7620 *Inorg. Chem.* **1996,** *35,* 7620−7625

Synthesis and Characterization of $[Yb(NH_3)_8][Cu(S_4)_2]\cdot NH_3$, $[Yb(NH_3)_8][Ag(S_4)_2]\cdot 2NH_3$, and $[La(NH_3)_9][Cu(S_4)_2]$ in Supercritical Ammonia: Metal Sulfide Salts of the First Homoleptic Lanthanide Ammine Complexes

Dianna M. Young, George L. Schimek, and Joseph W. Kolis*

Department of Chemistry, Clemson University, Clemson, South Carolina 29634-1905

Received February 8, 1996[⊗]

Three new lanthanide metal polysulfides have been synthesized in supercritical ammonia: $[Yb(NH_3)_8][Cu(S_4)_2]\cdot NH_3$ (**I**), $[Yb(NH_3)_8][Ag(S_4)_2]\cdot 2NH_3$ (**II**), $[La(NH_3)_9][Cu(S_4)_2]$ (**III**). Compounds were prepared in sealed quartz tubes which were filled to one-third volume with liquid ammonia and heated at 170 °C for 3 days. Compounds **I** and **II** were obtained from the reaction of a premade ytterbium polysulfide with M and S in the ratio of 1:1:4, while $[La(NH_3)_9][Cu(S_4)_2]$, **III**, was obtained by reacting La, Cu, and S in the ratio of 1:1:8. In all these compounds, the lanthanide cation is coordinated only by ammonia, while the M^+ is chelated by S_4^{2-} to form metal tetrasulfide rings. $[Yb(NH_3)_8][Cu(S_4)_2]\cdot NH_3$ and $[Yb(NH_3)_8][Ag(S_4)_2]\cdot 2NH_3$ contain $[M(S_4)_2]^{3-}$ anionic units with M^+ in a distorted tetrahedral coordination environment chelated by two S_4^{2-} groups. Compound **III**, $[La(NH_3)_9][Cu(S_4)_2]$, also contains anionic $[Cu(S_4)_2]^{3-}$ units; however, Cu^+ is in a trigonal planar coordination geometry due to the presence of one monodentate S_4^{2-}. All the compounds are unstable with respect to loss of ammonia, and decomposition yielded known ternary and binary phases. Crystallographic data for the compounds are the following: **I**, space group = $I\bar{4}$, $Z = 2$, $a = 10.024(4)$ Å, $c = 9.752(4)$ Å; **II**, space group = $P2_12_12_1$, $Z = 4$, $a = 11.177(4)$ Å, $b = 20.472(6)$ Å, $c = 9.754(3)$ Å; **III**, space group = $P2_1/n$, $Z = 4$, $a = 9.891(2)$ Å, $b = 12.600(3)$ Å, $c = 17.812(3)$ Å, $\beta = 103.57(2)°$.

Introduction

The use of supercritical ammonia as a synthetic medium for the preparation of novel inorganic compounds is a relatively unexplored technique. Jacobs and Schmidt[1] have thus far been the primary contributors to ammonothermal synthesis, and they have examined several systems that include amides, nitrides, chalcogenides and polychalcogenides. In their studies, the temperatures (≥500 °C) and pressures (≥6 kbar) used far exceed the minimum values necessary to obtain supercritical ammonia conditions. We recently demonstrated that performing reactions in supercritical ammonia at 160 °C is a unique and fruitful method of obtaining new metastable inorganic solids. For example we have prepared a number of new complex quaternary phases that have the general formula $A_wM_xE_yQ_z$ (A = K, Rb, Cs; M = Cu, Ag; E = As, Sb; Q = S, Se) like A_2AgSbS_4 and $A_2Ag_3Sb_3S_8$.[2] These new metal sulfide phases often have complicated, low-dimensional structures. The alkali metals act as isolated cations, while the anionic frameworks are made of clusters or polymers of 15/16 anions, for example SbS_4^{3-} or $Sb(S_2)_\infty^-$, held together by Ag^+ or Cu^+. We have systematically prepared an extensive array of compounds having this general formula. While they are structurally unique and interesting, they all contain a closed shell transition metal with a valence-precise main group building block. Thus, all of the solids are electronically precise compounds and most of them are diamagnetic, wide-bandgap semiconductors.

In an effort to prepare more electronically interesting solids, we have begun trying to introduce open-shelled di- and trivalent metal centers into the extended framework. Our initial effort involved attempts to substitute lanthanide ions for the alkali metal ions, as it is known that lanthanides will combine with metal sulfides to form a variety of new lanthanide−transition metal sulfide phases.[3] It is well-known that lanthanide metals dissolve in ammonia to form reducing solutions much like alkali and alkaline earth metals.[4] We anticipated that the lanthanides would behave like the alkali metals, reducing sulfur in liquid ammonia to form polysulfides, which would in turn, react with elemental Ag or Cu. This might then lead to new ternary solids with trivalent lanthanides within the framework, much like alkali-metal-containing ternaries.[5]

$$4Ln + 3S_8 \rightarrow 4Ln^{3+} + 6S_4^{2-}$$

$$4Ln^{3+} + 6S_4^{2-} + M \rightarrow Ln_xM_yS_z$$

Instead, we observed that the solvent ammonia ligates to the trivalent metal ions, forming metal ammine complexes. The polysulfides react with the Ag or Cu to form metal sulfides, but the ammonia coordinated to the lanthanide centers effectively prevents them from becoming part of the metal sulfide framework.

