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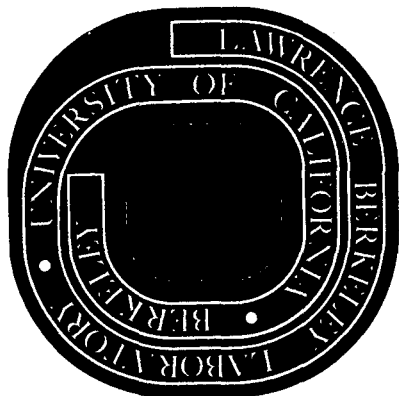
Kenneth A. Strom and William L. Jolly

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THE REACTION OF HYDROGEN WITH COPPER(I)
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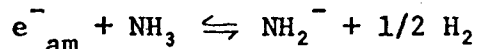
The Department of Chemistry, University of California, and the
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Abstract- Molecular hydrogen reacts with liquid ammonia solutions containing CuI and excess of either KNH_2 or CsNH_2 to form thermally unstable orange-red solids with the approximate compositions $\text{K}_2\text{Cu}_3\text{H}_5 \cdot x\text{NH}_3$ and $\text{CsCuH}_2 \cdot x\text{NH}_3$. The compounds have been characterized by elemental analysis, X-ray powder diffractometry, and, in the case of the potassium compound, Raman spectroscopy and magnetic measurements.

A. INTRODUCTION

Only a few reactions of molecular hydrogen have been studied in liquid ammonia. The amide-catalyzed para-ortho conversion [1] and isotope exchange [1,2,3] reactions have been found to be first order in amide concentration and first order in hydrogen concentration.

The reaction



has been found to be reversible [4]. Hydrogenation of trans 1,2-diphenylethylene and diphenylacetylene in the presence of potassium amide and a reduced iron oxide catalyst has been reported [5].

We now wish to report the reaction of hydrogen with copper(I) amide complex (probably $\text{Cu}(\text{NH}_2)_2^-$) in the presence of excess potassium amide or cesium amide. The products are thermally unstable orange-red crystalline ternary hydrides with the approximate formulas $\text{K}_2\text{Cu}_3\text{H}_5 \cdot x\text{NH}_3$ and $\text{CsCuH}_2 \cdot x\text{NH}_3$.

B. EXPERIMENTAL

Apparatus

A two-legged glass reaction vessel (O.D. 32 mm) similar to the one described by Fernelius and Johnson was used [6]. One leg had two side arms (O.D. 10 mm) each with a break-seal and ball joint assembly. One side arm was used in the hydrolysis experiments (described below), and the other served to connect the vessel to the vacuum line after

the preparation. When a capillary containing reaction product was needed, Pyrex tubing (O.D. 5 mm) was attached to the leg and a capillary was drawn from the tubing.

A side arm (O.D. 22 mm) attached to the other leg via a short length of glass tubing (O.D. 4 mm) served as a still for the introduction of alkali metal by distillation. This leg also was equipped with a ball joint. A very thin platinum black coating in this leg catalyzed the reaction of the metal with ammonia, producing alkali metal amide and hydrogen.

A General Electric camera with a graphite monochromator was used to obtain the X-ray powder diffraction patterns. The tube voltage (CuK_{α_1}) was 35 kV; filament current was 20 mA; exposure time was 72 hours. The samples were contained in capillaries drawn from Pyrex tubing. The capillaries were kept at -170° to -190° during exposure by an Enraf-Nonius Universal Low Temperature Device, which employs a cold inner stream of nitrogen for cooling and a warm outer stream of nitrogen to prevent icing. The density of $\text{K}_2\text{Cu}_3\text{H}_5 \cdot x\text{NH}_3$ was estimated by a helium displacement technique [7].

The magnetic susceptibility of $\text{K}_2\text{Cu}_3\text{H}_5 \cdot x\text{NH}_3$ at room temperature was determined by the Gouy method using an electromagnet (Spectromagnetic Industries, Model 4-100), with 1-inch diameter pole faces and 1-inch gap, powered with a Spectromagnetic Industries Model T.C. 200-8 power supply.

The infrared spectra of Nujol mulls of the potassium compound at -196° were obtained. The mulls were prepared in a dry box

(Vacuum/Atmospheres Corp. Model HE-193-1) and placed in a low temperature cell similar to that described by Shriver [8].

