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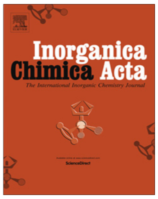

Dithiocarbamate copper(I) and silver(I) complexes: Synthesis, structure and thermal behavior

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ABSTRACT

Complexes $[M(PBu_3)_n(S_2CNRR')]$ (M = Cu, Ag; n = 1, 2, 3; R = R′ = $CH_2CH{=}CH_2$, $(CH_2)_4$, C_2H_4OH; R = Me, R′ = C_2H_4OH; R = Bu, R′ = C_2H_4OH) (**4**–**9**) are accessible by the reaction of $[Cu(PBu_3)_nCl]$ (**1a**–**c**) or $[Ag(PBu_3)_n(NO_3)]$ (**2a**–**c**) with $[K(S_2CNRR')]$ (**3a**–**e**). The respective silver(I) dithiocarbamates **7**–**9** and $[Ag(PPh_3)_2(S_2CNRR')]$ (**12a**, R = Me; **12b**, R = Bu) could be synthesized by the subsequent treatment of **3** with $[AgNO_3]$ (**10**) giving $[AgS_2CNRR']$ (**11**) followed by addition of n equivalents of the phosphine L (L = PBu_3, PPh_3). Exemplary, the $^{31}P\{^1H\}$ NMR spectra of $[Ag(PBu_3)_n(S_2CNMe(C_2H_4OH))]$ (n = 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5) were investigated in the temperature range of 308–178 K showing phosphine ligand exchange processes in solution. The molecular structures of **12a**,**b** in the solid state are reported confirming the monomeric architecture with coordination number 4 at silver, which is setup by a chelate-bonded (κ^2-S,S′) $S_2CNR(C_2H_4OH)$ unit and two coordinated PPh_3 ligands. The thermal behavior of selected samples was studied by thermogravimetry. Depending on R, R′ and the number of phosphines n, decomposition occurs in varying temperature ranges giving different decomposition residues (Cu_xS, x = 1.96, 2; Ag, Ag_2S), which were characterized by XRPD.

1. Introduction

Dithiocarbamate-containing coordination compounds represent a class of transition metal complexes, which are accessible by using different synthetic methodologies [1]. Over the last decades, a versatile chemistry has been developed around them and a wide-ranging field of applications including analytical chemistry [2], material sciences [3], homogeneous catalysis [4], and biology [5] has been established. The enormous interest in dithiocarbamate compounds results from their ability to coordinate different metals in diverse bonding modes [1,6], which, for example, allows the simultaneous determination of copper and silver in wastewater [7]. For all applications, consolidated knowledge of the coordinating behavior of the respective dithiocarbamates complexes is of prime importance. Though, with exclusion of limited examples, the interaction between copper(I) and/or silver(I) dithiocarbamates and phosphines regarding spectroscopic and structural features is only rarely described in literature [8]. Hence, we got interested in the investigation of the interaction between selected copper(I) and silver(I) dithiocarbamates with phosphines PR_3 (R = Bu, Ph) and their use as precursors in deposition processes.

Herein, we discuss the synthesis, properties, characterization, and thermal behavior of a series of phosphine copper(I) and silver(I) dithiocarbamate complexes of structural type $[ML_n(S_2CNRR')]$ (M = Cu, Ag; L = PBu_3, PPh_3; n = 1, 2, 3; R = R′ = $CH_2CH{=}CH_2$, $(CH_2)_4$, C_2H_4OH; R = Me, R′ = C_2H_4OH; R = Bu, R′ = C_2H_4OH).

2. Results and discussion

Phosphine copper(I) and silver(I) dithiocarbamate complexes of type $[M(PBu_3)_n(S_2CNRR')]$ (M = Cu, Ag; n = 1, 2, 3; R = R′ = $CH_2CH{=}CH_2$, $(CH_2)_4$, C_2H_4OH; R = Me, R′ = C_2H_4OH; R = Bu, R′ = C_2H_4OH) (**4**–**9**) have been prepared by reacting $[Cu(PBu_3)_nCl]$ (**1a**–**c**) or $[Ag(PBu_3)_n(NO_3)]$ (**2a**–**c**) with $[K(S_2CNRR')]$ (**3a**–**e**) as shown in Scheme 1 (Table 1). The potassium dithiocarbamate salts **3a**–**e** were accessible by treatment of the secondary amines diallylamine, pyrrolidine, diethanolamine, 2-(methylamino)ethanol, or 2-(butylamino)ethanol with an excess of carbon disulfide in ethanolic potassium hydroxide solutions at 0 °C [9]. Another synthetic methodology to prepare the phosphine silver(I) dithiocarbamates **7**–**9** and additional $[Ag(PPh_3)_2(S_2CNR(C_2H_4OH))]$ (**12a**, R = Me; **12b**, R = Bu) relates upon the subsequent reaction of **3d**,**e** with stoichiometric amounts of $[AgNO_3]$ (**10**) to afford $[AgS_2CNR(C_2H_4OH)]$ (**11a**, R = Me; **11b**, R = Bu) followed by addition of n equivalents of the phosphine PR_3 (n = 1, 2, 3) (Scheme 1)

