

Reactivity of Ammonium Chloride/Mercuric Chloride Mixtures with Monel Containers. The New Compounds $(\text{NH}_4)_2(\text{NH}_3)_x[\text{Ni}(\text{NH}_3)_2\text{Cl}_4]$ and $(\text{NH}_4)_5\text{Cl}_2[\text{CuCl}_2][\text{CuCl}_4]$

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Received February 27, 2001; in revised form June 6, 2001; accepted June 20, 2001; published online August 28, 2001

IN HONOR OF PROFESSOR PAUL HAGENMULLER ON THE OCCASION OF HIS 80TH BIRTHDAY

Ammonium chloride/mercuric chloride mixtures (molar ratio 2:1) react at 350°C with Monel (Cu68Ni32) to yield $(\text{NH}_4)\text{NiCl}_3$ and mercury and copper amalgam, respectively. With larger amounts of $(\text{NH}_4)\text{Cl}$ in the reaction mixture, dark green $(\text{NH}_4)_2(\text{NH}_3)_x[\text{Ni}(\text{NH}_3)_2\text{Cl}_4]$ ($x \approx 0.77$) (1) is also formed as a main product. Light blue crystals of the mixed-valent copper(I,II) chloride $(\text{NH}_4)_5\text{Cl}_2[\text{CuCl}_2][\text{CuCl}_4]$ (2) were obtained as a minor byproduct from a 4:1 reaction mixture. The crystal structures were determined from single crystal X-ray data; (1): tetragonal, $I4/mmm$, $a = 770.9(1)$, $c = 794.2(2)$ pm, 190 reflections, $R_1 = 0.0263$; (2): tetragonal, $I4/mcm$, $a = 874.8(1)$, $c = 2329.2(3)$ pm, 451 reflections, $R_1 = 0.0736$. In (1) Ni^{2+} resides in *trans*- $[\text{Ni}(\text{NH}_3)_2\text{Cl}_4]^{2-}$ octahedra, and in (2) copper(I) is linearly two-coordinated in $[\text{CuCl}_2]^-$ and copper(II) resides in a flattened tetrahedron $[\text{CuCl}_4]^{2-}$ with a tetrahedrality of 89%. © 2001 Elsevier Science

Key Words: reactivity; ammonium chloride; mercuric chloride; crystal structure.

1. INTRODUCTION

Ammonium chloride, $(\text{NH}_4)\text{Cl}$, acts as an oxidant for many metals (1), producing a number of ternary ammonium chlorides or ammine complexes. Aluminum may serve as an example; the action of ammonium chloride on aluminum in sealed Monel (Cu68Ni32) containers yields $(\text{NH}_4)\text{AlCl}_4$ and $\text{AlCl}_3 \cdot 3\text{NH}_3 \equiv [\text{Al}(\text{NH}_3)_4\text{Cl}_2]^+ [\text{Al}(\text{NH}_3)_2\text{Cl}_4]^-$ (2), depending upon the actual reaction conditions.

As the oxidant is actually the proton of the ammonium ion, noble metals such as mercury normally cannot be oxidized and, therefore, mercury does not react with ammonium chloride in a Monel container. The less noble homologues of mercury, zinc and cadmium, do, of course, react with ammonium chloride, yielding the ternary

chlorides $(\text{NH}_4)\text{MX}_3$ and $(\text{NH}_4)_2\text{MX}_4$ ($M = \text{Zn}, \text{Cd}$), respectively, also in the presence of mercury, which does perhaps enhance the reactivity of zinc and cadmium (3).

Analogous ternary ammonium mercuric chlorides, $(\text{NH}_4)\text{HgX}_3$ and $(\text{NH}_4)_2\text{HgX}_4$, and those with the composition $(\text{NH}_4)\text{Cl}:\text{HgCl}_2$ of 2:9, 1:2, and 4:1 have been reported in a phase diagram investigation (4). Our own work has resulted in the synthesis and crystal structure determination of a new chloride, $(\text{NH}_4)_{10}\text{Hg}_3\text{Cl}_{16}$ (5), close to the reported 4:1 phase. These reactions were carried out in Pyrex ampoules. In sealed Monel containers, however, these reactions go in a different direction as the Monel container is quite obviously not so inert against ammonium chloride/mercuric chloride mixtures as are Pyrex ampoules.

