Mg(NH$_3$)$_6$Hg$_{22}$, a Mercury Intercalation Compound

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Received March 17, 2000

Abstract: Very pure Mg dissolves in liquid NH$_3$ with a blue color. Attempts to isolate solid Mg(NH$_3$)$_x$ were not met with success. MgHg alloy reacts with liquid NH$_3$ with formation of Mg(NH$_3$)$_6$Hg$_{22}$, as established by a single-crystal structure determination. The octahedral Mg(NH$_3$)$_6$ units have Mg–N distances typical for Mg(NH$_3$)$_6{}^{2+}$. They are embedded in layers into cavities of the mercury metal matrix, resulting in a layered structure. T_c of this superconducting material is 3.6 K, which is lower than that of pure Hg (4.19 K).

Introduction

Blue solutions of certain metals in liquid HH$_3$ have been known for a very long time[1,2] and have been under continuous investigation over the years. Some of the NH$_3$ soluble metals, such as Ca, Sr, and Ba, form solid ammonia adducts M(NH$_3$)$_x$ which have a metal-like appearance, e.g. are often bronze colored. Structures based on neutron diffraction powder data are known for Ca(ND$_3$)$_6$ and Li(ND$_3$)$_4$. The CaN$_6$ skeleton of Ca(ND$_3$)$_6$ is regularly octahedral; the ND$_3$ molecules are found to be strongly distorted from the usual ammonia geometry, based on a disorder model.[3–5] Li(ND$_3$)$_4$ has an elongated tetrahedral structure, with one Li–N bond much longer (248.8(16) pm) than the other three Li–N bonds (198.4(4) pm). The ammonia molecules appear normal.[6,7] To shed more light on the solid metal–ammonia complex structures, we have attempted to prepare such complexes with magnesium as the metal atom, since it lies between Ca and Li in its chemical behavior.

The literature of the system Mg/NH$_3$ is controversial. Some reports say that Mg does not dissolve in liquid NH$_3$.[8,9] Others say that a weak blue solution is obtained if Mg with a clean surface is contacted with NH$_3$.[10,11] Another approach has been tried by reacting a Mg/Hg alloy with liquid ammonia, and a compound so obtained was analyzed as Mg(NH$_3$)$_6$, however containing large amounts of mercury due to the method of preparation.[10]

Experimental Section

General. X-ray measurements: A Bruker Smart CCD 1000 TM diffractometer with Mo Kα radiation and a graphite monochromator was used. Magnetic susceptibility was measured with a squid magne-

tometer. Hg and Mg were handled in a drybox with automatic argon cyclization, guaranteeing oxygen and water contents between 0.1 and 1 ppm.

Starting compounds: Mercury, 99.9999% purity, was purchased from Johnson Mathey Co. and distilled in a vacuum. Magnesium, 99.99% purity, was purchased from Heraeus Co. and sublimed at 1.5 × 10^{-5} mbar and 600 °C in a stainless steel sublimation apparatus.

Ammonia, 99.98 purity, was purchased from Air Liquide Co. and stored briefly with some Na. ND$_3$, ^{15}NH$_3$, and ^{15}ND$_3$, all 98% purity, were purchased from Cambridge Isotope Laboratories and purified as described for NH$_3$.

Mg(NH$_3$)$_6$Hg$_{22}$. 18.56 g (90.52 mmol) of mercury and 100 mg (4.11 mmol) of magnesium were weighed into a thoroughly dried glass ampule. The ampule was evacuated, and with help of a glass vacuum line about 4 mL of purified NH$_3$ was condensed into the ampule. After sealing, the ampule was shaken briefly to make sure that all Mg–Hg particles dropped to the bottom. The sample was stored almost horizontally to bring a large metal surface into contact with NH$_3$. After 1 day the metallic surface was covered with very small crystals. Suitable crystal sizes were obtained only after weeks. Samples for magnetic susceptibility measurements were treated with ultrasound at room temperature for 1 day to obtain complete conversion.

A single crystal with dimensions of 0.2 × 0.2 × 0.05 mm^3 was fixed on the tip of a glass capillary under nitrogen and at low temperatures with the help of a special device.[12] The setup was mounted on the X-ray diffractometer under permanent cooling to −90 or −143 °C. A scan width of 0−3 in ω, an exposure time of 30 s/frame, and a detector-crystal distance of 4.0 cm were used. A full shell of data up to 2θ = 66° was measured by 1800 frames. Data were reduced to intensities, corrected for background, and an empirical absorption correction was done by equalizing multiple symmetry equivalent reflections ("Sadabs"). Structures were solved and refined by the SHELX programs.[13,14] For further details see Table 1. Results are combined in Tables 2 and 3.

Mg(NH$_3$)$_6$Cl$_2$. Anhydrous Mg(CF$_3$CO$_3$)$_2$, prepared from MgCO$_3$ and excess CF$_3$SO$_3$H and drying at 90 °C/10^{-2} mbar, was dissolved in CH$_2$Cl$_2$. After adding a few milliliters of anhydrous NH$_3$ by distillation, the ampule was sealed. Within weeks at −35 °C there appeared colorless crystals of Mg(NH$_3$)$_6$Cl$_2$. The single-crystal structure determination in space group *Fm3m* (K$_2$PtCl$_6$ type) resulted in Mg(0,0,0), Cl(1/4, 1/4, 1/4), and N(0,0,0.2156(4)), with a Mg–N distance of 219.7-(3) pm. For further details see Table 1.

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Table 1

compd	$Mg(NH_3)_6Hg_{22}$		$Mg(NH_3)_6Cl_2$
mol weight [g mol^{-1}]	4539.48		789.66
temperature [°C]	−90		−143
a [pm]	755.6(1)		10.1899(4)
c [pm]	2725.7(4)		
volume [pm^3]	1556.33×10^6		1058.06×10^6
crystal system	tetragonal		cubic
space group	$14/m$	$I4/mmm$	$Fm3m$
	(No. 87)	(No. 139)	(No. 225)
Z	2	2	4
ρ_{calcd} [g cm^{-3}]	9.07	9.07	1.239
μ [mm^{-1}]	108.04	108.04	0.62
measured reflcns	9372	9372	622
θ_{max} [deg]	30.6	30.6	30
independent reflcns	753	753	132
R_{int}	0.1305	0.1305	0.0643
parameters	40	30	11
R	0.0392	0.0402	0.057
R_w^2	0.1072	0.1138	0.145

Table 2. Fractional Atomic Coordinates, Site Occupational Factor (s.o.f), and Isotropic Vibrational Parameters [pm^2] of $Mg(CH_3)_6Hg_{22}{}^a$

	x	y	z	s.o.f.	U_{eq}
Hg1	0	0	0.29074(5)	0.25	196(3)
	0	0	0.29074(5)	0.125	197(3)
Hg2	0.30803(10)	0.00168(53)	0.37865(3)	1.0	275(3)
	0.30803(10)	0	0.37866(3)	0.5	276(3)
Hg3	0.29876(30)	0.30201(31	0.30333(3)	1.0	288(3)
	0.30039(8)	0.30039(8)	0.30333(3)	0.5	290(3)
Hg4	0	0	0.44779(5)	0.25	313(4)
	0	0	0.44779(5)	0.125	316(4)
Hg5	0.5	0	0.25	0.25	232(3)
	0.5	0	0.25	0.125	232(4)
Mg	0	0	0	0.125	90(26)
	0	0	0	0.0625	84(25)
N1	0	0	0.08090(115)	0.25	247(65)
	0	0	0.08105(118)	0.125	232(64)
N2	0.0352(47)	0.2832(44)	0	0.5	368(115)
	0.03471(42)	0.2876(37)	0	0.25	259(72)

^{a} First number: space group $I4/m$. Second number: space group $I4/mmm$

Table 3. Bond Lengths within $Mg(NH_3)_6Hg_{22}$ [pm], Space Group $I4/m{}^a$

Hg1−Hg2	334.1(1)	Hg3−Hg3	301.7(2), 310.1(2)
Hg1−Hg3	322.8(1), 333.6(1)	Hg3−Hg5	307.4(3), 310.4(3)
Hg2−Hg2	290.1(1), 329.2(1)	Hg4−Hg4	284.6(3)
Hg2−Hg3	304.8(3), 307.4(3)	Mg−N1	220.5(31)
Hg2−Hg4	299.5(1)	Mg−N2	215.7(33)
Hg2−Hg5	325.8(2)		

^{a} Values for space group $I4/mmm$ do not differ by more than 0.1 pm.