Raman spectra were recorded below -100° with a Jarrell-Ash Raman Spectrometer (Model No. 25-300) equipped with a 30 mW helium-neon laser (exciting line, 6328 \AA), with a slit width of 10 cm^{-1} .

Chemicals

Copper(I) iodide was prepared by a standard method [9]. Potassium (Mallinkrodt Chemical Works; under petroleum hydrocarbons) and cesium (Research Organic/Inorganic Chemical Corp.; 99.95%) were distilled prior to use. Ammonia (Matheson; 99.999%) was distilled from sodium. Deuterium oxide (I. C. N. Corp.; 98.8%) was used as received.

Procedure

Copper(I) iodide (5 mmol) was placed in one leg. Ammonia (50 ml) was distilled onto 60 mmol of alkali metal in the other leg. The ball joint connection to the vacuum line was removed by glass-blowing. The hydrogen pressure in the vessel from the platinum black-catalyzed reaction between alkali metal and ammonia reached about 2 atm. (Caution: This is a sealed tube reaction. The reaction vessel must be kept cold (ca. -40°) and handled with heavy gloves behind a safety shield.) The copper(I) iodide was dissolved in 25 ml of ammonia^{which} was distilled from the other leg. The amide solution was slowly poured into the copper(I) solution at -78° , whereupon a white precipitate of copper(I) amide appeared and then quickly dissolved as excess amide entered the solution [10]. An orange-red solid appeared throughout the

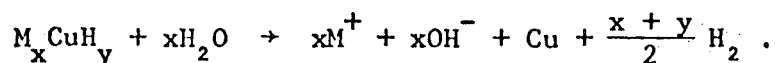
solution a few minutes later; thereafter, the solid formed at the gas-liquid interface. On occasion the reaction time was decreased by stirring the reactants with a glass-encased magnet.

After a reaction time of 12-18 hours at -78° the solid was washed by repeated decantation and distillation of ammonia from the decantate back onto the precipitate. The vessel was opened to a vacuum line; the pressure was reduced to less than 1 atm, and the leg containing the ammonia plus washings was removed by glass-blowing. The product was dried by keeping it under high vacuum for 24 hours at -78° . The product was transferred to the side arms, which were then removed and stored at -196° . The thermal instability of the hydrides (at room temperature, the potassium and cesium compounds blacken in 60 and 10 minutes, respectively) and their insolubility in solvents with which they do not react (benzene, cyclohexene) discouraged further purification attempts. Yield (based on copper) was typically 40%.

Experiments were performed without hydrogen by degassing the amide solution prior to sealing the vessel. No products formed.

Analysis

Accurately weighed samples were treated with water (or D_2O) at room temperature, and the evolved hydrogen was measured. Hydrogen evolution was due to the reaction



Subsequent heating of the solution and residue for 10 hours at 80° did not cause additional hydrogen evolution, indicating that the hydrolysis

had gone to completion at room temperature. Basic solutions catalyze the decomposition of wurzite copper hydride [11], therefore the hydrolysis was expected to be complete. No significant amounts of CuO or Cu₂O were formed, inasmuch as only trace amounts of copper species could be washed from the hydrolysis residue with 6 M HCl. Other workers have also found that hydrolysis of ternary hydrides often results in reduction to metal [12].

The ammonia content of the hydrolysis solution was determined by the Kjeldahl method [13]. Alkali metals were determined as their perchlorate salts [14], and copper was determined iodometrically [15]. No other species were present in significant amounts (see percent compositions below).

C. RESULTS

The ternary hydrides are thermally unstable orange-red crystalline nonvolatile solids, reactive to moisture and insoluble in common solvents. Eight different samples of the potassium compound were analyzed. Two typical sets of results are: K, 26%; Cu, 66%; NH₃, 6%; and K, 28%; Cu, 62%; NH₃, 6%. Calc for K₂Cu₃H₅·NH₃: K, 26%; Cu, 65.4%; NH₃, 6.1%. Three preparations of the cesium compound were analyzed. The results are: (1) Cs, 64%; Cu, 32%; NH₃, 3%; (2) Cs, 63%; Cu, 34%; NH₃, 2%; and (3) Cs, 61%; Cu, 32%, NH₃, 2%. Calc for CsCuH₂·1/4 NH₃: Cs, 65.6%; Cu, 31.4%; NH₃, 2.1%. The ammonia content of the solids decreased to less than 1% after prolonged pumping, but unfortunately the hydrogen content also decreased, so that the compounds could not be prepared free