2. EXPERIMENTAL DETAILS

In an argon dry box (M. Braun, Garching/München), mixtures of $(\text{NH}_4)\text{Cl}$ and HgCl_2 (*p.a.*, Merck, Darmstadt) in 2:1, 4:1, and 6:1 molar ratios (for example, 2:1, 53.5 mg $(\text{NH}_4)\text{Cl}$ and 543.0 mg HgCl_2) were weighed into previously cleaned (nitric acid) and at one end sealed Monel containers (i.d. 6 mm, length 5 cm), which were then sealed in a He arc welder. The Monel containers were jacketed with a Pyrex or silica ampoule under a light vacuum. The whole ensemble was then put in a tubular furnace and heated to 350°C for 28 days. The Monel containers were opened in the argon dry box with a pair of scissors.

X-ray powder diffractograms were recorded with representative samples of the products (θ - 2θ diffractometer, STADI P, Stoe, Darmstadt). Single crystals were selected in an argon dry box with the aid of a microscope and sealed in thin-walled glass capillaries. Lattice constants were determined from single-crystal data (Stoe Image Plate Diffraction System, IPDS) and from powder diffractograms

TABLE 1
Crystallographic Data for (NH₄)₂(NH₃)[Ni(NH₃)₂Cl₄] and (NH₄)₅Cl₂[CuCl₂][CuCl₄]

	(NH ₄) ₂ (NH ₃)[Ni(NH ₃) ₂ Cl ₄]	(NH ₄) ₅ Cl ₂ [CuCl ₂][CuCl ₄]
Crystal system	Tetragonal	Tetragonal
Space group	<i>I4/mmm</i>	<i>I4/mcm</i>
Lattice constants <i>a</i> (pm)	770.9(1)	874.8(1)
<i>c</i> (pm)	794.2(2)	2329.2(3)
Formula units per cell	2	4
Density (X ray) (g cm ⁻³)	2.000	1.791
Crystal size (mm ³)	0.2 × 0.2 × 0.3	0.2 × 0.2 × 0.2
Diffractometer	IPDS (Stoe)	
Radiation	MoK α (λ = 71.07 pm)	
Temperature (K)	293(2)	293(2)
Scan range	3.68° < 2 θ < 49.97°	6.58° < 2 θ < 49.98°
<i>F</i> (000)	280	996
Absorption coefficient μ (mm ⁻¹)	3.133	3.567
Absorption correction	Numerical after optimization of the crystal shape, programs X-SHAPE, X-RED (6)	
Images/Distance from detector	100/60 mm	100/60 mm
Exposure time (min)	4	4
Reflections measured	1939	5878
Reflections with <i>I</i> > 2 σ (<i>I</i>)	187	451
Unique reflections	190	451
Internal <i>R</i> value <i>R</i> _{int}	0.0402	0.0600
Structure solution and refinement	Programs SHELXS-97 and SHELXL-97 (7); full-matrix least-squares on <i>F</i> ²	
Scattering factors	From <i>International Tables</i> , Vol. C (8)	
Goodness of fit	1.236	1.134
<i>R</i> values for <i>I</i> > 2 σ (<i>I</i>)	<i>R</i> ₁ = 0.027; w <i>R</i> ₂ = 0.0745	<i>R</i> ₁ = 0.0582; w <i>R</i> ₂ = 0.1630
<i>R</i> values for all data	<i>R</i> ₁ = 0.0263; w <i>R</i> ₂ = 0.0751	<i>R</i> ₁ = 0.0736; w <i>R</i> ₂ = 0.1740
Residual electron density (e/Å ³)	0.341/–0.622	1.09/–0.93

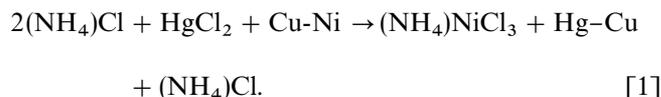
whenever possible. Data collection on single crystals were carried out with the IPDS; for details see Table 1.

Infrared and UV-Vis-NIR spectra were recorded with a CARY 5E spectrometer (Varian, Australia). Thermal analysis was carried out with a thermal analyzer (simultaneous thermogravimetry and difference thermal analysis; STA 429, Netzsch, Selb) to which a quadrupole mass spectrometer (Balzers) was attached.

3. RESULTS AND DISCUSSION

In all three cases, i.e., reactions with molar ratios of the educts (NH₄)Cl and HgCl₂ of 2:1, 4:1, and 6:1, no ternary

mercuric chloride was detected. Rather, mercuric chloride reacted with the Monel container, yielding elemental mercury and copper amalgam and the ternary (NH₄)NiCl₃, according to the reaction scheme



With the 2:1 ratio, these are the only products. When larger amounts of (NH₄)Cl are applied, the hitherto

TABLE 2
Atomic Parameters and Equivalent and Anisotropic Displacement Factors in 10⁻¹ pm² for (NH₄)₂(NH₃)[Ni(NH₃)₂Cl₄], Space Group *I4/mmm*

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂ ^a
N1 (NH ₄ ⁺)	4d	0	0.5	0.25	27.8(8)	30(1)	<i>U</i> ₁₁	23(2)	0
N2 (NH ₃)	4e	0	0	0.2584(4)	24.5(8)	28(1)	<i>U</i> ₁₁	17(2)	0
N3 (NH ₃) ^b	4c	0	0.5	0	21(1)	28(4)	16(3)	19(3)	0
Ni	2a	0	0	0	20.4(4)	22.8(4)	<i>U</i> ₁₁	15.8(5)	0
Cl	8h	0.22915(7)	<i>x</i>	0	27.5(4)	28.8(4)	<i>U</i> ₁₁	24.8(5)	–6.7(3)

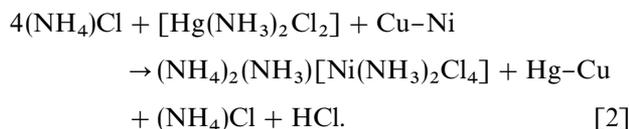
^a*U*₂₃ = *U*₁₃ = 0.

^bOccupation factor 0.77(5).

TABLE 3
**Atomic Parameters and Equivalent and Anisotropic Displacement Factors in 10^{-1} pm^2 for $(\text{NH}_4)_5\text{Cl}_2[\text{CuCl}_2][\text{CuCl}_4]$,
 Space Group $I4/mcm$**

Atom	Site	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{12}
N1 (NH_4^+)	16l	0.3457(5)	0.1543(5)	0.0910(3)	36.3(17)	32(2)	U_{11}	44(4)	$U_{23} = -U_{13} = -2(2); U_{12} = 2(3)$
N2 (NH_4^+)	4a	0	0	0.25	61.0(48)	70(8)	U_{11}	42(9)	$U_{23} = U_{13} = U_{12} = 0$
Cu1 (I)	4c	0.5	0.5	0.5	98.0(14)	131(2)	U_{11}	32(1)	$U_{23} = U_{13} = U_{12} = 0$
Cu2 (II)	4b	0.5	0	0.25	43.6(8)	50(1)	U_{11}	30(1)	$U_{23} = U_{13} = U_{12} = 0$
Cl1	8f	0	0	0.09387(11)	33.5(7)	29(1)	U_{11}	43(2)	$U_{23} = U_{13} = U_{12} = 0$
Cl2	16l	0.3514(2)	0.1486(2)	0.31204(9)	45.1(7)	51(1)	U_{11}	33(1)	$U_{23} = U_{13} = -6(6); U_{12} = 16(1)$
Cl3	8h	0.3543(3)	0.1457(3)	0.5	57.5(11)	71(2)	U_{11}	31(2)	$U_{23} = U_{13} = 0; U_{12} = 30(2)$

unknown complex compound $(\text{NH}_4)_2(\text{NH}_3)_x[\text{Ni}(\text{NH}_3)_2\text{Cl}_4]$ is obtained as dark green crystals (see Tables 1 and 2 for crystallographic data). As this could be written as $(\text{NH}_4)_2\text{NiCl}_4 \cdot (2+x)\text{NH}_3$, one can imagine that it must be the higher partial pressure of ammonia that is created in these ampoules at the reaction temperature when larger amounts of $(\text{NH}_4)\text{Cl}$ are applied, which stabilizes the new $(\text{NH}_4)_2(\text{NH}_3)_x[\text{Ni}(\text{NH}_3)_2\text{Cl}_4]$. This assumption is supported by the observation that $(\text{NH}_4)_2(\text{NH}_3)_x[\text{Ni}(\text{NH}_3)_2\text{Cl}_4]$ is the only product (except the Cu–Hg amalgam) of the reaction of $(\text{NH}_4)\text{Cl}$ and $[\text{Hg}(\text{NH}_3)_2\text{Cl}_2]$ in a molar ratio of 4:1 at 350°C (3), where the higher pressure of ammonia is at least partially produced by decomposition of $[\text{Hg}(\text{NH}_3)_2\text{Cl}_2]$ into HgCl_2 and 2NH_3 :



The content of the crystal ammonia x in $(\text{NH}_4)_2(\text{NH}_3)_x[\text{Ni}(\text{NH}_3)_2\text{Cl}_4]$ is subject to crystal structure refinement around 0.77 (see below). No information is available at present as to whether this ammonia content is dependent upon pressure and temperature.

A few light blue crystals of an also hitherto unknown compound of the analytical composition $(\text{NH}_4)_5\text{Cu}_2\text{Cl}_8$ (almost $(\text{NH}_4)_2\text{CuCl}_4$!) were obtained from the 4:1 reaction. This is a mixed-valent Cu(I)/Cu(II) chloride that should be written as $(\text{NH}_4)_5\text{Cl}_2[\text{CuCl}_2][\text{CuCl}_4]$ (see Tables 1 and 3 for crystallographic data). This is surprising as $(\text{NH}_4)\text{Cl}$ reacts with copper (as the wall of a copper reaction container) only to form $(\text{NH}_4)_2\text{CuCl}_3$ with monovalent copper. The oxidation to divalent copper in the present case (in a Monel container!) might be due to the relatively high hydrogen chloride pressure that builds up when ammonia is consumed for the production of one of the main products, $(\text{NH}_4)_2(\text{NH}_3)_x[\text{Ni}(\text{NH}_3)_2\text{Cl}_4]$, because HCl is not only an acid but also an oxidant.

$(\text{NH}_4)\text{NiCl}_3$. This compound, whose crystal structure has been refined recently (9), crystallizes with the hexagonal CsNiCl_3 -type structure (10) with the lattice constants obtained from powder diffractometry being $a = 695.2(1)$, $c = 592.8(1)$ pm. In this structure the $[\text{NiCl}_6]$ octahedra share common faces in the $[001]$ direction.

$(\text{NH}_4)_2(\text{NH}_3)_x[\text{Ni}(\text{NH}_3)_2\text{Cl}_4]$. This compound contains isolated *trans*-configured $[\text{Ni}(\text{NH}_3)_2\text{Cl}_4]^{2-}$ octahedra with the *trans* $(\text{H}_3\text{N})\text{-Ni-(NH}_3)$ moieties on the crystallographic c axis, Fig. 1. With distances $\text{Ni}^{2+}\text{-N}(\text{H}_3)$ of 205 pm, the N–N distances in this direction are 384 pm (Table 4). Unfortunately, we have no information on the hydrogen positions. The $\text{Ni}^{2+}\text{-Cl}^-$ distances of almost 250 pm are in fair agreement with those found in CsNiCl_3 , i.e., 244 pm (10).