In this paper we report the synthesis, structural characterization and thermal behavior of three new compounds, $[Yb(NH_3)_8][Cu(S_4)_2]\cdot NH_3$, $[Yb(NH_3)_8][Ag(S_4)_2]\cdot 2NH_3$ and $[La(NH_3)_9][Cu(S_4)_2]$. These ammine complexes act as relatively large countercations which lead to the formation of molecular salts. The complexes are believed to be the first homoleptic lanthanide ammine complexes.

[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1996.

(1) Jacobs, H., Schmidt, D. In *Current Topics in Materials Science*; Kaldis, E., Ed.; North Holland Publishing Co.: Lausanne, Switzerland, 1982.

(2) (a) Schimek, G. L.; Pennington, W. T.; Wood, P. T.; Kolis, J. W. *J. Solid State Chem.* **1996**, *123*, 277. (b) Wood, P. T.; Schimek, G. L.; Kolis, J. W. *Chem. Mater.* **1996**, *8*, 721.

(3) (a) Christuk, A. E.; Wu, P.; Ibers, J. A. *J. Solid State Chem.* **1994**, *110*, 330. (b) Wu, P.; Christuk, A. E.; Ibers, J. A. *J. Solid State Chem.* **1994**, *110*, 337.

(4) Nicholls, D. *Inorganic Chemistry in Liquid Ammonia*; Elsevier-North Holland: Lausanne, Switzerland, 1979.

(5) Wood, P. T.; Pennington, W. T.; Kolis, J. W. *Inorg. Chem.* **1994**, *33*, 1556.

S0020-1669(96)00140-1 CCC: $12.00

Experimental Section

All elemental powders were purchased from commercial vendors (S from Mallinckrodt (reagent grade); the metals Cu, Ag, La and Yb from Strem (99.9%)) and used without further purification. The anhydrous ammonia was obtained from LaRoche Industries. In initial experiments, we further dried the ammonia by distilling it from elemental sodium, but subsequent work demonstrated that it emerges from the cylinder in sufficient purity for our purposes, so we continue to use it directly. The methods used to perform syntheses in supercritical amines are based on the modification of procedures used by Rabenau.[6] The air-sensitive starting material "$[Yb(NH_3)_x(S_y)]$" was prepared by loading the elements Yb and S in a 1:8 mole ratio (170 mg scale) in fused-silica tubes in an argon-filled drybox. The tubes were then filled to 40% volume with NH_3 and sealed under vacuum. The reactions were then placed in a Parr reaction vessel (internal volume 71 mL) and subsequently counter pressured to 3500 psi. Reactions were heated in the vessel at 170 °C for 3 days. The starting material was collected as an orange powder. We have found that using this premade starting material, instead of elemental Yb and S, in the synthesis of the title compounds **I** and **II** yielded single crystals, while direct reaction of the elements Yb, M and S yielded only powders. We have not structurally characterized "$[Yb(NH_3)_x(S_y)]$" , but its IR contains a broad band at 597 cm^{-1} and sharp peaks at 487 cm^{-1}, suggesting the presence of metal ammine linkages as well as polysulfide groups (*vide infra*). On the basis of results with the lanthanide system, it is most likely an ammine complex of Yb with a polysulfide anion such as $[Yb(NH_3)_x]S_y$ ($x \approx 8-9$, $y \approx 6-8$).

Synthesis of $[Yb(NH_3)_8][Cu(S_4)_2]\cdot NH_3$ (I) $[Yb(NH_3)_8][Ag(S_4)_2]\cdot 2NH_3$ (II). The title compounds **I** and **II** were synthesized in a similar fashion using a modification of methods developed by Rabenau. In an argon filled drybox, "$[Yb(NH_3)_x(S_y)]$" , copper or silver powders, and S in 1:1:8 ratios (50−60 mg scale) were loaded in fused-silica tubes. Reaction tubes were then filled with NH_3 (40% fill), sealed under vacuum and subsequently placed in a Parr reaction vessel that was then counter-pressured to 3500 psi and then heated at 170 °C for 3 days. Compounds $[Yb(NH_3)_8][Cu(S_4)_2]\cdot NH_3$ and $[Yb(NH_3)_8][Ag(S_4)_2]\cdot 2NH_3$ were collected as well-formed orange and yellow crystals with yields of 31% and 25%, respectively.

Synthesis of $[La(NH_3)_9][Cu(S_4)_2]$ (III). Compound **III** (50−60 mg scale) was prepared by loading stoichiometric amounts of the elements in powdered form (La, Cu and S) in fused-silica tubes in an argon filled drybox. Reaction tubes were then filled with NH_3 (40% fill), sealed under vacuum and subsequently placed in a Parr reaction vessel that was then counter pressured to 3500 psi and heated at 170 °C for 3 days. $[La(NH_3)_9][Cu(S_4)_2]$ single crystals were orange. The amorphous starting material "$[La(NH_3)_x(S_y)]$" was also prepared in the same fashion as the ytterbium analog and loaded in reaction tubes in the same stoichiometric amounts as for the preparation of the Yb compounds. However, single crystal yields and quality of compound **III** were poor. In contrast to the Yb system, using the elements (La, Cu, and S) in a direct reaction led to higher yields (68%) and better quality single crystals of $[La(NH_3)_9][Cu(S_4)_2]$.