of ammonia. These results suggest the formulation of the products as ammoniates. If we assume oxidation states of +1, +1, and -1 for K, Cu, and H, respectively, we calculate a closer approximation to charge neutrality for an ammoniate formulation, $K_x CuH_y \cdot 0.33 NH_3$, than for an amide formulation, $K_x CuH_y (NH_2)_{0.33}$. (The analytical data, which do not distinguish between these formulations, correspond to an N/Cu ratio of approximately 1/3). The Raman spectral data (discussed below) also support the formulation of the potassium compound as an ammoniate.

The values of x and y calculated from the analytical data for the potassium and cesium compounds are given in Table 1. It will be noted that the y values are below the values corresponding to the formulations $K_2Cu_3H_5$ and $CsCuH_2$ (1.67 and 2, respectively). However, it is not uncommon for hydrolytic determinations of hydrogen for ternary hydrides to be low [11, 12, 16]. Indeed, prior to hydrolysis the cesium compound was noticeably darkened because of partial decomposition; so the values of y for that compound were expected to be low.

Treatment of the potassium compound with D_2O yielded hydrogen with an isotopic distribution (H_2 , 57%; HD, 41%; D_2 , 2%) similar to that found for soluble CuH [11]. Thermal decomposition of the solid at 80° for 2 hours yielded ca. 0.5 mmol of hydrogen per mmol of copper. Treatment of the residue with D_2O yielded ca. 0.67 mmol of the mixture H_2 , 31%; HD, 67%; D_2 , 2%, per mmol of copper.

The potassium compound showed no infrared bands between 4000 and 400 cm^{-1} . The compound is diamagnetic, as expected for a copper(I) compound, with $\chi_g = -0.8 \times 10^{-6}$ e.m.u. (c.g.s.). The Raman spectrum of the potassium compound has bands at 4225 cm^{-1} (s), 3450 cm^{-1} (w), and 3367 cm^{-1} (s). The intensity of the peak at 4225 cm^{-1} decreased with time; moving the laser beam to a new area of the sample caused a momentary increase in intensity. Fluorescence prevented observation of bands below 1000 cm^{-1} .

The X-ray powder patterns are summarized in Tables 2, 3, 4, and 5. In Table 2, the face-centered cubic phase with $a_0 = 3.91\text{ \AA}$ corresponds to lines in the powder pattern that are distinctly sharper than the others. A face-centered cubic phase with $a_0 = 8.00\text{ \AA}$ and a metallic copper phase account for the remaining lines. The copper lines are very broad, and in some cases overlap other lines that are sharper (for example, the line at 1.823 \AA is the leading edge of the copper 1.808 \AA line).

The X-ray powder pattern of the cesium compound has extremely weak lines. Nevertheless, the pattern was indexed (Table 3) as an orthorhombic phase using the analytical procedure of Hesse and Lipson [17].

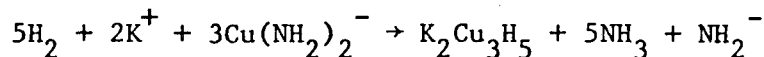
The cell constants (refined by least squares analysis) were found to be:

$$a_0 = 8.54 \pm 0.012 \text{ \AA}; b_0 = 10.59 \pm 0.03 \text{ \AA}; c_0 = 7.70 \pm 0.011 \text{ \AA}.$$

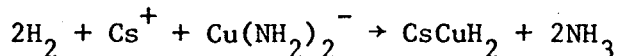
The hydrides were decomposed thermally, and the X-ray powder diffraction patterns of the residues were obtained (Tables 4 and 5). Broad and intense lines due to copper were found, and the residue from the cesium compound showed lines due to cesium metal ($a_0 = 6.067 \text{ \AA}$; literature [18], $a_0 = 6.067 \text{ \AA}$ at 78°K). Apparently neither the cesium nor the potassium compound decomposes to crystalline metal hydride. We have been unable to assign or to index about half of the lines in the powder pattern of the potassium compound's residue.

