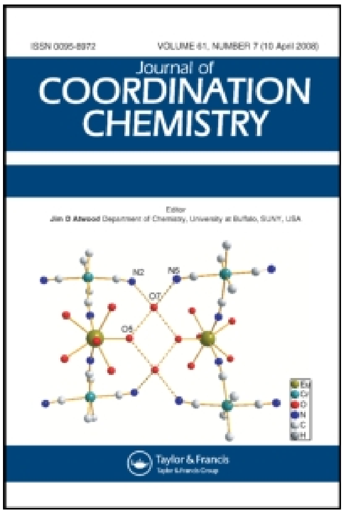

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COPPER(I) COMPLEXES OF TETRAMETHYLTHIURAM MONOSULFIDE

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Copper(I) complexes of tetramethylthiuram monosulfide (Me_4TMS) of the type $Cu(Me_4TMS)X$ where X = Cl, Br or I have been prepared in high yield. The $Cu(Me_4TMS)X$ species possess a dimeric halogen-bridged structure as inferred from IR and Raman spectra. The reaction of Me_4TMS with $Cu(PPh_3)_2NO_3$ produces the mixed-ligand complex $[Cu(PPh_3)_2(Me_4TMS)]NO_3$, in which the copper atom is coordinated by two phosphorus and two sulfur atoms giving a pseudotetrahedral C_{2v} CuS_2P_2 skeleton. The nitrate anion acts merely as a counterion.

Keywords: Copper(I), tetramethylthiuram, monosulfide, complexes, Raman, binding

INTRODUCTION

In the course of our investigation on the reactivity of tetraalkylthiuram monosulfides (R_4TMS) toward metallic ions, we have been able to find three types of reactions: a) formation of a true coordination compound if the metal ion does not undergo a redox reaction. This is the case with group II metal ions.[1] Under special conditions Co(II)[2,3] and Cr(III)[4] also seem to behave in this way; b) when reacting with a transition metal ion such as Cu(II) or Fe(III) a dithiocarbamate complex is obtained; c) formation of the trithiolane cation (R_4bitt)[5,6] when treated with a powerful oxidating agent such as chlorine or bromine. This five-membered ring has been stabilized either in salts of $FeCl_4^{2-}$, $Cu_2Br_6^{2-}$, $Hg_2I_6^{2-}$[6] or CuX_3^{2-} (X = Cl, Br or I).[7]

In fact, the reaction of Me_4TMS with copper(II) halides in ethanol yields a mixture of the Me_4TMS coordination compounds of Cu(I) and the corresponding salt $[Me_4bitt]CuX_3$.[7] In the present work we have prepared coordination compounds of Cu(I) halides and investigated their structure by means of IR and Raman spectroscopy. Me_4TMS has also been reacted with $Cu(PPh_3)_2NO_3$ in the hope of replacing the bidentate nitrate ligand. In previous work the nitrate ligand was found to change its coordination mode, though the entering ligand was an *N*-donor.[8]

EXPERIMENTAL

Preparative

[Cu(Me₄TMS)X]

The coordination compounds of the type $[Cu(Me_4TMS)X]$ (X = Cl, Br or I) were prepared as follows. The corresponding copper(I) halide (20 mmol) was suspended in

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TABLE I

Analytical and conductivity data for Me_4TMS ($C_6H_{12}N_2S_3$) complexes of copper(I); (calc. values in parentheses).

Complex	C%	H%	N%	X%	Cu%	Melting point(°C)	20^b Λ_M
$Cu(Me_4TMS)Cl$	23.8 (23.5)	3.6 (3.9)	9.3 (9.1)	11.9 (11.5)	19.5 (20.5)	90[a]	97
$Cu(Me_4TMS)Br$	20.7 (20.5)	3.6 (3.4)	7.8 (8.0)	22.3 (22.7)	17.9 (18.1)	167[a]	98
$Cu(Me_4TMS)I$	18.0 (18.1)	3.2 (3.0)	7.3 (7.0)	31.6 (31.8)	15.4 (15.9)	180[a]	148
$[Cu(PPh_3)_2(Me_4TMS)]NO_3$	58.5 (58.8)	5.0 (4.9)	4.6 (4.9)		7.4 (7.4)	125	117

[a] Decomposes before melting. [b] Molar conductivities for mM solutions in acetonitrile.

a solution of Me_4TMS (20 mmol) in acetone and left with stirring for 10–15 hrs at room temperature (bromide and iodide) or at 0°C (chloride). The red to orange products were filtered off, washed with the same solvent and pumped dry.

$[Cu(PPh_3)(Me_4TMS)]NO_3$

To a solution of 50 mmol of Me_4TMS in acetonitrile and kept at 0°C was added a solution containing 50 mmol of $Cu(PPh_3)NO_3$ dissolved in the same solvent. The solution was stirred for two hours and the solvent partially pumped off. The yellow solid was filtered off, washed with a few cm^3 of acetone and pumped dry.