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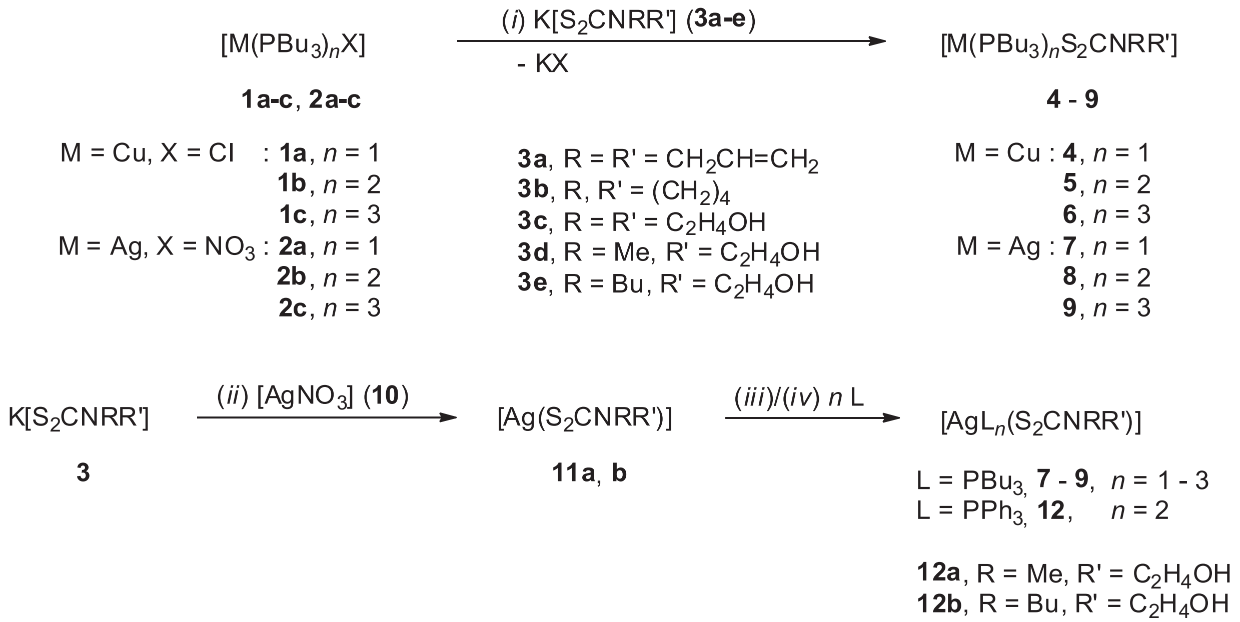

Scheme 1. Synthesis of **4–9**, **11** and **12** (Table 1). ((i) pentane, 0 °C; (ii) acetonitrile/ethanol (ratio 1:50, v/v), 0 °C; (iii) L = PBu_3, pentane, 0 °C; (iv) L = PPh_3, dichloromethane, 25 °C).

Table 1
Complexes $[ML_n(S_2CNRR')]$ (**4–9**, **11** and **12**).