D. DISCUSSION

The preparation of the ternary hydrides can be represented by the equations

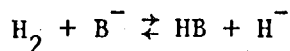


and



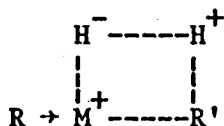
The mechanism probably involves either the intermediate formation of hydride ion from the reaction of hydrogen with amide, or a concerted reaction involving a $\text{Cu}^+-\text{H}_2-\text{NH}_2^-$ complex. Examples of both types of mechanism are known.

The reaction of hydrogen with a strong base, B^- , may be written:



Hydride ions have been proposed to be the initial product of the reaction of hydrogen with hydroxide ion in water [19] and with amide ion in liquid ammonia [1,2,3]. The *t*-butoxide-catalyzed hydrogenation of benzophenone [20] and the reduction by hydrogen of silver(I) [21] are also thought to involve intermediate formation of hydride ions.

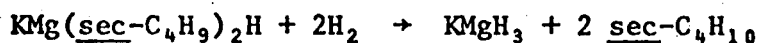
The activation of hydrogen by copper(I) in aqueous acid [22,23] and in several organic solvents [24,25] is believed to involve the reaction $\text{Cu(I)} + \text{H}_2 \rightarrow \text{CuH} + \text{H}^+$ where $k = 10^{-1} \text{ M sec}^{-1}$. It was found that basic solvents enhance the rate of reaction. Cyclic intermediates were suggested for the reactions of copper(I) [26] and silver(I) [27] with hydrogen in organic solvents:



where M^+ is the metal ion and R and R' are bases (such as amines).

We cannot determine from our data which type of mechanism is involved in the formation of the potassium and cesium ternary hydrides.

It is interesting to note that an analogous preparative reaction, in which the $\text{sec-C}_4\text{H}_9^-$ anion may serve to aid the deprotonation of molecular hydrogen, has been reported [28]



where the strong base is the $\text{sec-C}_4\text{H}_9^-$ anion.

X-Ray Data

The face-centered cubic phase with $a_0 = 3.91 \text{ \AA}$ observed in the powder pattern of the potassium compound may be cubic CuH, in view of the fact that the lattice constant for the cubic form of CuH has been predicted to be 4.04 \AA [29]. The value (3.91 \AA) of a_0 that is observed suggests a high degree of covalent character in the CuH bond. The absence of a Cu-H band in the infrared spectrum of the potassium compound is indicative of low bond polarity [30] and is consistent with the absence of Cu-H bands in the infrared spectra of soluble CuH [11], wurzite CuH [30], and $[\text{CuHP}(\text{C}_6\text{H}_5)_3]_6$ [32].

The synthesis of an unstable ternary hydride of lithium and copper with the composition LiCuH_2 has recently been reported [32]. The existence of this compound and the analytical data (above) suggest that the face-centered cubic phase with $a_0 = 8.00 \text{ \AA}$ is KCuH_2 . Thus the formula $\text{K}_2\text{Cu}_3\text{H}_5 \cdot x\text{NH}_3$ may be written $(\text{KCuH}_2)_2 \cdot \text{CuH} \cdot x\text{NH}_3$. The mole ratio was consistently $2\text{KCuH}_2 : 1\text{CuH}$ even though the reaction ratio of NH_2^- to Cu(I) was varied by a factor of four. This suggests that perhaps $\text{K}_2\text{Cu}_3\text{H}_5 \cdot \text{NH}_3$ was the original compound, and that it decomposed to KCuH_2 and CuH, a reaction that is similar to the decomposition of $\text{NaZn}_2(\text{CH}_3)_2\text{H}_3$ to NaZnH_3 and $\text{Zn}(\text{CH}_3)_2$ [33]. Assuming a 2:1 molar mixture for the phases KCuH_2 and CuH and allowing 8 formula units of KCuH_2 [34] per unit cell (to fill space) [35] and 4 formula units of CuH per unit cell the density is calculated to be 3.55 gm/ml which is consistent with the observed density of $4.0 \pm 0.5 \text{ gm/ml}$.

There are numerous examples of cubic ternary hydrides: the ternary hydrides of calcium and strontium with iridium, rhodium, and ruthenium (space group Fm3m) [12]; KMgH_3 [28]; SrLiH_3 , BaLiH_3 , and EuLiH_3 (perovskite structure) [36]; Sr_2PdH , SrPd_2H (8 formula units per unit cell, space group Fd3m) and $\text{Ca}_3\text{Pd}_2\text{H}_4$ [34]. The space groups $F\bar{4}3m$, Fd3m, F23, Fd3, and $F4_132$ are the only ones possible for KCuH_2 since only these space groups allow 8 molecules of KCuH_2 per unit cell.

The non-cubic lattice of the cesium compound may result from distortion of a cubic lattice by the large Cs^+ cation [37]; BaNiO_2 has an orthorhombic structure due to this cause [38].

The X-ray data for the thermally decomposed potassium compound suggests that the increased amount of HD resulting from treatment of the residue with D_2O does not come from reaction with alkali metal hydride. The potassium compound decomposes in a complex way, reminiscent of the thermal decomposition of LiAlH_4 [39], where Li_3AlH_6 and "LiAl" have been postulated as products. The compound K_2CuH_3 (analogous to the compound $\text{K}_2\text{Cu}(\text{NH}_2)_3$ [10]) is a probable decomposition product, but formation of "KCu" is unlikely, because potassium and copper do not form alloys [40].

The cubic phase ($a_0 = 6.067 \text{ \AA}$) detected in the powder pattern of the decomposed CsCuH_2 is undoubtedly cesium metal ($a_0 = 6.067$ at 78°K [18]). The decomposition reaction appears to be: $\text{CsCuH}_2 \rightarrow \text{Cs} + \text{Cu} + \text{H}_2$.

Raman Data

The band at 4225 cm^{-1} in the Raman spectrum of the potassium compound is ascribed to molecular hydrogen. The decrease in the

intensity of the band that accompanies blackening of the surface of the sample suggests that hydrogen molecules trapped in the solid are responsible for the absorption, and that they escape during the disruption of the solid structure. The difference between the observed frequency and 4161 cm^{-1} (the normal stretching frequency of H_2 [41]) can be explained by postulating that the hydrogen molecules are trapped in very small holes. Positive vibration frequency shifts, $\nu_{\text{matrix}} - \nu_{\text{gas}}$, of diatomic molecules in inert gas matrices at low temperatures are observed when the substitutional site (i.e. the vacancy created by removing a matrix element) is very small, with the result that the repulsion interaction has become larger than the electrostatic, inductive, and dispersive interactions. Hydrogen chloride in an argon matrix has a calculated repulsion term of $+60.8 \text{ cm}^{-1}$ [42,43,44], indicating that our observed shift of $+64 \text{ cm}^{-1}$ is not unreasonable.

An alternative explanation [45] is that holes in the solid are doubly occupied by hydrogen molecules. Interaction between their vibrational states would result in a higher frequency Raman active symmetric vibrational mode (corresponding to the observed band at 4225 cm^{-1}) and a lower frequency Raman inactive antisymmetric vibrational mode.

The fact that the Raman bands of the potassium compound at 3450 and 3367 cm^{-1} do not decrease in intensity or shift in frequency when the compound blackens is consistent with their identification as ammonia bands (cf. 3414 , 3336 cm^{-1} [42]) and the formulation of the compound as an ammoniate. The frequencies are too high to be

attributed to potassium amide (which has infrared bands at 3210 and 3258 cm^{-1} [46]) or to strongly coordinated ammonia (for example, $[\text{Ni}(\text{NH}_3)_6](\text{ClO}_4)_2$ has bands at 3397 and 3312 cm^{-1} [41]).

Acknowledgements.- We wish to thank Robert Snyder of the Shell Development Co. for recording the Raman spectra and for lending us the low temperature infrared cell, Professor Neil Bartlett for the use of the dry box and the powder camera, and Professor Kenneth Raymond for the use of the low temperature device. This research was supported by the U. S. Atomic Energy Commission.

Table 1

Values of the parameters x and y
calculated from analytical data (see hydrolysis equation)

	x	y
Potassium compound:	0.65	1.25
	0.63	1.29
	0.68	1.28
	0.68	1.36
	0.64	1.42
	0.63	1.53
	0.73	1.47
	0.67	1.63
Cesium compound:	0.96	1.54
	0.89	1.71
	0.91	1.29

Table 2

X-Ray Powder Data (d, Å) for $K_2Cu_3H_5 \cdot xNH_3$

Observed ^a	KCuH ₂ (calc.)	hkl	CuH (calc.)	hkl	Copper(metal) ^b	I/I ₀
4.635 (s)	4.640	111				
4.014 (w)	4.010	200				
2.832 (s)	2.830	220				
2.408 (m)	2.412	311				
2.260 (m)			2.26	111		
2.081 (m)					2.088	100
1.957 (w)			1.957	200		
1.823 (w)	1.820	331			1.808	46
1.628 (m)	1.633	422				
1.542 (w)	1.540	333				
1.382 (w)			1.384	220		
1.350 (w)	1.350	531				
1.269 (w)					1.278	20
1.179 (m)			1.180	311		
1.129 (w)			1.129	222		
1.086 (vw)					1.0900	17
1.038 (vw)					1.0436	5
0.8980 (vw)			0.8980	331	0.9038	3
0.8760 (w)			0.8755	420	0.8293	9
0.8000 (w)	.8000	860			0.8083	8

^a Line intensities estimated visually

^b Powder Diffraction File of the Joint Committee on Powder Diffraction Standards, Philadelphia, Pa.

Table 3

X-Ray Powder Data (d, Å) for $\text{CsCuH}_2 \cdot x\text{NH}_3$

Observed ^a	Calculated	hkl
4.128 (m)	4.128	200
3.965 (m)	3.965	210
3.742 (m)	3.740	201
3.213 (w)	3.205	031
3.058 (s)	3.052	221
2.888 (vw)	2.863	202
2.777 (w)	2.765	212
2.153 (m)	2.145	241
2.074 (m)	2.078	033
1.955 (vw)	1.943	242
1.866 (vw)	1.884	104, 313
1.770 (m)	1.770	124
1.691 (vw)	1.690	015, 034
1.623 (vw)	1.622	413
1.514 (vw)	1.515	105
1.355 (vvw)	1.360	305
1.280 (vvw)	1.282	462
1.242 (vvw)	1.241	415
1.205 (vvw)	1.205	701
0.8869 (vvw)	0.8869	367
0.8256 (vvw)	0.8256	864

^a Line intensities estimated visually

Table 4

X-Ray Powder Data (d, Å) for thermally decomposed $K_2Cu_3H_5 \cdot xNH_3$ ^a

Decomposed at 23° for 15 hours	Decomposed at 90° for 24 hours	Copper (metal) ^b	I/I ₀
2.161 (vww)	3.532 (w)		
2.831 (s)	3.325 (w)		
2.478 (vw)	3.034 (w)		
2.298 (vww)	2.881 (w)		
2.193 (vw)	2.490 (vww)		
2.083 (vs)	2.085 (vs)	2.088	100
	2.031 (vw)		
1.821 (m)	1.807 (s)	1.808	46
	1.731 (vw)		
1.636 (vw)	1.661 (vww)		
	1.582 (vww)		
	1.440 (vww)		
1.281 (m)	1.276 (s)	1.278	20
1.093 (m)	1.089 (s)	1.0900	17
1.049 (vw)	1.042 (m)	1.0436	5
	0.903 (vww)	0.9038	3
0.828 (vww)	0.829 (m)	0.8293	9
	0.808 (m)	0.8083	8

^a Line intensities estimated visually

^b Footnote b, Table 2

Table 5

X-Ray Powder Data for Thermally Decomposed $\text{CsCuH}_2 \cdot x\text{NH}_3$

Observed ^a	Cesium ^b	Copper (metal) ^c	I/I ₀
3.510 (vww)	3.503		
3.032 (vww)	3.033		
2.141 (vww)	2.145		
2.081 (vs)		2.088	100
1.796 (s)		1.808	46
1.392 (vww)	1.392		
1.272 (s)		1.278	20
1.088 (s)		1.0900	17
1.041 (w)		1.0436	5
0.9010 (vww)		0.9038	3
0.8276 (m)		0.8293	9
0.8078 (m)		0.8083	8

^a Line intensities estimated visually

^b Reference 18

^c Footnote b, Table 2

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