The UV-Vis-NIR spectrum of $(\text{NH}_4)_2(\text{NH}_3)_x[\text{Ni}(\text{NH}_3)_2\text{Cl}_4]$ exhibits three absorption bands at 27500, 19000, and 9000 cm^{-1} , which can be assigned to the

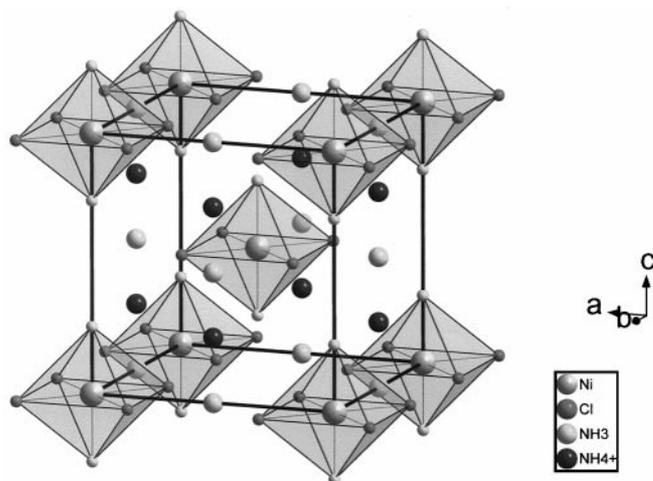


FIG. 1. Perspective view of the crystal structure of $(\text{NH}_4)_2(\text{NH}_3)_x[\text{Ni}(\text{NH}_3)_2\text{Cl}_4]$.

TABLE 4
Important Internuclear Distances in pm for
 $(\text{NH}_4)_2(\text{NH}_3)_x[\text{Ni}(\text{NH}_3)_2\text{Cl}_4]$ and $(\text{NH}_4)_5\text{Cl}_2[\text{CuCl}_2][\text{CuCl}_4]$

	$(\text{NH}_4)_2(\text{NH}_3)_x[\text{Ni}(\text{NH}_3)_2\text{Cl}_4]$
Ni	(Cl, $4 \times 249.8(1)$; NH_3 , $2 \times 205.4(3)$)
$(\text{NH}_4)^+$	(Cl, $8 \times 338.1(1)$)
	$(\text{NH}_4)_5\text{Cl}_2[\text{CuCl}_2][\text{CuCl}_4]$
Cu1	(Cl1, $2 \times 218.6(3)$)
Cu2	(Cl2, $4 \times 233.9(2)$)
$(\text{NH}_4)^+1$	(Cl1, $325.9(7)$, $2 \times 337.6(6)$; Cl2, $2 \times 331.2(3)$; Cl3, $332.2(7)$, $2 \times 348.1(6)$)
$(\text{NH}_4)^+2$	(Cl2, $2 \times 363.6(3)$; Cl3, $8 \times 363.7(1)$)

transition from the $^3A_{2g}(\text{F})$ ground state to the $^3T_{1g}(\text{P})$, $^3T_{1g}(\text{F})$, and $^3T_{2g}(\text{F})$ excited states, in accordance with spectra known for $[\text{Ni}(\text{NH}_3)_6]^{2+}$ complexes (11). This also means that considerable amounts of copper(II) replacing nickel(II) in this compound cannot be present.

The infrared spectrum shows the typical vibrational modes of $(\text{NH}_4)^+$ and NH_3 . The assignment is in accordance with the literature (12) and agrees well with similar compounds containing either the ammonium ion or the ammine ligand, see Table 5.

The $[\text{Ni}(\text{NH}_3)_2\text{Cl}_4]^{2-}$ octahedra form a tetragonal body-centered lattice of dimensions $a = 771$ and $c = 795$ pm into which a primitive lattice of $(\text{NH}_4)^+$ cations is imposed with a translation vector of $[0, \frac{1}{2}, \frac{1}{4}]$. The $(\text{NH}_4)^+$ cations thereby are eight-coordinated by chloride in a cube-like arrangement with $d((\text{NH}_4)^+ - \text{Cl}^-) = 338$ pm. One problem of the crystal structure is the ammonia molecule on the $0, \frac{1}{2}, 0$ position. These crystal ammonia molecules form a row with the $(\text{NH}_4)^+$ ions parallel to the $[001]$ direction with distances of only $c/4 = 199$ pm. Although they add to the coordination sphere of $(\text{NH}_4)^+$ and can make plausible why the c axis is some 20 pm longer than the a axis, an $(\text{NH}_4)^+ - \text{NH}_3$ distance of 199 pm is too short even when hydrogen bonding is present and can be assumed from the infrared spectrum. An explanation might be that the occupation factor of the N3 position is only about 0.77.

TABLE 5
Assignment of the Infrared Active Vibrational Modes
in $(\text{NH}_4)_2(\text{NH}_3)_x[\text{Ni}(\text{NH}_3)_2\text{Cl}_4]$ (in cm^{-1})

3037	$\nu_1(\text{NH}_4^+)$	3337	$\nu_a(\text{NH}_3)$
1663	$\nu_2(\text{NH}_4^+)$	3243	$\nu_{st}(\text{NH}_3)$
3141	$\nu_3(\text{NH}_4^+)$	1627	$\delta_s(\text{HNH}/\text{NH}_3)$
1407	$\nu_4(\text{NH}_4^+)$	1246	$\delta_s(\text{HNH}/\text{NH}_3)$
1975	$\nu_2 + \nu_6(\text{NH}_4^+)$	648	$\rho_r(\text{NH}_3)$
1737	$\nu_4 + \nu_6(\text{NH}_4^+)$		
2812	$2\nu_4(\text{NH}_4^+)$		

Thermal analysis in combination with mass spectrometry (Fig. 2) shows that $(\text{NH}_4)_2(\text{NH}_3)_x[\text{Ni}(\text{NH}_3)_2\text{Cl}_4]$ decomposes thermally in a two-step mechanism at 250 and 320°C, respectively, leading to $(\text{NH}_4)\text{NiCl}_3$ and finally to NiCl_2 , also proven by X-ray power diffractometry.

The lattice constants of $(\text{NH}_4)_2(\text{NH}_3)_x[\text{Ni}(\text{NH}_3)_2\text{Cl}_4]$ determined from single-crystal data ($a = 770.93(13)$, $c = 794.94(15)$ pm) are in good agreement with those refined from X-ray powder diffractometer data for the 0° to 90° range in 2θ , $a = 769.33(4)$, $c = 793.57(6)$ pm.

$(\text{NH}_4)_5\text{Cl}_2[\text{CuCl}_2][\text{CuCl}_4]$. This compound also crystallizes with the tetragonal system, although with a c/a ratio of 2.66 (see Table 1) and with four formula units per unit cell, Fig. 3. Monovalent copper, Cu1, occupies the atomic positions (4c) and divalent copper, Cu2, positions (4b). Thus, copper alone builds up a tetragonally distorted (elongated) cubic closest-packed lattice with two unit cells

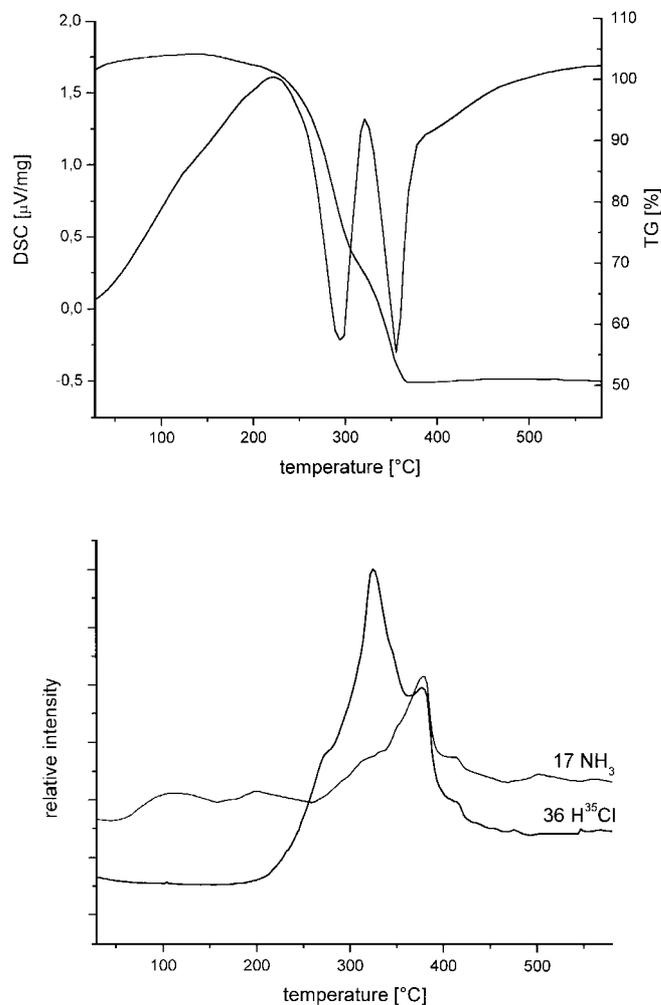


FIG. 2. Simultaneous thermogravimetry (TG) and difference thermal analysis (DTA) (top) and mass spectra for $(\text{NH}_4)_2(\text{NH}_3)_x[\text{Ni}(\text{NH}_3)_2\text{Cl}_4]$.

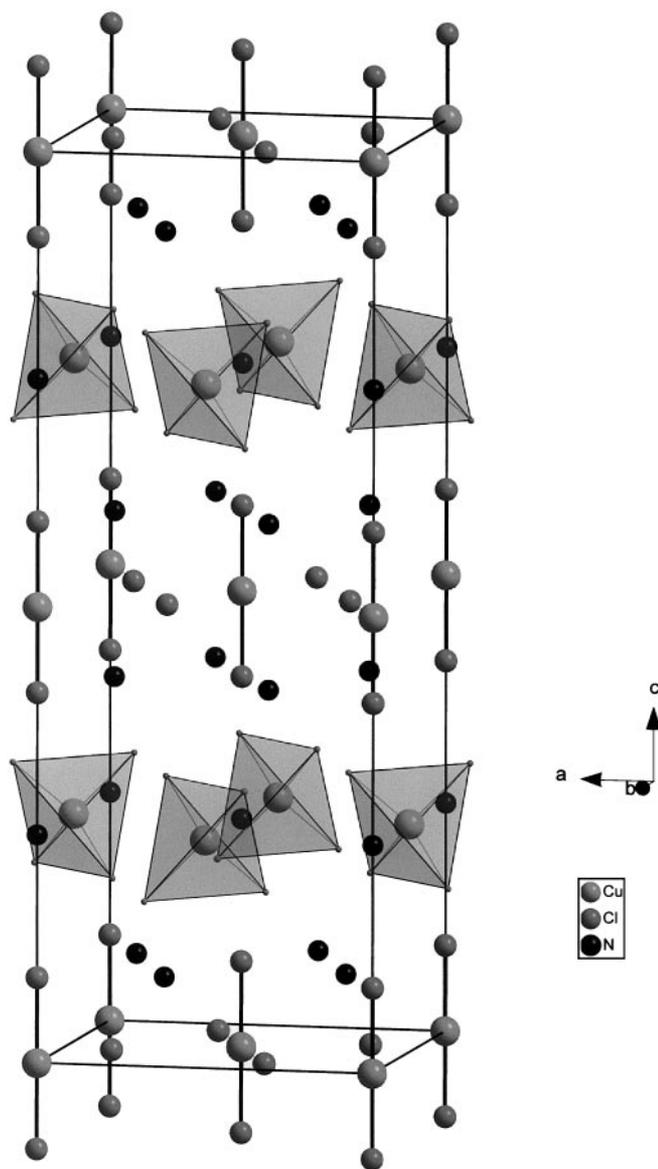


FIG. 3. Perspective view of the crystal structure of $(\text{NH}_4)_5\text{Cl}_2[\text{CuCl}_2][\text{CuCl}_4]$.

stacked in the $[001]$ direction. The elongation with $0.5c/a = 1.33$ is subject to two-coordinated copper(I). Its ligands Cl1, on the 8f positions $(0, 0, 0.09)$, are 219 pm apart (Table 4). These distances appear a bit large when compared to four-coordinated copper(I) in CsCu_2Cl_3 , 217 pm (13). However, four out of twenty $(\text{NH}_4)^+$ cations are also located on the c axis such that the sequence in the $[001]$ direction is Cu(I)–Cl1– $(\text{NH}_4)_2$ –Cl1–Cu(I)–Cl1– $(\text{NH}_4)_2$ –Cl1–Cu(I). These $(\text{NH}_4)^+$ cations have a coordination number of 10.

Divalent copper, Cu2, is four-coordinated, although in the unusual tetrahedral rather than square-planar coordination, with a tetrahedrality of 89% (for a definition see (14)).

Cu^{2+} – Cl^- distances (Cu2, Cl2) are 234 pm, which are larger than those in Cs_2CuCl_4 (average 223 pm (15)) where flattened tetrahedra are present, and are close to distances of 230 and 233 pm found in $(\text{NH}_4)_2\text{CuCl}_4$ (16), although there a square-planar coordination is present.

Except for Cl1 and Cl2 that do belong to Cu1 and Cu2, respectively, there are two chloride ions per formula unit in the unit cell that do not coordinate to either Cu1 or Cu2. They belong to $(\text{NH}_4^+)_1$ only. This one has coordination number 8 and the $(\text{NH}_4^+)_1$ – Cl^- distances cover a similar range (331 to 348 pm), as do the $(\text{NH}_4^+)_2$ – Cl^- distances: 364 pm ($10 \times$).

Unfortunately, we have so far obtained only a few single crystals of $(\text{NH}_4)_5\text{Cl}_2[\text{CuCl}_2][\text{CuCl}_4]$ as byproducts in reactions such as $(\text{NH}_4)\text{Cl}/\text{HgCl}_2/\text{Cu-Ni}$ or $(\text{NH}_4)\text{Cl}/\text{Hg}(\text{NH}_3)_2\text{Cl}_2/\text{Cu-Ni}$. Therefore, we could not obtain any spectra or magnetic measurements to learn more about this most interesting mixed-valent copper chloride. It does not contain any significant amount of nickel(II) subject to an EDX analysis of single crystals.

4. CONCLUSIONS

Mercuric chloride, HgCl_2 , reacts in the presence of $(\text{NH}_4)\text{Cl}$ (molar ratio 1:2) with the Monel alloy, $\text{Cu}68\text{Ni}32$, to form elemental mercury and copper amalgam and the ternary $(\text{NH}_4)\text{NiCl}_3$. Further $(\text{NH}_4)\text{Cl}$ (reactant ratio 1:4) yields the new dark green $(\text{NH}_4)_2(\text{NH}_3)_x[\text{Ni}(\text{NH}_3)_2\text{Cl}_4]$, making use of the high ammonia partial pressure in the Monel reaction container. A few crystals of the light blue hitherto unknown mixed-valent copper(I,II) chloride $(\text{NH}_4)_5\text{Cl}_2[\text{CuCl}_2][\text{CuCl}_4]$ have also been obtained and the structures were determined from X-ray single-crystal data. $(\text{NH}_4)_2(\text{NH}_3)_x[\text{Ni}(\text{NH}_3)_2\text{Cl}_4]$, also characterized by infrared and UV-Vis-NIR spectra, decomposes thermally via $(\text{NH}_4)\text{NiCl}_3$ (250°C) to NiCl_2 (320°C).

ACKNOWLEDGMENTS

This work has been supported by the Deutsche Forschungsgemeinschaft, Bonn, as one project in the Schwerpunktprogramm "Reaktivität von Festkörpern," and by the Fonds der Chemischen Industrie, Frankfurt am Main.

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