Compd.	M	L	*n*	R	R′	Yield [%][a]
4	Cu	PBu_3	1	C_2H_4OH	Me	93
5a	Cu	PBu_3	2	C_2H_4OH	Me	94
5b	Cu	PBu_3	2	C_2H_4OH	C_2H_4OH	91
5c	Cu	PBu_3	2	$CH_2CH{=}CH_2$	$CH_2CH{=}CH_2$	87
6a	Cu	PBu_3	3	C_2H_4OH	Me	93
6b	Cu	PBu_3	3	C_2H_4OH	C_2H_4OH	90
6c	Cu	PBu_3	3	$CH_2CH{=}CH_2$	$CH_2CH{=}CH_2$	86
6d	Cu	PBu_3	3	$(CH_2)_4$		88
7	Ag	PBu_3	1	C_2H_4OH	Me	92[b]
8a	Ag	PBu_3	2	C_2H_4OH	Me	91[b]
8b	Ag	PBu_3	2	$CH_2CH{=}CH_2$	$CH_2CH{=}CH_2$	88[b]
9a	Ag	PBu_3	3	C_2H_4OH	Me	92[b]
9b	Ag	PBu_3	3	$CH_2CH{=}CH_2$	$CH_2CH{=}CH_2$	86[b]
11a	Ag			C_2H_4OH	Me	96[c]
11b	Ag			C_2H_4OH	Bu	89[c]
12a	Ag	PPh_3	2	C_2H_4OH	Me	93[d]
12b	Ag	PPh_3	2	C_2H_4OH	Bu	96[d]

[a] Based on charged **1a**–**c** or **2a**–**c**.
[b] Reaction pathway (*i*).
[c] Based on charged **3**.
[d] Based on charged **11**.

(Section 4). After appropriate work-up, the PPh_3-based compounds were obtained as solids, while the respective PBu_3-functionalized transition metal complexes are liquids. Further conspicuous is that the appropriate pale yellow copper(I) complexes are sensitive to air- and moisture, while the off-white silver(I) derivatives are stable under similar conditions, however, upon exposure to light they decompose in between days forming elemental silver. The tri-*n*-butylphosphine metal complexes **4–9** are soluble in most common polar and non-polar organic solvents, while the PPh_3 ligands in **12a**,**b** are responsible for the less solubility of these complexes (Section 4).

Complexes **4–9**, **11** and **12** were characterized by elemental analysis, IR and NMR (^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$) spectroscopy (Section 4). The thermal behavior of selected samples was studied by TG (=Thermogravimetry). The molecular structures of **12a**,**b** in the solid state are reported.

The IR spectra of **4–9**, **11** and **12** are characterized by distinct absorptions typical for the dithiocarbamate units with vibrations at ca. 1500 cm^{-1} ($\tilde{\nu}_{C-N}$) and 1000 cm^{-1} ($\tilde{\nu}_{C-S}$) (Section 4) [1]. Generally, the Bonati and Ugo [10] criterion based on the number and splitting of $\tilde{\nu}_{C-S}$ bands at 1050–950 cm^{-1} is used for the differentiation of chelating and monodentate binding modes of dithiocarbamates. More lately, Kellner et al. [11] proposed interligand coupling of the CS ligand as origin of the splitting and hence ruled out the possibility of predicting the dithiocarbamate binding motif from IR vibrations. Nevertheless, the presence of solely one CS band indicates a chelating binding type as also discussed in the dynamic NMR section and the solid state structure (see below).

As expected, the hydroxyl functionality gives rise to a broad band at 3350 cm^{-1}. All vibrations proposed for the phosphine ligand, if present in the respective compound, were found, being only slightly shifted with respect to those of the free donors (Section 4).

^1H NMR spectroscopy allows the assignment of all organic groups present (Section 4). As exemplary shown for $[Ag(PBu_3)_2(S_2CNMe(C_2H_4OH))]$ (**8a**) (Fig. 1), upon decreasing the temperature the resonance signals for the dithiocarbamate functionality are slightly shifted to higher field. The signal corresponding to the OH proton is most affected and shifted to lower field, which is likely caused by the formation of stronger hydrogen-bonds [12].

In addition, $^{13}C\{^1H\}$ NMR spectroscopy can be used for monitoring the progress of the formation of **4–9**, **11** and **12** starting from **3**, which is accompanied by a distinctive shift of the resonance signals of the quaternary dithiocarbamate carbon atoms to higher field (**3a–e**, 214.5–208.0 ppm; **4–9**, **11** and **12**, 213.0–203.7 ppm) (Section 4). The data are in agreement with similar dithiocarbamate transition metal complexes [8a].

The coordination of the phosphine ligands to copper(I) or silver(I) in dithiocarbamates **4–9** and **12** can best be monitored by $^{31}P\{^1H\}$ NMR spectroscopy, since the respective chemical shift gives evidence of the bonding behavior between the phosphorus and the transition metal atom (Section 4) [13]. Additional evidence comes from the $J_{^{107}Ag^{31}P}$ and $J_{^{109}Ag^{31}P}$ coupling constants of the appropriate silver(I) species (Fig. 2). Furthermore, with increasing number of phosphine ligands at silver following trends were observed: