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Versatile bridging ability of secondary thioamide group for constructing metal cluster based on pincer complex

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ABSTRACT

The crystallization of the SCS pincer platinum complex with secondary thioamide groups, [4-methyl-2,6-bis(anilinothiocarbonyl)-κ^2S,S'-phenyl-κC^1]chloroplatinum(II), spontaneously forms a trinuclear cluster complex accompanied by liberating HCl in DMSO/EtOH mixture. The crystal structure of the SNS pincer copper complex with secondary thioamide groups, [2,5-bis(benzylaminothiocarbonyl)-κ^2S,S'-pyrrolyl-κN^1]chlorocopper(II), exhibits a dimer structure bearing the bridging thioamide group. The thioamide group acts as the bridging ligand of the multimetallic complexes in different anionic and neutral manners.

1. Introduction

Metal chalcogenido clusters are of great interest because of their unique electrical, magnetical, chemical, and catalytical properties [1]. Sulfur containing ligands such as thiols [2], thiosemicarbazone [3], and mercaptonicotinic acid [4] are often used as bridging ligands for constructing metal clusters due to their strong coordination property. However, the number of examples of thioamide-based metal clusters is limited. A thioamide group is one of the sulfur-based donating groups for constructing organometallic compounds [5,6]. Upon deprotonation, a secondary thioamide group forms thioamidate and iminothiolate as resonance structures (Scheme 1). The deprotonation gives a dramatically change in terms of bridging ability of a thioamide group. Therefore, the secondary thioamide group serves as a bridging ligand in three manners such as neutral thioamide, thioamidate and iminothiolate. The versatility of the thioamide group as bridging ligand is expected to afford a new metal clusters.

Pincer complexes generally have a tridentate ligand (ECE ligand) composed of a cyclometalating carbon and donating groups such as PR_2, NR_2 and SR [7]. The pincer complexes bearing thioamide groups as a donating group were also investigated [5]. Since the secondary thioamide group has potential for bridging the metal centers, the pincer complexes would assemble to form metal cluster based on pincer complexes. Herein, we report a formation of two kinds of cluster complexes from the monometallic pincer Pt and Cu complexes having the secondary thioamide moiety. The secondary thioamide group in each complex acts as a bridging ligand in different manners.

2. Results and discussion

2.1. Synthesis and X-ray diffraction study of the trinuclear complex **2**

The Pt pincer complex **1** was prepared in accordance with the method in the previous report [5d]. The crystallization of **1** from DMSO gives single crystals having monometallic structure [5d]. In contrast, crystallization of **1** in a mixture of DMSO and EtOH gives different crystals having monoclinic lattice in 4% yield. The single X-ray diffractional analysis revealed the trimetallic structure as shown in Fig. 1. The chloride ligand on the Pt center and one of the proton in the N–H groups disappear in the trimetallic structure compared with the structure of the parent complex **1** (Scheme 2). These results indicate that HCl was liberated during the crystallization process. The deprotonation of the secondary thioamide group provides iminothiolate moieties bridging Pt centers.

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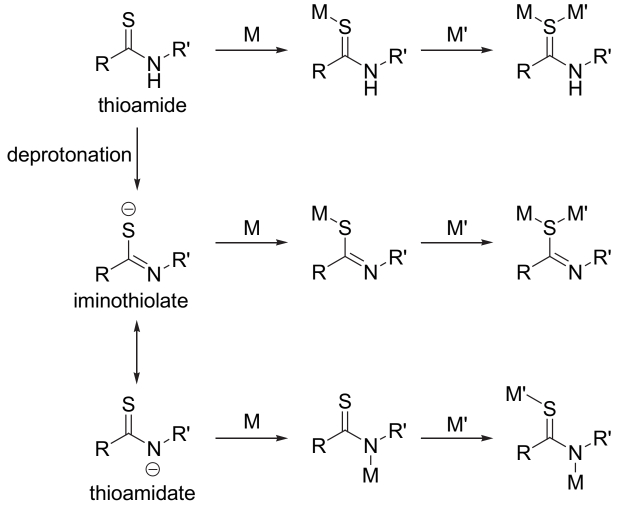
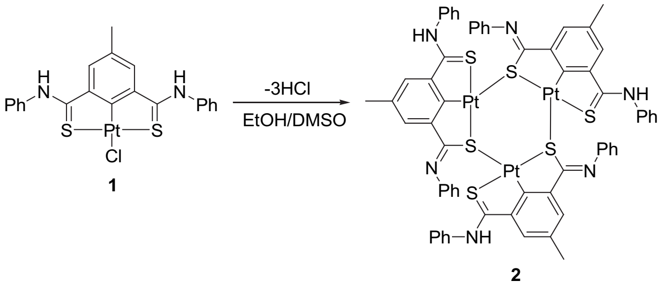


Scheme 1. The neutral and anionic forms of a secondary thioamide group and presumable coordination mode as a building block of metal clusters.



Scheme 2.

Since the total of the bond angles around the Pt centers are close to 360°, the each Pt center retains a distorted square planar structure in the trimetallic structure. The core of trimetallic cluster **2** consists of a six-membered ring of alternating Pt and S atoms (Fig. 1b). In terms of the lengths of six Pt–S bond in the six-membered ring, the Pt–S bonds in each SCS pincer structure is 2.304 Å on average, which is shorter than the Pt–S bonds connecting each pincer complex (2.415 Å on average) (Table 1). The bond angles involving bridging sulfur atoms are as follows: Pt1-S2-Pt2, 88.79(10)°; Pt2–S3–Pt3, 98.92(9)°; Pt1-S1-Pt3, 100.45(10)°. The average bond distances between the carbon atom and the bridging S atom such as S1–C2 in cluster **2** is 1.823 Å, which is longer than the average of C–S bonds in parent complex **1** (1.707 Å). These changes of bond lengths are consistent with formations of S–C single bonds of iminothiolate moieties in the cluster structure. In addition, the C–N distances of the iminothiolate moiety (1.261 Å on average) are shorter than those of the thioamide groups in complex **1** (1.318 Å) and **2** (1.34 Å) owing to a double bond character of the iminothiolate structure. The distances between the Pt centers (Pt1–Pt2 3.3135(6) Å; Pt2–Pt3 3.5741(7) Å; Pt1–Pt3 3.6207(7) Å) indicate that there is no direct bond between the Pt atoms. Lei et al. reported SNS pincer Pd complexes having a centered 2,6-pyridine unit bearing secondary thioamide groups [8]; deprotonation of the secondary thioamide groups by strong base affords tetrametallic or trimetallic cluster depending on the substituent on thioamide group. The structure of the trimetallic cluster is similar to that of **2**. In the case of these clusters, both of thioamide groups are deprotonated during the formation of the cluster because the SNS pincer ligand is neutral.

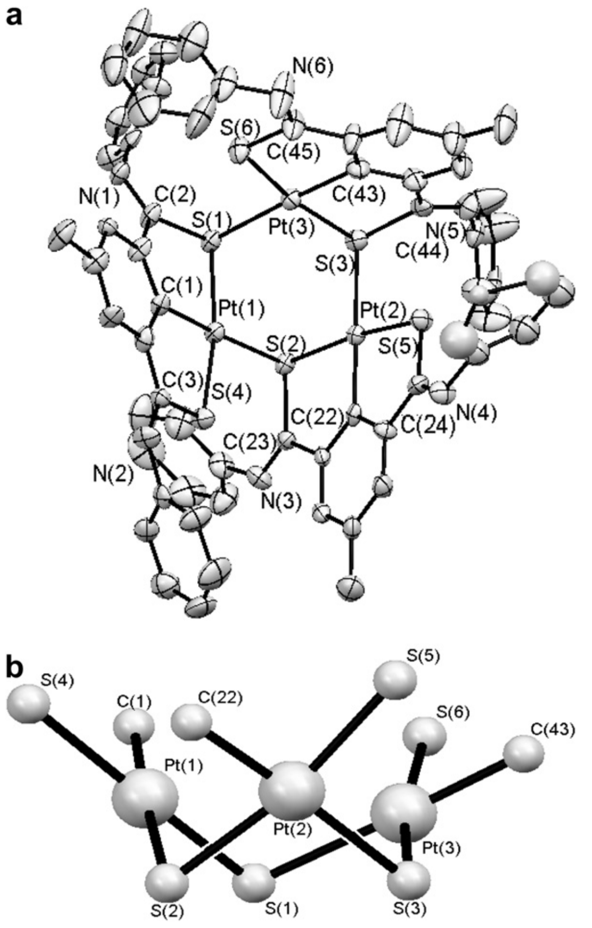


Fig. 1. (a) ORTEP drawing of **2** with thermal ellipsoids shown in 50% probability level and (b) ball and stick model viewed along the Pt_3S_3 core. Solvating molecules are omitted for clarity.

Table 1
Selected bond length (Å) and angles (deg) for complexes **1** and **2**

1[a]		2			
Pt1–C2	1.957(7)	Pt1–C1	1.992(11)	Pt1–S1	2.310(2)
		Pt2–C22	1.985(10)	Pt1–S2	2.440(2)
		Pt3–C43	1.968(13)	Pt1–S4	2.292(2)
S1–C8[b]	1.700(7)	S1–C2[c]	1.815(12)	Pt2–S2	2.293(2)
S2–C15[b]	1.714(7)	S2–C23[c]	1.821(11)	Pt2–S3	2.401(2)
		S3–C44[c]	1.833(13)	Pt2–S5	2.292(3)
		S4–C3[b]	1.724(12)	Pt3–S1	2.401(2)
		S5–C24[b]	1.712(12)	Pt3–S3	2.301(3)
		S6–C45[b]	1.690(14)	Pt3–S6	2.289(3)
N1–C8[b]	1.328(8)	N1–C2[c]	1.256(15)		
N2–C15[b]	1.307(8)	N2–C3[b]	1.348(13)		
		N3–C23[c]	1.274(16)		
		N4–C24[b]	1.328(17)		
		N5–C44[c]	1.252(15)		
		N6–C45[b]	1.35(2)		
S1–Pt1–S2	170.77(6)	S1–Pt1–S4	169.06(10)	S1–Pt1–S2	93.36(9)
		S2–Pt2–S5	169.60(9)	S2–Pt1–S4	97.24(10)
		S3–Pt3–S6	169.99(11)	S2–Pt2–S3	92.23(10)
		S1–Pt1–C1	85.6(3)	S3–Pt2–S5	97.47(10)
		S4–Pt1–C1	83.9(3)	S1–Pt3–S3	93.28(10)
		S2–Pt2–C22	85.2(3)	S1–Pt3–S6	96.71(11)
		S5–Pt2–C22	85.2(3)		
		S3–Pt3–C43	85.4(4)		
		S6–Pt3–C43	84.6(4)		

[a] From Ref. [5d].

[b] Thioamide moiety.

[c] Imino-thiolate moiety.