Single-Crystal X-ray Diffraction and Refinement. Single crystals of the title phases are very air and thermally sensitive, particularly with respect to ammonia loss. Single crystals of compound **II**, being extremely air sensitive, were isolated and mounted (glass fiber) with epoxy on a frit under cold N_2[7] and quickly moved into an N_2 cold stream on the single crystal X-ray diffractometer. Single crystals of **I** and **III** were mounted in capillary tubes with epoxy at room temperature. Table 1 lists crystallographic data for compounds **I**, **II** and **III**. The single crystal X-ray diffraction data for **I** and **II** were collected at low temperature on a four-circle Rigaku AFC7R diffractometer (Mo Kα, $\lambda = 0.710\,73$ Å, graphite monochromator). Compound **III** was collected on a four circle Nicolet R3mV at room temperature (Mo Kα, $\lambda = 0.710\,73$ Å, graphite monochromator). The unit cells of **I**, **II** and **III** were based on the indexing of 25, 25, and 42 reflections at $12° \leq 2\theta \leq 25°$, $13° \leq 2\theta \leq 15°$, and $12° \leq 2\theta \leq 28°$, respectively, using the automatic indexing routine of the diffractometer. On the basis of 3 check reflections every 100 reflections, there was no decomposition of the crystals during data collection. The data were corrected for Lorentz and polarization effects. Compounds **I** and **III** were solved by direct methods with SHELXS-86 and refined with SHELXTL-PLUS programs.[8] Compound **II** was solved by direct methods using the SHELXS-86 format in teXsan[9] and final refinements were performed in SHELXTL-PLUS. The atoms were assigned to relevant intensity peaks and refined with isotropic *U*'s. Table 2 lists atomic coordinates and isotropic *U*'s. The absorption correction program XABS, a modified version of DIFABS[10] was utilized for compounds **I** and **III**. A ψ scan absorption correction was applied to compound **II**. Hydrogen atoms were placed on nitrogen atoms as rigid groups and refined isotropically with a group thermal parameter. Upon refinement with anisotropic *U*'s (with H's remaining isotropic) the Fourier difference maps were flat. Anisotropic *U*'s are provided in the Supporting Information. Since **I** and **II** were refined in noncentrosymmetric space groups, both configurations were refined. The results presented correspond to the configuration with the lowest residuals.

Table 1. Crystallographic Parameters for Compounds **I**, **II**, and **III**

	I	**II**	**III**
empirical formula	$YbCuS_8N_9H_{27}$	$YbAgS_8N_{10}H_{30}$	$LaCuS_8N_9H_{27}$
fw	646.4	707.7	612.2
space group	$I\bar{4}$	$P2_12_12_1$	$P2_1/n$
Z	2	4	4
a (Å)	10.024(4)	11.177(4)	9.891(2)
b (Å)		20.472(6)	12.600(3)
c (Å)	9.752(4)	9.754(3)	17.812 (3)
β (deg)			103.57(2)
V	979.9(7)	2232(1)	2157.9(8)
d (Mg/m^3)	2.191	2.089	1.884
abs coeff (mm^{-1})	6.680	5.797	3.713
T (K)	203	150	298
λ (Å)	0.710 73	0.710 73	0.710 73
R (%)^a	4.15	3.86	4.62
R_w (%)^b	5.19	5.28	6.46

$^a\ R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b\ R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.

Decomposition Studies. Single crystals obtained of each of the title phases were loaded into quartz tubes, placed on a vacuum line and pumped for several hours to remove as much ammonia as possible. The crystals were noticably decomposed based on their appearance. They had obviously turned to powder and their color changed to darker shades. The samples were then sealed in quartz tubes under vacuum and heated to 450 °C overnight. The resultant black decomposition products (powders) were then isolated in air and phases were determined by X-ray powder diffraction. Decomposition products of all three title phases were then identified by X-ray powder diffraction using a Scintag XDS 2000 powder diffractometer at room temperature. Products were determined by matching sample patterns to known phases.[11]

Results and Discussion

Compound **I**, $[Yb(NH_3)_8][Cu(S_4)_2]\cdot NH_3$, crystallizes in the space group $I\bar{4}$ with isolated $[Yb(NH_3)_8]^{3+}$ cations and $[Cu(S_4)_2]^{3-}$ anionic units (Figure 1). Free ammonia molecules are located between cations as viewed down the *c* axis. A Yb^{3+} cation sits on the origin and is ligated by eight ammonia molecules arranged in a slightly distorted square antiprismatic coordination environment (Figure 2). The ammonia ligands are rotated to create a 30° dihedral angle relative to an ideal cube, generating a coordination environment between cubic and square antipris-

---

(6) Rabenau, A. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1026.

(7) Drake, G. W.; Schimek, G. L.; Kolis, J. W. *Inorg. Chim. Acta* **1995**, *240*. 63.

(8) (a) Sheldrick, G. M. In *Crystallographic Computing 3*; Sheldrick, G. M., Krüger, C., Goddard, R., Eds.; Oxford University Press: Oxford, U.K., pp 175−189. (b) Sheldrick, G. M. *SHELXTL-PLUS*; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1990.

(9) *teXsan: Single Crystal Structure Analysis Software, Version 1.6b*; Molecular Structure Corp.: The Woodlands, TX 77381, 1993.

(10) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

(11) (a) DMS 2000 Diffraction Management System, version 2.86, Scintag, Inc., Sunnyvale CA. 94086. (b) JCPDS-ICDD database Joint Commission on Powder Diffraction Standards-International Center Diffraction Data, Swarthmore, PA 19081.

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic *U*'s (Å$^2 \times 10^3$)

atom	x	y	z	U(eq)^a
$[Yb(NH_3)_8][Cu(S_4)_2]\cdot NH_3$				
Yb(1)	0	0	0	18(1)
Cu(1)	0	5000	2500	29(1)
S(1)	−1662(4)	4391(5)	974(5)	31(1)
S(1′)	1712(16)	4400(20)	957(5)	31(5)
S(2)	−1040(4)	5125(4)	−865(4)	37(1)
N(1)	−1175(14)	1014(15)	1953(12)	44(4)
N(2)	1509(14)	1730(15)	922(13)	46(4)
N(3)	0	0	5000	103(16)
$[Yb(NH_3)_8][Ag(S_4)_2]\cdot 2NH_3$				
Yb(1)	272(1)	3750(1)	2135(1)	13(1)
Ag(1)	5184(1)	3697(1)	2576(1)	21(1)
S(1)	6204(3)	4625(2)	3839(4)	21(1)
S(2)	6241(3)	5294(2)	2269(4)	25(1)
S(3)	4552(3)	5299(2)	1411(4)	24(1)
S(4)	4303(3)	4389(2)	558(3)	23(1)
S(5)	4063(3)	2894(2)	4104(3)	20(1)
S(6)	4209(3)	2037(2)	2881(4)	23(1)
S(7)	5992(3)	2001(2)	2348(4)	23(1)
S(8)	6389(3)	2829(2)	1255(4)	25(1)
N(1)	2084(10)	3213(5)	1322(11)	17(3)
N(2)	−370(11)	2649(5)	1502(13)	22(3)
N(3)	1015(11)	4359(5)	123(12)	21(3)
N(4)	−1417(10)	3869(6)	539(13)	27(4)
N(5)	−586(10)	4819(5)	2682(13)	25(3)
N(6)	−1432(10)	3526(6)	3644(13)	28(4)
N(7)	1936(10)	4417(5)	3100(10)	19(3)
N(8)	1006(11)	3182(6)	4151(12)	27(4)
N(9)	8510(12)	900(6)	3207(18)	44(5)
N(10)	1226(13)	1571(7)	3039(29)	86(10)
$[La(NH_3)_9][Cu(S_4)_2]$				
La(1)	1813(1)	2570(1)	9040(1)	24(1)
Cu(1)	548(2)	2910(2)	2288(1)	44(1)
S(1)	1550(5)	3483(4)	3481(2)	53(2)
S(2)	1727(6)	5082(4)	3261(3)	63(2)
S(3)	2397(5)	5104(3)	2252(3)	57(2)
S(4)	826(5)	4267(3)	1511(2)	48(2)
S(5)	−588(5)	1446(3)	1912(2)	47(1)
S(6)	−1909(6)	1774(3)	844(2)	59(2)
S(7)	−3879(6)	2120(3)	1012(3)	63(2)
S(8)	−4250(6)	3696(4)	1101(3)	58(2)
N(1)	2304(15)	2332(9)	10592(6)	50(5)
N(2)	−557(13)	3241(9)	9403(7)	40(4)
N(3)	1764(15)	4117(10)	7989(6)	47(5)
N(4)	2260(16)	4470(9)	9786(8)	57(6)
N(5)	−416(13)	2274(10)	7804(7)	44(5)
N(6)	4442(13)	3261(9)	9130(7)	43(4)
N(7)	3621(15)	927(9)	9560(8)	53(5)
N(8)	308(15)	842(9)	9236(8)	55(5)
N(9)	2624(16)	1486(11)	7940(7)	57(5)

^{a} Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

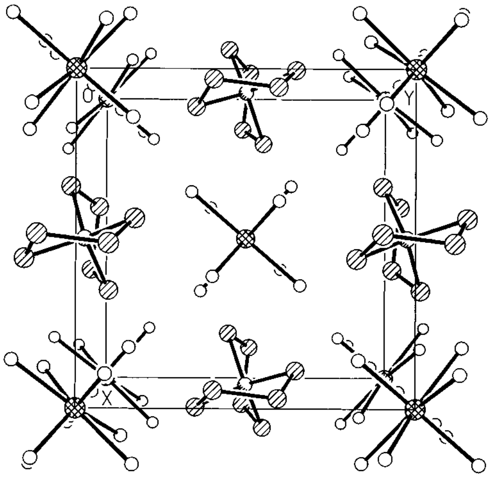

Figure 1. Perspective view down the *c* axis of $[Yb(NH_3)_8][Cu(S_4)_2]\cdot NH_3$, **I**: Yb atoms, cross-hatched; Cu, highlighted; S, striped; N, open; H, omitted for clarity.

