

Contribution from the Institute of Crystallography, BSP Dorigny, CH-1015 Lausanne, Switzerland, and the Institute of Inorganic and Analytical Chemistry, Place du Château 3, University of Lausanne, CH-1005 Lausanne, Switzerland

## Structure of the Red Copper(II)-Doped Methylammonium Tetrachloromanganate(II)

GERVAIS CHAPUIS,\* GEORGES BRUNISHOLZ, COLETTE JAVET, and RAYMOND ROULET

Received April 2, 1982

The phase diagram of  $(\text{CH}_3\text{NH}_3)_2\text{Mn}_{1-x}\text{Cu}_x\text{Cl}_4$  obtained by chemical analysis and powder diffraction shows a large miscibility gap in the range  $0.03 < x < 0.96$ . For  $x = 0.03$ , the crystals are dark red and a structure analysis was performed from single-crystal X-ray diffraction measurements up to  $(\sin \theta)/\lambda = 0.71$ . The structure refined to  $R_w = 0.021$  including isotropic H atoms. The structure is isomorphous with the corresponding Mn compound and can be described by an infinite sequence of alternating layers of  $\text{MnCl}_6$  octahedra and  $(\text{CH}_3\text{NH}_3)^+$  ions. The Cu atoms are stochastically distributed among the Mn sites. A difference Fourier synthesis revealed two peaks that are interpreted as Cl atoms bonded to Cu. The copper coordination is thus an octahedron compressed along the normal to the layer with  $4/mmm (D_{4h})$  symmetry.

### Introduction

Mixed-metal salts of compounds with low-dimensional structures have been studied recently to understand their magnetic behavior both from the theoretical and from the experimental point of view.<sup>1</sup> In the two-dimensional layer compounds  $(\text{CH}_3\text{NH}_3)_2\text{Cu}_x\text{Mn}_{1-x}\text{Cl}_4$  (abbreviated ClCuMn) some remarkable features have been found on EPR spectra.<sup>2</sup> In addition to the Mn and Cu lines, a new signal has been observed for which numerous hypotheses based on the Jahn-Teller distortion of Cu have been proposed. Most of the Cu-doped Mn salts of the mono- or dialkylammonium tetrachlorometallate type exhibit a dark red color, which is observed neither in the pure Mn (pink) nor in the pure Cu salt (yellow). For an explanation of the origin of this color, single crystals of Cu-doped ethylenediammonium tetrachloromanganate were studied by absorption spectroscopy.<sup>3</sup> On the basis of their measurements, the authors proposed a new Cu coordination of the Cl atoms with  $mmm (D_{2h})$  or  $4/mmm (D_{4h})$  symmetry.

The aim of the present study is twofold. First, we wish to know to what extent Cu atoms can be incorporated in single crystals of ClCuMn. Second, can we deduce from X-ray diffraction of a Cu-doped single crystal of ClMn the coordination of copper? In this work, we present the phase diagram of the system  $(\text{CH}_3\text{NH}_3)_2\text{MnCl}_4-(\text{CH}_3\text{NH}_3)_2\text{CuCl}_4-\text{CH}_3\text{OH}$  established by chemical analysis, the powder diffractograms of different members of the series, and the results of a structural analysis based on single-crystal diffraction.

### Experimental Section

**Phase Diagram.**  $(\text{CH}_3\text{NH}_3)_2\text{MCl}_4$  complexes ( $M = \text{Mn}, \text{Cu}$ ) were obtained by evaporation of solutions containing  $\text{CH}_3\text{NH}_3\text{Cl}$  and  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  or  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (molar ratio 2:1) in ethanol-methanol. A series of Pyrex tubes containing ca. 1 g of  $(\text{CH}_3\text{NH}_3)_2\text{MCl}_4$  with various Mn:Cu ratios, ca. 6 g dry methanol, and a Pyrex rod were fixed on a rotating wheel immersed in a thermostated bath at  $20.0 \pm 0.1$  °C (the technique used to equilibrate mixed crystals has been described elsewhere<sup>4</sup>). The Pyrex rod was used to avoid the formation of large crystals, and the phase equilibrium was considered achieved when two successive analyses of the mother liquor and the microcrystals were identical. Equilibrium was reached after 3 weeks. The metal contents of the methanol solutions and the centrifuged microcrystals were analyzed separately. Manganese was determined by complexometry with KCN as masking ligand.<sup>5</sup> Copper was determined by titration with triethylenetetramine in the presence of calcein W under filtered UV light.<sup>6</sup> Chemical analysis was checked for several batches of crystals by ARL microprobe analysis, which gave identical results within experimental error (ca. 1%).