Results

The System Mg/NH₃. Freshly sublimed Mg and NH₃ (distilled from a Na/NH₃ solution) were combined in a sealed vessel to yield a blue solution. The color could be intensified by prolonged shaking. However, a visible loss of Mg could not be seen. We therefore assume that the solution remained very dilute. When lower temperatures and ultrasound were applied, the color intensified, until a metal mirror appeared on the wall of the glass tube at the meniscus of the blue solution. Below −80 °C a phase separation occurs. The upper phase was solid, colorless NH₃. The lower phase remained liquid, and was very dark and nontransparent (in a tube of 8 mm diameter). Upon further cooling to −90 °C the lower phase solidified also, and was completely colorless and transparent, with very small metallic spangles that appeared in this solid. These phase

transitions are completely reversible, and we assume that the metallic spangles are some $Mg(NH_3)_x$ material, however in such a small amount that no attempt was made to isolate it. We should keep in mind that phase separation is also observed in concentrated metal/ammonia solutions at low temperatures, with metals such as Na, Ca, Sr, and Ba.[15]

The system Mg/Hg/NH₃. If all components are thoroughly purified, and also if the glass vessel is thoroughly dried to remove superficial water, the liquid Mg−Hg alloy and the liquid NH₃ combine at room temperature to a microcrystalline solid of metallic appearance. At best, crystallites appeared as very thin quadratic platelets of about $0.5 \times 0.5 \times 0.01$ mm^3. The thickness of the platelets is so small that the value of 0.01 mm remains only an estimate. These crystals decompose irreversibly at room temperature with loss of NH₃, and it is obvious that they represent the same material as the one described as Mg-$(NH_3)_6$ in 1922. This was been accurately analyzed as containing Mg and NH₃ in the ratio 1:6, but also high contamination by mercury was noted.[10]

The proper choice of crystal size was essential in solving the crystal structure. Crystals larger than $0.2 \times 0.2 \times 0.01$ mm^3 refract very little due to the strong absorption ($\mu = 108$ mm^{-1}), while crystals smaller than $0.1 \times 0.1 \times 0.01$ mm^3 refract very little. The structure could be solved in either of two space groups: twinned (with 010, 100, 00−1) in $I4/m$ (No. 87) or disordered in $I4/mmm$ (No. 139). In the case of space group $I4/m$ (twinned) all atoms could be refined anisotropically. In space group $I4/mmm$ the disordered nitrogen position was refined isotropically, since in this model the disordered N atom positions of N2 are only 50 pm apart. No attempts were undertaken to locate the hydrogen positions. The location of the hydrogen atoms is hampered not only by their small refractive power but also by the expected disorder. The three hydrogen atoms at N1 are at best disordered over 12, at most over 24 positions (3-fold symmetry of the NH₃ unit assumed). The three hydrogen atoms on any of the four disordered N positions may indeed be located at three distinct positions, but only in $I4/m$ and when one of the hydrogen positions is in $x,y,0$. Otherwise they can be disordered again by as much as 24 positions. For two reasons the use of neutron diffraction data on a powder sample to detect hydrogen positions was not even tried: Hg strongly absorbs neutrons, and the large Z-axis would result in an overlap of many reflections.

$Mg(NH_3)_6Hg_{22}$ has a layered structure. One layer consists of only mercury atoms while the layers between are composed of $Mg(NH_3)_6$ units. The layers are oriented in the a, b plane of the tetragonal, body centered lattice and thus dominate the external appearance of the crystals (see Figure 1). The crystallographic a and b axes are parallel to the long edges of the square platelets, while the c axis is normal to the large crystal faces.