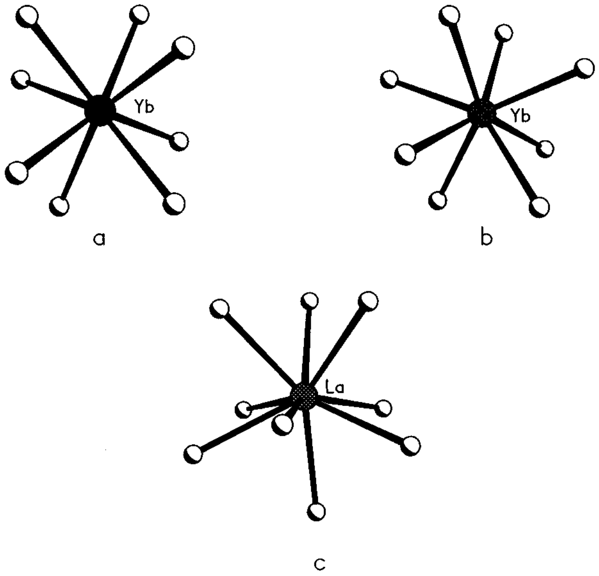

Figure 2. Coordination environments around (a) the $[Yb(NH_3)_8]^{3+}$ cation in compound **I**, (b) the $[Yb(NH_3)_8]^{3+}$ cation in compound **II**, and (c) the $[La(NH_3)_9]^{3+}$ cation in compound **III**.

matic. Table 3 lists selected bond distances and angles for the title compounds. Yb−N distances range from 2.470(14) to 2.459(13) Å. Typical Yb−N distances reported in other molecular compounds containing $Yb-NH_3$ coordination also vary between 2.4−2.5 Å.[12] The copper ion is formally in a +1 oxidation state and it sits on a site in a distorted tetrahedral coordination environment, with two chelating S_4^{2-} ligands forming CuS_4 rings. S(1)−Cu(1)−S(1) angles range from 100.0(2) to 114.4(1)°.

The tetrasulfide ligand coordinates to Cu(I) in a number of different coordination environments[13] and it is well-known that tetrasulfides readily coordinate to transition metal centers.[14] The distorted tetrahedral coordination environment is very common for divalent metal centers with S_4^{2-} chelates. Surprisingly, however, this type of geometry has not yet been reported for either Cu(I) or Ag(I) metal centers. It is much more common for the metal centers to form polynuclear clusters or low-dimensional solids, with the polysulfide acting as a bridging ligand.[15] We attribute this to the higher charge buildup per metal ion in the mononuclear complexes such as $[Cu(S_4)_2]^{3-}$. The presence of a trivalent charge will lead to a substantial decrease in the solubility of such a complex, and thus lessen the possibility of observing the formation of well-formed crystalline products in more conventional solvents. The formation of multinuclear complexes leads to a lower anionic charge on the metal complex. The ability of supercritical fluids to enhance the solubility of some normally intractable molecules may lead to the formation of well formed single crystals of **I**−**III**, with the higher anionic charge.

---

(12) (a) Wayda, A. L.; Dye, J. L.; Rogers, R. D. *Organometallics* **1984**, *3*, 1605. (b) Zalkin, A.; Henly, T. J.; Andersen, R. A. *Acta Crystallogr.* **1987**, *C43*, 233.

(13) Kanatzidis, M. G.; Park, Y. *J. Am. Chem. Soc.* **1989**, *111*, 3767.

(14) (a) Draganjac, M.; Rauchfuss, T. B. *Angew. Chem., Int. Ed. Engl .* **1985**, *24*, 742. (b) Müller, A.; Diemann, E. *Adv. Inorg. Chem.* **1987**, *31*, 89.

(15) (a) Kanatzidis, M. G. *Chem. Mater.* **1990**, *2*, 353. (b) Huang, S. P.; Kanatzidis, M. G. *Inorg. Chem.* **1991**, *30*, 1455.

Table 3. Selected Bond Distances (Å) and Angles (deg)

	$[Yb(NH_3)_8][Cu(S_4)_2]\cdot NH_3$		
Cu(1)−S(1)	2.316(4)	S(1)−Cu(1)−S(1a)	100.0(2)
Cu(1)−S(1′)	2.360(18)	S(1)−Cu(1)−S(1b)	114.4(1)
S(1)−S(1′)	1.212(20)	S(1′)−Cu(1)−S(1′a)	100.8(9)
S(1)−S(2)	2.036(6)	S(1′)−Cu(1)−S(1′a)	114.0(1)
S(1′)−S(2)	1.959(20)	S(2a)−S(2)−S(1)	105.1(2)
S(2)−S(2a)	2.100(8)	S(2a)−S(2)−S(1′)	111.7(5)
Yb(1)−N(1)	2.459(13)	Cu(1)−S(1)−S(2)	104.5(2)
Yb(1)−N(2)	2.470(14)	Cu(1)−S(1′)−S(2)	105.4(7)
	$[Yb(NH_3)_8][Ag(S_4)_2]\cdot 2NH_3$		
Ag(1)−S(1)	2.535(4)	S(1)−Ag(1)−S(4)	97.3(1)
Ag(1)−S(4)	2.617(4)	S(1)−Ag(1)−S(5)	114.9(1)
Ag(1)−S(5)	2.547(4)	S(4)−Ag(1)−S(5)	127.2(1)
Ag(1)−S(8)	2.576(4)	S(1)−Ag(1)−S(8)	121.7(1)
S(1)−S(2)	2.056(5)	S(4)−Ag(1)−S(8)	101.3(1)
S(2)−S(3)	2.063(5)	S(5)−Ag(1)−S(8)	95.9(1)
S(3)−S(4)	2.060(5)	Ag(1)−S(1)−S(2)	98.5(2)
S(5)−S(6)	2.070(5)	S(1)−S(2)−S(3)	106.6(2)
S(6)−S(7)	2.063(5)	S(2)−S(3)−S(4)	106.4(2)
S(7)−S(8)	2.052(5)	Ag(1)−S(4)−S(3)	97.8(2)
Yb(1)−N(1)	2.435(11)	Ag(1)−S(5)−S(6)	98.6(2)
Yb(1)−N(2)	2.445(10)	S(5)−S(6)−S(7)	106.2(2)
Yb(1)−N(3)	2.468(11)	S(6)−S(7)−S(8)	106.3(2)
Yb(1)−N(4)	2.457(12)	Ag(1)−S(8)−S(7)	101.5(2)
Yb(1)−N(5)	2.451(11)		
Yb(1)−N(6)	2.449(12)		
Yb(1)−N(7)	2.492(11)		
Yb(1)−N(8)	2.426(12)		
	$[La(NH_3)_9][Cu(S_4)_2]$		
Cu(1)−S(1)	2.244(4)	S(1)−Cu(1)−S(4)	104.3(2)
Cu(1)−S(4)	2.257(5)	S(1)−Cu(1)−S(5)	130.1(2)
Cu(1)−S(5)	2.181(4)	S(4)−Cu(1)−S(5)	125.5(2)
S(1)−S(2)	2.068(7)	Cu(1)−S(1)−S(2)	99.9(2)
S(2)−S(3)	2.058(8)	S(1)−S(2)−S(3)	103.8(3)
S(3)−S(4)	2.075(6)	S(2)−S(3)−S(4)	101.6(3)
S(5)−S(6)	2.080(6)	Cu(1)−S(4)−S(3)	100.2(2)
S(6)−S(7)	2.086(8)	Cu(1)−S(5)−S(6)	106.3(2)
S(7)−S(8)	2.032(6)	S(5)−S(6)−S(7)	108.5(3)
La(1)−N(1)	2.710(10)	S(6)−S(7)−S(8)	114.0(3)
La(1)−N(2)	2.710(13)		
La(1)−N(3)	2.695(12)		
La(1)−N(4)	2.725(12)		
La(1)−N(5)	2.751(11)		
La(1)−N(6)	2.711(13)		
La(1)−N(7)	2.750(12)		
La(1)−N(8)	2.706(13)		
La(1)−N(9)	2.661(14)		

The Cu−S bond distances in the $[Cu(S_4)_2]^{3-}$ anion of compound **I** range from 2.316(4) to 2.360(18) Å, and these are consistent with known compounds.[13,16] S(1) is the sulfur atom bonded to Cu(1) to form the tetrahedron and it sits on a general position. S(1) is positionally disordered and well modeled as S(1) and S(1′) which are each 50% occupied. The S(1)−S(2) bond distance is 2.100(8) Å, typical for S−S bonds, and the modelled disorder also exhibits reasonable bond distances and angles.

Figure 3 shows a perspective unit cell view down the *c* axis of $[Yb(NH_3)_8][Ag(S_4)_2]\cdot 2NH_3$. It crystallizes in the orthorhombic space group $P2_12_12_1$ and is the molecular analog of compound **I** in which $[Yb(NH_3)_8]^{3+}$ cations and $[Ag(S_4)_2]^{3-}$ anions are present. Like compound **I**, Yb(III) is coordinated to 8 ammonia molecules in a square antiprismatic fashion (Figure 2). The dihedral angle between ammonia ligands is 42°, creating an almost ideal antiprismatic coordination environment . The Yb−N distances are 2.435(11)−2.492(11) Å as listed in Table 3 and are also comparable to previously reported Yb ammine complexes.[12] Two free ammonia molecules are located near the $[Ag(S_4)_2]^{3-}$ anions, as shown in Figure 3. The Ag(I) metal center is in a distorted tetrahedral environment in which S−Ag−S angles range from 97.3(1) to 127.2(1)°. The Ag tetrahedron is somewhat more distorted as compared to the Cu tetrahedron found in $[Cu(S_4)_2]^{3-}$ of compound **I**. This increase in distortion is attributed to the closer proximity of both the $[Yb(NH_3)_8]^{3+}$ cation and the free ammonia molecules located near $[Ag(S_4)_2]^{3-}$, relative to the copper analog. Ag−S distances are 2.535(4)-2.576(4) Å and are typical when compared to those of molecular $[Ag_2(S_6)_2]^{2-}$ (Ag−S = 2.415(2)-2.500(2) Å).[17] S−S bond distances in **II** are 2.052(5)-2.070(5) Å, typical for polysulfide bond distances.

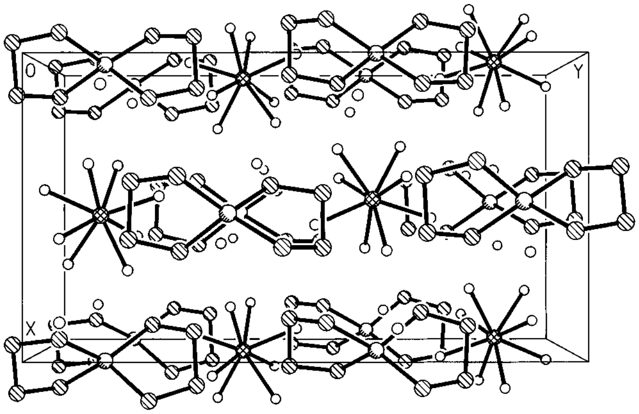

Figure 3. Perspective view down the *c* axis of $[Yb(NH_3)_8][Ag(S_4)_2]\cdot 2NH_3$, **II** (atom types same as in Figure 1).

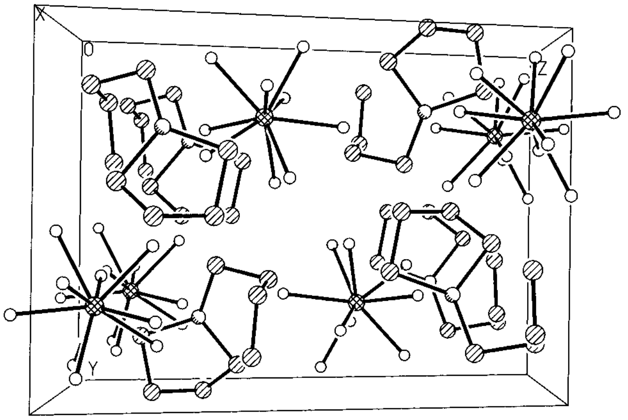

Figure 4. Perspective view down the *a* axis of $[La(NH_3)_9][Cu(S_4)_2]$, **III** (atom types same as in Figure 1).

Figure 4 shows a perspective view down the *a* axis of $[La(NH_3)_9][Cu(S_4)_2]$. The structure crystallizes in the monoclinic space group $P2_1/n$. Compound **III** is different from **I** and **II** in that La is coordinated to 9 ammonia molecules. La−N distances are 2.661(4)−2.751(1) Å. The La^{3+} coordination environment can be best described as a monocapped square antiprism, as shown in Figure 2. The Cu^+ in **III** is in a trigonal planar coordination environment with two S_4^{2-} ligands. Surprisingly only one S_4^{2-} is bidentate, forming a five-membered ring. The other S_4^{2-} ligand is monodentate to the metal center. Cu−S distances are 2.181(4)−2.257(5) Å. The trigonal planar Cu−S distances found in **III** are slightly shorter than the tetrahedral Cu−S distances found in **I** (2.316(4)−2.360(18) Å). Furthermore, both Cu coordination environments and each of their corresponding Cu−S distances match well with literature values (ca. 2.3 Å), as expected. It should be noted that the terminal S−S distance in the monodentate tetrasulfide is

---

(16) Müller A.; Bauman, W. F.; Bögge, H.; Schimtz, K. *Z. Anorg. Allg. Chem.* **1985**, *521*, 89.

(17) Müller, A.; Krickemeyer, E.; Zimmermann, M.; Römer, M.; Bögge, H.; Schmitz, K. *Inorg. Chim. Acta* **1984**, *90*, L69.

substantially shorter than any other S−S bond (2.032(6) Å vs an average distance of 2.073(15) Å for the coordinated polysulfides). Trigonal planar coordination of Cu by S is not uncommon for Cu(I), and has also been reported for Se[18] and Te[19] polychalcogenide anionic units. Monodentate polychalcogenide ligands are somewhat rare, but examples have been observed previously.[20] However, in these previous cases, the metal center is still coordinatively saturated (usually square planar four-coordinate). In the case of **III**, the Cu(I) is only three-coordinate. This is in marked contrast to **I,** where the Cu(I) center is four-coordinate. It is unclear to us why the metal center would eschew the free energy of chelation and choose to remain three-coordinate.

It should be noted that several attempts were made to synthesize the silver analog of compound **III**, both by direct reaction of the elements (La, Ag and S) in supercritical ammonia and by using premade "$[La(NH_3)_x(S_y)]$" with silver and sulfur powder. However, none of these reactions were successful, and only very poor quality single crystals of $[La(NH_3)_9]S_x$ ($x = 5$ or 6) and other amorphous powders were obtained. In no case could we induce silver to become incorporated into the framework. Given the similarity of the Cu(I) and Ag(I) polysulfide complexes in **I** and **II**, it is not at all clear to us why the silver analog of **III** does not form.

A number of distinct bands are observed in the IR and far-IR spectra for all three compounds. Weak broad bands are observed at 3300−3500 cm^{-1} for all three compounds due to N−H stretches. In all three cases, strong broad bands are also observed between 500 and 600 cm^{-1}. These are assigned to the metal−nitrogen stretches. The broadness of the bands is attributed to the instability of the products relative to ammonia loss and the likely presence of a number of different coordination environments around the metal after mulling at room temperature. In the case of **I** and **II**, two sharper stretches are observed at 474 and 401 cm^{-1} for **I** and 480 and 412 cm^{-1} for **II**. This is a typical region for S−S stretches[21] and they are assigned as such. In **III**, there are no sharp bands observed in the S−S stretching region. We attribute this to excessive broadening of the La−N stretches into the S−S stretching region. The increased broadening correlates well with extreme instability of these compounds. There are a few weak shoulders which appear in this spectrum at 400 cm^{-1} and they may be due to S−S stretching, but this assignment is tentative at best. Lower lying bands around 265 cm^{-1} can be assigned to metal sulfur stretches.