All analytical and conductivity data are collected in Table I.

Physical Measurements

The conductivity and magnetic measurements were carried out as described previously.[9] The electronic spectra were obtained in acetonitrile using a Perkin-Elmer 356 spectrophotometer. The IR spectra were run in CsI pellets on a Perkin-Elmer 457 spectrophotometer whereas the Raman spectra were recorded on powdered solids in capillary tubes as described elsewhere.[10]

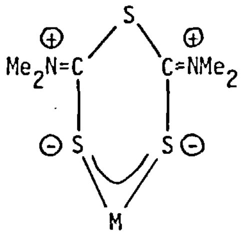
RESULTS AND DISCUSSION

The conductivity measurements in acetonitrile yielded molar conductivities in the range of 100–150 mhos cm^2 mol^{-1}. These values are around the lower limit for a 1:1 electrolyte in this solvent[11] implying that for $Cu(Me_4TMS)X$ partial dissociation takes place. The value for $Cu(PPh_3)_2(Me_4TMS)NO_3$ agrees well with a formula containing ionic nitrate as is confirmed by its IR spectrum. The molar conductivity of $Cu(PPh_3)_2NO_3$ in acetonitrile is 120 mhos cm^2 mol^{-1}, *i.e.*, the bidentate nitrate is replaced by two molecules of solvent to produce $Cu(PPh_3)_2(CH_3CN)_2NO_3$. The magnetic data of all compounds indicate that they are diamagnetic and hence can be confidently formulated as Cu(I) complexes.

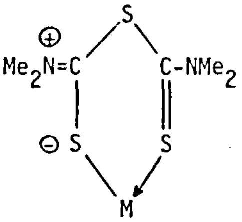
The IR spectra show typical bands of Me_4TMS modified by coordination. Table II lists some of the more important bands in the compounds reported here. The IR spectra in the middle frequency region can be interpreted in terms of four important modes: a) the so called "thiureide" band located at *ca* 1500 cm^{-1} and due to a ν(C$\overset{\cdots}{-}$N vibration, b) a band at *ca* 1240 cm^{-1} corresponding to the C–N stretching mode involving the methyl groups, c) coupled bands in the region of 940–990 cm^{-1} assigned to the C=S stretching vibrations and d) medium to weak bands in the region of 850–870 cm^{-1} due to the C–S stretching mode involving the bridging sulfur atom.

The frequency of the thiureide band is assigned to the C$\overset{\cdots}{-}$N stretching vibration since it lies between a double ν(C=N) mode (1640–1690 cm^{-1}) and a single C–N vibration (1250–1350 cm^{-1}). In the complexes reported here this band is close to the value observed in the free ligand. In fact, shifts no greater than 3 cm^{-1} are observed. These frequencies are much lower than those detected for some Co(II),[2,3] Cr(III)[4] and Hg(II)[1] complexes, implying that the polar structures **Ib** and **Ic** (see below) contribute strongly to the group state of these species. The presence of other ligands such as halogen or PPh_3 seems to exert no influence on this band.

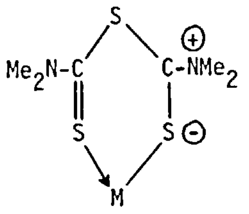
In the region of *ca* 1000 cm^{-1} the free ligand as well as its complexes show two absorptions. In this sense the thiurams behave as the *S*-methyl ester of the dimethylthiocarbamate. In fact, the spectra in this region can be interpreted in terms of an *S*-dimethylthiocarbamoyl ester of the dithiocarbamic acid. The origin of the doublet at *ca* 990 and 950 cm^{-1} is still uncertain and no theoretical foundation has been found for it.[12,13] A similar situation has been observed for the doublet located at 870–860 cm^{-1} assigned to the C–S stretching mode involving the bridging sulfur atom. This doublet has been used to differentiate a thiuram from a dithiocarbamate complex since no such bands are observed in the latter. It is worth noting that in general the assignment of the vibrational bands in the free thiurams and their complexes is approximate since normal coordinate analysis[14] clearly shows that all modes are strongly coupled.



Ia



Ib



Ic

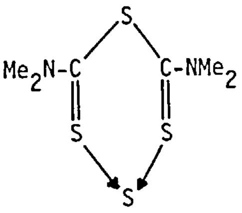


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TABLE II
Selected IR bands for the Me$_4$TMS complexes of copper(I).