The $Mg(NH_3)_6$ Subunits. The $Mg(NH_3)_6$ units are located in ellipsoidal holes within the mercury lattice. These holes are 755.6 pm wide in two dimensions and 1073 pm long and are made up of 32 mercury atoms. The $Mg(NH_3)_6$ units are separated from each other by only a rectangular array of mercury atoms Hg4. In fact the N2 atoms of neighboring $Mg(NH_3)_6$ units are quite close to each other: 331.9 pm. This is the only part of the structure that is dependent on the choice of space group. In the disordered model ($I4/mmm$) these atoms are separated by 321 pm, see Figure 2. The atoms N1 are positioned at 0, 0,

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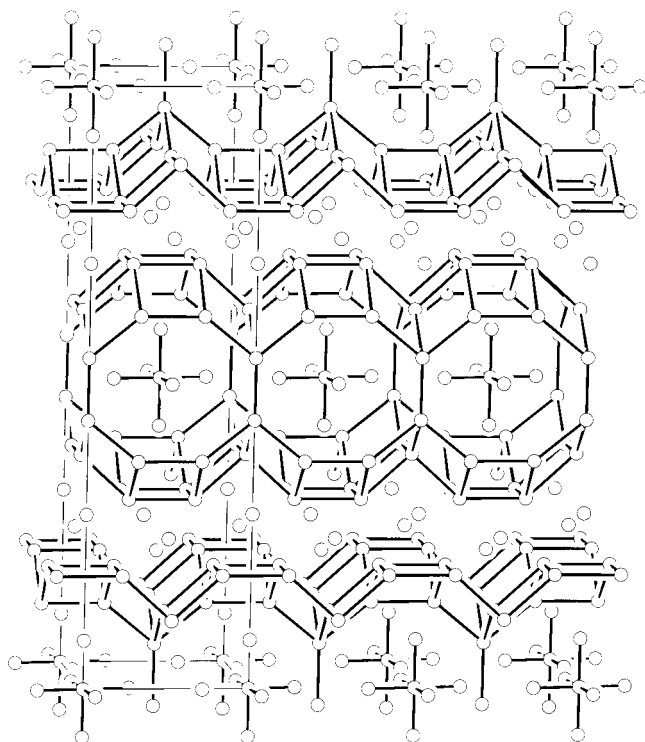
Figure 1. Three unit cells of $Mg(NH_3)_6Hg_{22}$. The 32 mercury atoms of the cavities surrounding the $Mg(NH_3)_6$ units are connected by solid lines.
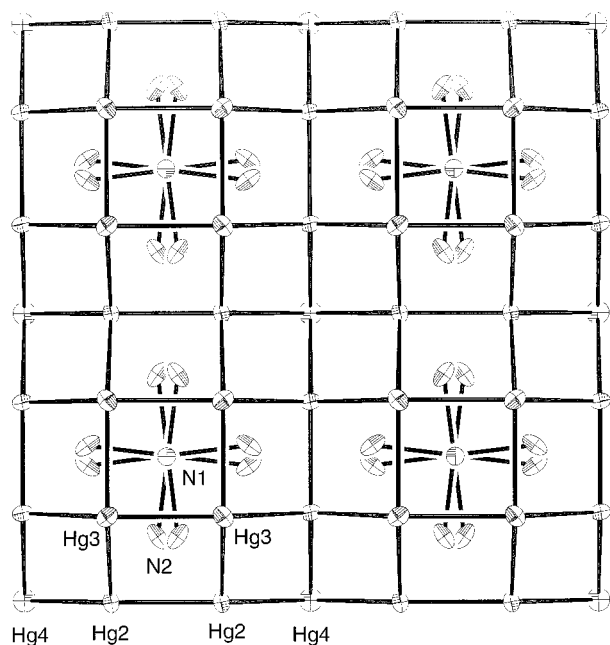

Figure 2. Projection into the *a, b* plane, Ortep, 50% probability ellipsoids. Sixteen mercury atoms, the upper half of the Hg_{32} cavity, are shown, also the disorder/twinning of the N2 positions.

$+z$, so that ideal octahedral angles are preserved. The question of whether all Mg–N bond lengths are equal or not cannot be answered with certainty. The two axial Mg–N bonds seem to be longer than the four equatorial Mg–N bonds, but the difference is well within three esd's. A literature search revealed no answer to the question of whether the observed Mg–N bond lengths of 215.6 and 220.5 pm are normal for the $Mg(NH_3)_6^{2+}$ ion, although it would be possible to make predictions by using ion and atomic radii. We therefore prepared single crystals of $Mg(NH_3)_6^{2+}(Cl^-)_2$, and found perfectly regular $Mg(NH_3)_6^{2+}$

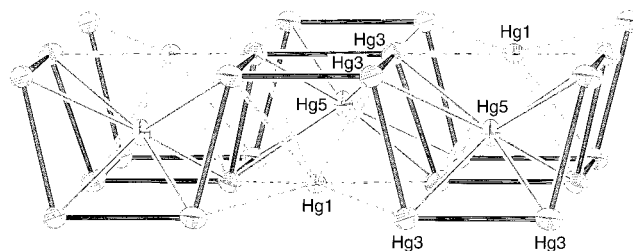**Figure 3.** The close to body centered mercury layers in $Mg(NH_3)_6$-Hg_{22}, consisting of Hg1, Hg3, and Hg5, Ortep, 50% probability ellipsoids.

units with a Mg–N distance of 219.7(3) pm. This is so close to the Mg–N distances in the title compound that the $Mg(NH_3)_6$ unit in $Mg(NH_3)_6Hg_{22}$ can be regarded as a double positive ion. For uncharged $Mg(NH_3)_6$ a much larger Mg–N distance is anticipated.

The Mercury Cavities around $Mg(NH_3)_6$. The $Mg(NH_3)_6$ units are surrounded by a three-dimensional network of 32 mercury atoms Hg2, Hg3, and Hg4, forming the previously mentioned cavities (see Figures 1 and 2). It is interesting to note that the Hg–Hg distances in the inner surface of the cavity atoms are mostly below 300 pm and no longer ones than 303 pm are observed. Thus it seems that these Hg–Hg distances are indicative of stronger than normal metallic bonding between them. This finding is not unusual, since in Hg-rich alloys with electropositive metals such shortening of Hg–Hg distances is also observed. Also the quadratic Hg_4 unit with bond distances below 300 pm is a common structural motif of such alloys.[16]

The compounds closest to $Mg(NH_3)_6Hg_{22}$ are possibly $MeHg_{11}$ (Me = K, Rb, Sr, Ba).[17-19] They are also built from a Hg matrix with large cavities that hold solely the metal atoms (or ions). Of course the cavities in those cases are much smaller than those in $Mg(NH_3)_6Hg_{22}$, namely 662 pm in case of BaHg, formed from 20 mercury atoms, and they are closer to spherical shape. For a view of this cavity see Figure 2 in ref 19.

The Mercury Layers. The mercury layers are formed by Hg1, Hg3, and Hg5, see Figure 3. The structure can be derived from β-Hg (tetragonal body centered, stable at high pressure (>4000 bar) or below −194 °C).[20,21] It consists of squares of Hg3 with (in contrast to β-Hg) alternating sizes. Hg5 is positioned body centered almost exactly between two large squares, and Hg1 is positioned between large and small squares, and shifted slightly in height (along the *z* axis) from the central position, see Figure 3. The Hg–Hg distances here are all larger than 306 pm, except the Hg3–Hg3 distance within the small squares, which is 299.1 pm. But we should keep in mind that the small squares belong to the $Mg(NH_3)_6$ environment. It may be noteworthy that MHg_{11} is structurally related to rhombohedral α-Hg, and $Mg(NH_3)_6Hg_{22}$ to body-centered tetragonal β-Hg.

$Mg(NH_3)_6Hg_{22}$ is obviously superconducting with a sharp critical temperature T_c at 3.6 K, as indicated by a magnetic susceptibility measurement, see Figure 4. This value is below the T_c of α-Hg (4.15 K) and also that of β-Hg (3.94 K).[20,21] It is known that most Hg alloys have a lower T_c than pure Hg including $MeHg_{11}$,[19] and those few with a higher T_c (Hg_xPb_{1-x},

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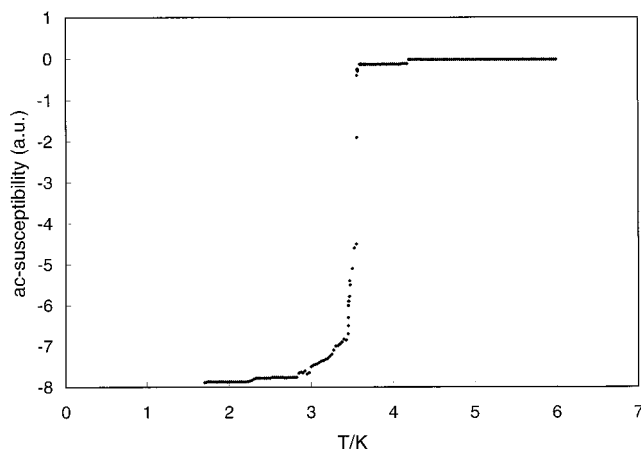(21) Schirber, J. E.; Swenson, C. A. *Phys. Rev. Lett.* **1959**, *2*, 296.

Figure 4. Magnetic susceptibility versus temperature plot of $Mg(NH_3)_6$-Hg_{22}. The insert shows presence of a small amount of metallic Hg with $T_c = 4.2$ K (lit. $T_c = 4.19$ K, ref 22).

Hg_xSn_{1-x}) lie very close to the value of 4.19 K of α-Hg.[22] We therefore assume that the superconductivity stems from the Hg part of the lattice, and that $Mg(NH_3)_6$ plays only the role of a diluent. We have also synthesized $Mg(^{15}NH_3)_6Hg_{22}$, $Mg(ND_3)_6$-Hg_{22}, and $Mg(^{15}ND_3)_6Hg_{22}$ to find out if there is any isotope effect influencing T_c. We only found that T_c of the samples varies slightly from sample to sample, possibly as a function of particle size, with an order similar to that expected from an isotope effect.

Discussion

The main question is whether this compound should be formulated as an alloy between $Mg(NH_3)_6$ and Hg_{22} or whether it is to be formulated as an ionic compound $Mg(NH_3)^{2+}Hg_{22}^{2-}$, or some state in between. The Mg−N bond lengths point clearly to an ionic description. For example, in $Ca(NH_3)_6$ the Ca−N bond length is 269 pm (3), whereas for $Ca(NH_3)_6^{2+}$ a Ca−N

bond length of only about 257 pm is to be expected from ionic radii considerations.

One can also speculate about the orientation of the $Mg(NH_3)_6$ octahedra. The position of N2 away from the vertical minor planes in *I4/mmm* leaves the impression that neighboring N2 atoms, or better their nonlocated hydrogen atoms, avoid each other. This could result in a partial or perfect orientation of all octahedra within one plane. No such influence can be established between the layers. So it is likely that there is no orientation of the octahedra in different layers. This particular model cannot be described exactly by either space group *I4/m* or *I4/mmm*. This problem is often encountered in layered intercalation compounds.

We wondered if other phases of similar type can be made. Preliminary results show that the $Mg(NH_3)_6Hg_{22}$ formation is so far unique. For instance Na, dissolved in NH_3 at −33 °C can be extracted from this solution completely into liquid Hg, forming the well-known Na−Hg alloy, leaving pure NH_3 behind.

We found it difficult to find any compounds related to Mg-$(NH_3)_6Hg_{22}$. Li/NH_3 intercalation into metallic TiS_2 results in $Li_{0.22}(NH_3)_{0.64}TiS_2$, idealized $Li(NH_3)_3(TiS_2)_{4.5}$, which may be the closest known relative.[23]

Supporting Information Available: Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic vibrational parameters for $Mg(NH_3)_6Hg_{22}$ (*I4/m*), $Mg(NH_3)_6Hg_{22}$ (*I4/mmm*), and Mg-$(NH_3)_6Cl_2$ (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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