To our knowledge, compounds **I**−**III** are the first well-characterized homoleptic lanthanide ammine complexes. Although it has been postulated that the lanthanide cations do form solid metal ammine complexes, none have been well characterized to date.[22] There have been a number of organometallic metal mono(ammonia) complexes reported,[12] but they always contain substantially different ancillary ligands. Given the well-known tendency for lanthanide elements to dissolve in ammonia, generating free electrons and soluble metal cations,[4] this discrepancy is somewhat surprising. We attribute the lack of results to the fact that the ammonia coordination sphere of the lanthanum cations appears to be highly unstable, as exhibited by the rate of decomposition of the crystals when removed from the ammonia solvent. The free ammonia incorporated into the lattice of **I** and **II** also contributes to their instability, especially since NH_3 is relatively isolated and is not trapped in the framework. This is evident by the immediate darkening of the crystals upon removal of the solvent. Within several hours of removal of the crystals from the liquid ammonia, the crystals blacken and their facets disappear at room temperature. We have also synthesized a number of other related transition metal hexaammine pnictide sulfides (e.g. $[Mn(NH_3)_6][CuAs_7S_{12}]\cdot NH_3$),[23] which contain free ammonia in the lattice, but this compound remains intact for hours after the removal of ammonia solvent. In this case, free ammonia in the manganese hexammine transition metal compound are tightly trapped between dense polymeric layers of the 15/16 anionic framework, and thus decomposition is not as rapid. In addition, the ammonia ligands coordinated to the transition metal center are not as labile as those coordinated to the lanthanides.

The instability of the compounds relative to loss of ammonia led us to investigate the identity of the decomposition products. It was hoped that clean removal of ammonia could lead to new ternary phases at low temperature. Decomposition of the title phases at room temperature by removal of ammonia under vacuum lead to amorphous uncharacterizable solids. Infrared spectra of several of these solids indicate that there is still some ammonia present, but the extreme broadening of the bands implies that the crystal structure has completely broken down. Similarly, powder diffraction of these powders showed no interpretable lines. Thermogravimetric analysis of the compounds reveals steady, almost linear, weight loss to about 320 °C. Further heating at 450 °C overnight leads to formation of black powders consisting of reasonably crystalline phases of known compounds. X-ray powder diffraction data showed that both $[Yb(NH_3)_8][Cu(S_4)_2]\cdot NH_3$ and $[Yb(NH_3)_8][Ag(S_4)_2]\cdot 2NH_3$ decompose to the same phase, Yb_2O_2S,[24] upon heating to 450 °C in evacuated-fused-silica tubes, while $[La(NH_3)_9][Cu(S_4)_2)]$ decomposes cleanly to LaS_2.[25] The fused-silica tube in which the sample was reheated is the most likely source of oxygen for Yb_2O_2S. There are no other peaks of any size in the X-ray powder pattern, so we are unable to determine the fate of copper or silver. They probably form amorphous metal sulfide phases. Unfortunately, there is no evidence for the formation of Ln/Cu/S phases at the relatively low temperatures that we are investigating.

In summary, three new lanthanide ammine metal sulfides can be synthesized in supercritical ammonia. These compounds can be best described as homoleptic ammine lanthanide tri-cations counterbalanced by molecular anionic metal sulfide complexes. The cations exist in a lattice surrounded by anionic copper or silver polysulfide clusters. The lability of the lanthanide ammine bond causes these molecules to be very unstable. However, the introduction of metals which form more stable metal ammine complexes (i.e. the d-block metals) should lead to a wide variety of new solids. We anticipate that use of more stable metal ammine complexes will allow us to tailor the sulfide frameworks, leading to extended arrays with Werner complexes acting as templates.[23] On the basis of what has been discovered in this laboratory involving supercritical ammonia, we feel that this synthetic route holds a great deal of promise for obtaining

---

[18] Müller, U.; Ha-Eierdanz, M.-L.; Kräuter, G.; Dehnicke, K. *Z. Naturforsch.* **1990**, *45B*, 1128.

[19] Fenske, D.; Schreiner, B.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1993**, *619*, 253.

[20] Park, Y.; Kanatzidis, M. G. *Angew. Chem., Int. Ed. Engl.* **1990**, *29* , 945.

[21] Nakamoto, K. *The Infrared Spectra of Inorganic and Coordination Compounds*; Wiley: New York, 1978.

[22] (a) Hart, F. A. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, U.K.; 1987, Vol. 3, p 1059. (b) Moeller, T.; Martin, D. F.; Thompson, L. C.; Ferrus, R.; Feistel, G. R.; Randell, W. J. *Chem. Rev.* **1965**, *65*, 1.

[23] Young, D. M.; Kolis, J. W. Manuscript in preparation.

[24] Ballestracci, R.; Rossat-Mignod, J. *Solid State Commun.* **1969**, *7*, 1011.

[25] Dugue, J.; Carre, D.; Guittard, M. *Acta Crystallogr.* **1978**, *B34*, 403.

a wide variety of combinations of new compounds with metal ammine complexes incorporated into metal sulfide frameworks.

Acknowledgment. We are indebted to the National Science Foundation (Grant CHE-9102548) and Clemson University for support of this work. We are also grateful to Bill Evans for helpful discussions regarding lanthanide ammine complexes.

Supporting Information Available: Tables giving complete crystallographic data, all bond angles, anisotropic thermal parameters, and hydrogen coordinates and isotropic thermal parameters, thermal ellipsoid views of all three compounds, and powder diffraction patterns (12 pages). Ordering information is given on any masthead page.

IC9601403