Compound	$\nu(\mathrm{C}\overset{...}{-}\mathrm{N})$	$\nu(\mathrm{C'}-\mathrm{N})^{a}$	$\nu(\mathrm{C}=\mathrm{S})$	$\nu(\mathrm{C}-\mathrm{S})$
Me$_4$TMS	1510 s 1499 vs	1246 s	998 m 956 vs	871 m 862 m
Cu(Me$_4$TMS)Cl	1512 s 1501 s	1242 m	980 m 940 s	872 w 859 w
Cu(Me$_4$TMS)Br	1510 s 1505 s	1240 s	983 m 949 s	865 w
Cu(Me$_4$TMS)I	1510 s 1500 vs	1241 m	990 m 950 m	868 w 863 w
[Cu(PPh$_3$)$_2$(Me$_4$TMS)]NO$_3$	1510 s	1241 ms	992 ms 940 m	868 w 857 w

[a] C–N Stretching mode of the methyl group.

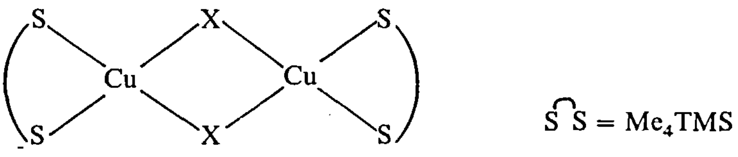
In the PPh$_3$ complex, the q, r and t "x-sensitive" fundamentals which involve P–C stretching modes are all shifted to higher values with respect to the free ligand. Thus, the q and r modes appear at 1095 and 702 cm^{-1} (free PPh$_3$ values: 1089 and 698, 692 cm^{-1}) respectively, whereas the t mode appears at 443 cm^{-1} (free PPh$_3$ $\sim$ 433, 423 cm^{-1}). These shifts have been taken as a criterion for phosphorus coordination in PPh$_3$ complexes.[15,16] Additional support for phosphorus coordination comes from the shift of *ca* 5 cm^{-1} observed in the planar ring deformation modes of the phenyl groups.[17]

TABLE III

Raman and IR bands of the Me$_4$TMS complexes of copper(I).

	ν(Cu–X)	ν(Cu–S)		ν(Cu–P)
Compound	Raman	IR	Raman	Raman
Cu(Me$_4$TMS)Cl	284 w 224 mw	347 s 310 m	339 vs 332 w	
Cu(Me$_4$TMS)Br	184 m 157 mw		340 vs 328 w	
Cu(Me$_4$TMS)I	120 vs 115 vs	365 s 325 ms	344 vs 331 w	
[Cu(PPh$_3$)$_2$(Me$_4$TMS)]NO$_3$			339 ms 304 w	185 s 147 vs

Raman and IR spectral data for the metal-ligand region are given in Table III. The assignments of the Cu–S, Cu–X and Cu–P stretching vibrations were made by comparison with previously reported data.[1,9,18,19] The Cu–X stretching modes show up in the typical region of bridging copper–halogen frequencies and hence the Cu(Me$_4$TMS)X species would possess a structure of D_{2h} symmetry involving halogen bridges (see below).



According to group theoretical methods in the above structure, four Cu–S stretching modes, two IR actives (B_{2u} + B_{3u}) and two Raman actives (A_g + B_{1g}) are to be observed. The Cu–X stretching modes are of A_g + B_{2g} (Raman) and B_{1u} + B_{3u} (IR) symmetries. In fact, Table III shows four ν(Cu–X) bands (two IR and two Raman) and the two Raman active ν(Cu–X) modes. Unfortunately our IR spectrophotometer does not permit the observation of the corresponding ν(Cu–X) vibrations.

In [Cu(PPh$_3$)$_2$(Me$_4$TMS)]NO$_3$, the coordination around the copper atom must be of pseudotetrahedral C_{2v} symmetry and hence one can expect to observe two Cu–S (A_1 + B_1) and two Cu–P (A_1 + B_2) stretching modes, both in the IR and the

Raman. In fact, we have obtained the Raman spectrum of this compound and found two Cu–S and two Cu–P frequencies. According to Edwards *et al.*,[19] the low frequencies of the Cu–P stretching modes suggest that no significant dπ–dπ interactions occur in this species. The ionic nitrate group was detected by its IR absorptions at 1372, 832 and 703 cm^{-1}.

The electronic spectra in acetonitrile of the compounds reported here show two bands located at *ca* 420 nm (ε ~ 2000) and *ca* 333 nm (ε ~ 3000). The former corresponds to a charge transfer band whereas the latter must be an internal transition in the thiuram ligand. Me_4TMS shows a band at 335 nm.

The reaction of Cu(II) salts with Me_4TMS produces $[Me_4Bitt]CuX_3$ and $Cu(Me_4TMS)X$ (X = Cl, Br or I) as a side product. Cu(I) complexes of thiuram have now been prepared by a direct method and the vibrational spectra show that they possess a dimeric halogen-bridged structure. Me_4TMS also reacts with the copper(I) species $Cu(PPh_3)_2NO_3$ to yield a mixed ligand complex of the type $[Cu(PPh_3)_2\text{-}Me_4TMS]NO_3$ where the copper atom is being coordinated by two phosphorus and two sulfur atoms in a pseudotetrahedral arrangement. The nitrate anion is not coordinated.

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