**Powder Diffractograms.** The following Guinier diffractograms were taken at room temperature and evaluated with the program LATCON<sup>7</sup> (from left to right:  $hkl, d$  (Å)).  $(\text{CH}_3\text{NH}_3)_2\text{MnCl}_4$  (abbreviated ClMn): 002, 9.668; 111, 4.940; 113, 4.005; 020, 3.627; 200, 3.599; 022, 3.397; 202, 3.372; 006, 3.225; 121, 3.199; 024, 2.905; 220, 2.559;

Table I. Comparison of Cell Parameters (Å)

compd	a	b	c	ref
ClMn powder	7.205 (3)	7.265 (2)	19.385 (9)	this work
single cryst	7.207 (1)	7.273 (1)	19.416 (2)	this work
single cryst	7.215 (3)	7.276 (3)	19.41 (1)	8
ClCu powder	7.265 (4)	7.364 (5)	18.64 (1)	this work
single cryst	7.276 (1) <sup>c</sup>	7.380 (1)	18.654 (2)	this work
single cryst <sup>a</sup>	7.30	7.54	7 × 18.55	9
ClCuMn <sup>b</sup> powder	7.205 (3)	7.265 (2)	19.395 (9)	this work
single cryst	7.209 (2)	7.272 (2)	19.402 (8)	this work

<sup>a</sup> Weissenberg films. <sup>b</sup>  $(\text{CH}_3\text{NH}_3)_2\text{Cu}_{0.03}\text{Mn}_{0.97}\text{Cl}_4$  (red). <sup>c</sup>  $\beta = 90.37$  (1)°.

222, 2.473; 171, 2.438; 008, 2.424; 131, 2.281; 040, 1.816; 400, 1.802; 042, 1.786; 228, 1.759.  $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_4$  (abbreviated ClCu): 002, 9.317; 111, 4.962; 113, 3.968; 200, 3.677; 020, 3.627; 006, 3.100; 204, 2.885; 024, 2.863; 220, 2.586; 222, 2.490; 117, 2.365; 311, 2.308; 131, 2.283; 226, 1.989; 0,0,10, 1.865; 400, 1.843; 040, 1.818; 228, 1.733.  $(\text{CH}_3\text{NH}_3)_2\text{Cu}_x\text{Mn}_{1-x}\text{Cl}_4$ : same powder diffractograms as ClMn for  $x < 0.03$  and ClCu for  $x > 0.96$ ; superposition of both for  $0.03 \leq x \leq 0.96$ .

A series of diffractograms were also recorded at temperatures between -20 and +35 °C for  $(\text{CH}_3\text{NH}_3)_2\text{Cu}_{0.03}\text{Mn}_{0.97}\text{Cl}_4$  to check for an eventual phase transition. No change could be observed in the whole temperature range with respect to the room-temperature diffractogram.

**Preparation of Single Crystals.** A mixture of ClMn and ClCu (9 mol % Cu) was dissolved in the minimum amount of methanol. Warm ethanol was added, and the solvents were allowed to evaporate at room temperature until ca. 2% of the tetrachlorometalate crystallized as red prisms. As a phase equilibrium is not ensured by this procedure, it is essential to limit the amount of crystals formed as well as their size. Crystallization of a large amount of tetrachlorometalate (ca. 20%) gave single crystals varying in composition. Crystallization by slow cooling of an unstirred solution gave larger crystals (ca. 1-2 mm), which were inhomogeneous as their color varied from red to yellow on going from the center to the top of the prism. Table I shows that the prepared single crystals have the same cell parameters as the microcrystals obtained in the phase equilibrium studies.

### Results and Discussion

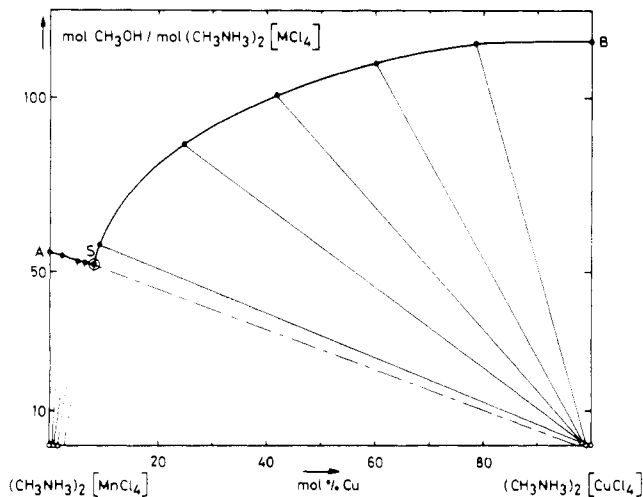
**1. Phase Diagram.** The Jänecke solubility diagram for the system  $(\text{CH}_3\text{NH}_3)_2\text{MnCl}_4-(\text{CH}_3\text{NH}_3)_2\text{CuCl}_4-\text{CH}_3\text{OH}$  at 20 °C presents a large miscibility gap for the solid  $(\text{CH}_3\text{NH}_3)_2\text{Cu}_x\text{Mn}_{1-x}\text{Cl}_4$  in the range  $0.028 < x < 0.960$

- (1) Birgeneau, R. J.; Shirane, G. *Phys. Today* 1978, 31, 32. Endoh, Y.; Heilmann, I. U.; Birgeneau, R. J.; Shirane, G.; McGurn, A. R.; Thorpe, M. F. *Phys. Rev. B: Condens. Matter* 1981, 23, 4582.
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- (9) Willett, R. D. *J. Chem. Phys.* 1964, 41, 2243.

\* To whom correspondence should be addressed at the Institute of Crystallography, BSP Dorigny.

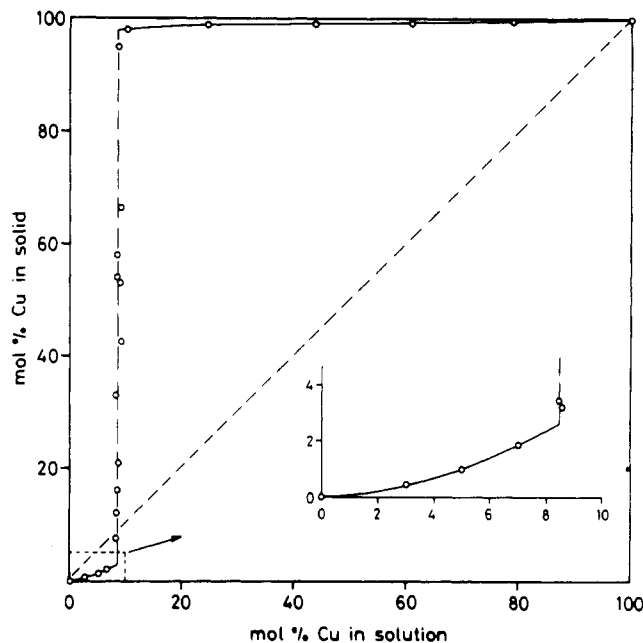
**Table II.** Summary of Crystal Data, Intensity Collection, and Refinement

formula	$(\text{CH}_3\text{NH}_3)_2\text{Cu}_x\text{Mn}_{1-x}\text{Cl}_4$ ( $x = 0.03$ )	radiation	Mo K $\alpha$ Nb filtered ( $\lambda = 0.71069 \text{ \AA}$ )
mol wt	260.9	$\mu$ , $\text{cm}^{-1}$	23.6
dimens, mm	$0.20 \times 0.20 \times 0.012$	min/max transmission	0.715/0.972
cryst class	orthorhombic	scan method	$2\theta-\theta$
$a$ , $\text{\AA}$	7.209 (2)	bkgd source	scan profile interpretation <sup>15</sup>
$b$ , $\text{\AA}$	7.272 (2)	$((\sin \theta)/\lambda)_{\text{max}}$	0.71
$c$ , $\text{\AA}$	19.402 (7)	data collected	$+h, +k, \pm l$
$V$ , $\text{\AA}^3$	1017.1 (5)	no. of unique reflns	800
$Z$	4	no. of reflns $> 3\sigma(I)$	452
$d_{\text{calcd}}$ , $\text{g/cm}^3$	1.703	no. of observns/no. of variables	14.6
$d_{\text{obsd}}$ , $\text{g/cm}^3$	1.709 (22 °C; $\text{CCl}_4\text{-CHBr}_3$ )	refinement method	full-matrix least squares
$F_{000}$	524	function minimized	$\sum w( F_o  -  F_c )^2$
space group	<i>Bmab</i> (No. 64)	$w$	$1/\sigma^2$
systematic absences	$hkl: h + l = 2n + 1$ $h0l: h = 2n + 1$ $hk0: k = 2n + 1$	$R$	0.028
		$R_w$	0.021
		goodness of fit	1.26

**Figure 1.** Jänecke phase diagram for the system  $(\text{CH}_3\text{NH}_3)_2\text{MnCl}_4\text{-(CH}_3\text{NH}_3)_2\text{CuCl}_4\text{-CH}_3\text{OH}$  at 20 °C: (A) 0, 55.96; (B) 100, 115.88; (S) 8.5, 51.81.

(Figure 1). The partition diagram (Figure 2) shows that the solids having a global Cu content within this range are mixtures of red crystals with the lower limit composition and of yellow crystals with the upper limit composition. The solution containing 8.5 mol % Cu (S) is in equilibrium with all these mixtures and represents an end point of crystallization. These results are at variance with a previous claim<sup>10</sup> that incorporation of copper in ClMn is unrestricted. All the yellow crystals in the range  $0.96 < x < 1$  have the same powder diffractograms as ClCu. The crystals in the range  $0 < x < 0.03$  are the only ones having the anomalous red color, and they all exhibit the same powder diffractograms and the same calculated cell constants as ClMn within  $1\sigma$ . The structure of a crystal with  $x = 0.03$  should thus be representative of this class of compounds.

**2. Structural Analysis of  $(\text{CH}_3\text{NH}_3)_2\text{Cu}_{0.03}\text{Mn}_{0.97}\text{Cl}_4$ .** Single-crystal diffraction intensities were collected on a Syntex P2<sub>1</sub> autodiffractometer. The crystal habit was a thin square plate delimited by the eight faces ( $\pm 1, \pm 1, 0$ ) and  $(0, 0, \pm 1)$ . The dimensions were  $0.20 \times 0.20 \times 0.012$  mm; owing to the asymmetric shape of the crystal, an absorption correction was performed. Lattice constants were determined by least-squares methods from 12 reflections centered on the diffractometer with  $11^\circ < 2\theta < 34^\circ$  (Mo K $\alpha$  radiation). The space group *Bmab* was determined from systematic absences of the intensities. A very large number of crystals were twinned along  $[110]$ , and a careful search was needed to find an untwinned sample under a polarizing microscope. The crystal was also

**Figure 2.** Partition diagram.**Table III.** Atomic Coordinates of ClCuMn with Population Parameter  $p$ 

atom	$x$	$y$	$z$	$p$
Mn	0	0	0	0.98 (1)
Cu	0	0	0	0.02
Cl(1)	0.25	0.25	0.01028 (4)	
Cl(2)	0	-0.0344 (1)	0.12751 (5)	
N	0.5	-0.0169 (7)	0.1157 (2)	
C	0.5	0.033 (1)	0.1875 (3)	
H(1)	0.5	-0.134 (6)	0.104 (2)	
H(2)	0.561 (9)	0.032 (6)	0.101 (3)	
H(3)	0.5	0.129 (7)	0.201 (3)	
H(4)	0.418 (5)	-0.036 (5)	0.209 (2)	

checked for twinning on the diffractometer. No reflection intensity of the type  $h + l = 2n + 1$  could be found up to  $2\theta = 25^\circ$ , as would be the case in the presence of a twin. Table II gives a summary of all relevant information on the crystal data. For the reduction of the intensities and refinement of the structure, the X-RAY 72 system of programs was used.<sup>11</sup> Atomic scattering factors calculated by Cromer and Mann<sup>12</sup> were assigned to Mn(II), Cu(II), Cl(-I), N, and C atoms. For H atoms the values calculated by Stewart et al.<sup>13</sup> were in-

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(11) Stewart, J. M.; Kundell, F. A.; Baldwin, J. C. X-RAY 72, version of June 1972, Technical Report TR-192 of the Computing Center, University of Maryland (as modified by D. Schwarzenbach).

(12) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *A24*, 321.(13) Stewart, R. G.; Davidson, E. R.; Simpson, W. T. *J. Phys. Chem.* **1965**, *42*, 3175.

Table IV. Thermal Parameters<sup>a</sup>

atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Mn	0.0189 (3)	0.0187 (4)	0.0302 (4)	0	0	0.0007 (3)
Cu	0.0189	0.0187	0.0302	0	0	0.0007
Cl(1)	0.0248 (4)	0.0267 (4)	0.0597 (6)	-0.0076 (3)	0	0
Cl(2)	0.0663 (6)	0.0454 (6)	0.0275 (5)	0	0	-0.0008 (4)
N	0.064 (2)	0.046 (2)	0.037 (2)	0	0	-0.001 (2)
C	0.102 (5)	0.080 (4)	0.034 (3)	0	0	-0.010 (3)

atom	$U, \text{\AA}^2$	atom	$U, \text{\AA}^2$	atom	$U, \text{\AA}^2$
H(1)	0.09 (2)	H(3)	0.12 (3)	H(4)	0.16 (2)
H(2)	0.21 (3)				

<sup>a</sup> The temperature factor has the form  $\exp(-T)$  where  $T = 8\pi^2 U((\sin \theta)/\lambda)^2$  for isotropic atoms and  $T = 2\pi^2 \sum h_i h_j a_i^* a_j^* U_{ij}$  for anisotropic atoms.  $a_i^*$  are reciprocal axial lengths, and  $h_i$  are coefficients of the scattering vector.

Table V. Bond Distances (Å) and Angles (deg)

Mn-Cl(1)	2.5677 (5)	C-H(3)	0.74 (5)
Mn-Cl(2)	2.487 (1)	C-H(4)	0.88 (3)
N-C	1.441 (6)	N...Cl(1)	3.346 (4)
N-H(1)	0.88 (5)	N...Cl(2) <sup>b</sup>	3.271 (5)
N-H(2)	0.63 (5)	Cl(1)-Mn-Cl(2)	89.65 (2)
		Cl(1)-Mn-Cl(1) <sup>a</sup>	89.16 (2)

<sup>a</sup>  $-x, y, z$ . <sup>b</sup>  $1/2 + x, -1/2 - y, z$ .

troduced in the structure factor calculations. Anomalous dispersion corrections<sup>14</sup> were applied to Cu and Mn atoms.

The atomic coordinates of the non-hydrogen atoms of ClMn<sup>8</sup> were transformed to fit the space group orientation and used as starting parameters for the refinement of the structure. A difference Fourier synthesis resulting from an anisotropic refinement of the non-hydrogen atoms revealed all the H atoms. They were subsequently refined with isotropic thermal coefficients. At this stage of refinement, a Cu atom was included in the model on the Mn site with an occupation of 0.03. The anisotropic temperature coefficients were constrained to be identical with those of the Mn atom, and the population parameter was refined subject to the condition  $p(\text{Mn}) + (1 - p)(\text{Cu}) = 1$ . The value of  $p$  converged to 0.98 (1) in accordance with the chemical analysis of the compound. A difference Fourier revealed two additional peaks, pk(1) and pk(2), with coordinates (0, 0.0467, 0.1273) and (0.25, 0.25, -0.0172) and densities of 0.79 and 0.57 e/Å<sup>3</sup>, respectively. An attempt to include these atoms as partially populated Cl atoms in the least-squares calculation failed owing to the large correlation between the population and the thermal parameters. The relevant information on the structure refinement is reported in Table II. Atomic coordinates, thermal parameters, and bond distances and angles are reported in Tables III-V, respectively. The list of structure factors is given as supplementary material.

**3. Description of the Structure and Discussion.** The structures of the Cu-doped compound and ClMn are essentially the same. The atomic coordinates of Mn, Cl, N, and C differ by less than  $5\sigma$ , for the two structures. Layers of corner-sharing MnCl<sub>6</sub> octahedra alternate with layers of (CH<sub>3</sub>NH<sub>3</sub>)<sup>+</sup> ions perpendicular to the  $c^*$  axis. The layers are linked together by means of hydrogen bonds between Cl and N atoms. The Cl octahedra are compressed in both cases along the axial Cl atoms. Figure 3 shows schematically the configuration of the ammonium hydrogen bonds with two equatorial (Cl(1)) and one axial (Cl(2)) atoms. This bonding scheme is responsible for the tilt of 5.8° of the octahedra about the [100] axis.

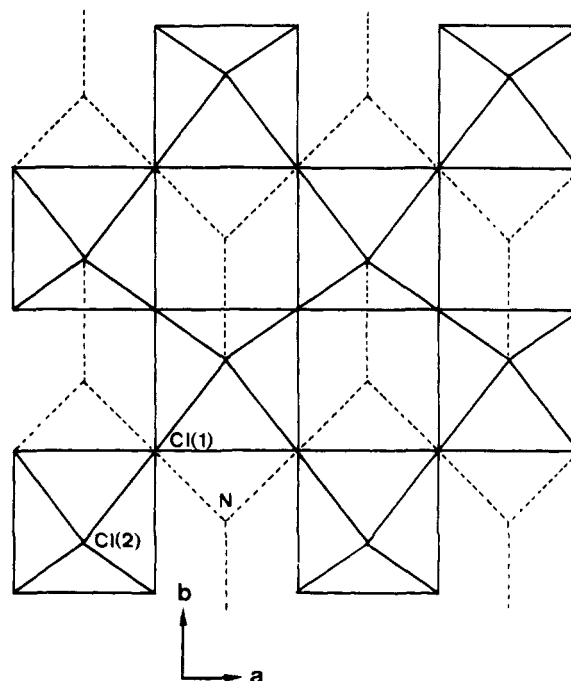


Figure 3. Schematic drawing of a single layer of ClCuMn. Cl octahedra are represented by solid lines. Dotted lines indicate the three N...Cl hydrogen bonds to one axial Cl(2) and two equatorial Cl(1) atoms. Metal and C atoms are omitted for clarity.

The distances to the Mn atom of the two additional peaks observed on the difference Fourier synthesis are 2.49 (pk(1)) and 2.58 Å (pk(2)). It is thus very likely that both can be interpreted as Cl atoms. The bond angles with Mn on the apex are nearly 90° (pk(1)-Mn-pk(2) = 88.2°, pk(2)-Mn-pk(2') = 88.5°). Thus the coordination figure formed by these two atoms and symmetry-related atoms is an octahedron compressed along the axial Cl atoms. It is tempting to interpret these two peaks as Cl atoms bonded to Cu. We have to evaluate first whether the Cu-bonded Cl atoms can be observed on a difference Fourier synthesis as we assume that their positions differ from the Cl bonded to Mn atoms. The Fourier transform of the atomic scattering factor  $f(s)$  gives the electron density of the corresponding atom in the crystal. If  $f(s) = \sum_1^5 a_i \exp(-b_i s^2)$ , where  $s = (\sin \theta)/\lambda$ , the Fourier transform is given by<sup>16</sup>

$$\rho(r) = 8\pi^{3/2} \sum_1^5 a_i b_i^{3/2} \exp(-4\pi^2 r^2 / b_i')$$

where  $b_i'$  represents the value of  $b_i$  including the temperature factor. The values of  $a_i$  and  $b_i$  are tabulated.<sup>17</sup> On the basis

(14) Cromer, D. T. *Acta Crystallogr.* **1965**, *18*, 17.

(15) Blessing, H.; Coppens, P.; Becker, P. *J. Appl. Crystallogr.* **1972**, *7*, 488. Schwarzenbach, D. Abstracts, Fourth European Crystallographic Meeting, 1977; p 134.

(16) Schwarzenbach, D.; Ngo Thong *Acta Crystallogr., Sect. A* **1979**, *A35*, 652.

of an isotropic temperature factor  $U = 0.06 \text{ \AA}^2$ , the ratio of the electron density of 0.03 Cl atom to that of a hydrogen is larger than 2 for  $r = 0.2$ . This result reinforces thus our hypothesis that pk(1) and pk(2) represent Cl atoms bonded to Cu.

In  $\text{ClCu}^{18}$  the Cl atoms form a tetragonal bipyramid with Cu-Cl distances of 2.29 Å in the basis and 2.91 Å along the pseudo-fourfold axis parallel to the layer plane. In  $\text{ClCuMn}$ , such a geometry cannot be realized for stochastically distributed Cu atoms as the coordination of the surrounding Mn atoms would be seriously modified. In our hypothesis, the equatorial Cu-bonded Cl atoms are constrained by the surrounding atoms whereas the axial Cl can be displaced more freely subject to the constraints of the hydrogen bonds. The symmetry of the Cu coordination would thus be approximately  $4/mmm$  ( $D_{4h}$ ) with the fourfold axis nearly parallel to the  $c$  axis. Our model derived by X-ray diffraction is very similar to one of the coordination models proposed for a similar compound on the basis of absorption spectroscopy measurements.<sup>3</sup> One of the distances ( $d(\text{Cu-Cl}) = 2.49 \text{ \AA}$ ) differs from the one proposed by the authors ( $d \approx 2.2\text{-}2.3 \text{ \AA}$ ) whereas the other Cu-Cl distances are in accordance.

There is however another interpretation that should not be overlooked. The octahedron formed by pk(1) and pk(2) is very similar to the one formed by Cl(1) and Cl(2). Both figures can be superposed by a rotation of  $12^\circ$  about the  $a$  axis. In

this hypothesis, pk(1) and pk(2) would result from a disorder in the packing of the  $\text{MnCl}_4$  layers where approximately 2% of the octahedra have an opposite tilt with respect to the normal to the layer. In view of the dimensions of the crystal ( $4.8 \times 10^{-4} \text{ mm}^3$ ), no diffuse scattering can be expected to be observed on X-ray film even if our hypothesis is valid. Larger single-crystal specimens tend to grow with a variable Cu concentration, as observed by the changing of color under the microscope. The diffraction pattern of a reasonably large crystal would thus not be considered as representative of the structure solved in this work. On the basis of the second hypothesis being true and in view of the electron density of the Cl atoms calculated by Fourier transform of the atomic scattering factor, we can postulate that the Cu atoms are distributed among the Mn sites with the same Cl coordination. In both hypotheses however, the Cu coordination remains the same.

In view of these arguments it is understandable why only a small percentage of Cu atoms can be incorporated into a  $\text{MnCl}_4$  framework as deduced from the phase diagram. The usual  $[4 + 2]$  Cu coordination found in this type of compounds cannot be realized without perturbation of the  $\text{MnCl}_4$  octahedra. The red color of the mixed compound originates thus very probably in the unusual octahedral coordination on the basis of absorption spectroscopy<sup>3</sup> and X-ray diffraction.

**Acknowledgment.** This work was supported by the Swiss National Science Foundation (Grant No. 2.067-0.81). We wish to thank Professor D. Schwarzenbach for helpful discussions.

**Registry No.**  $(\text{CH}_3\text{NH}_3)_2\text{MnCl}_4$ , 12121-86-7;  $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_4$ , 16950-47-3;  $\text{CH}_3\text{OH}$ , 67-56-1.

**Supplementary Material Available:** A listing of structure factor amplitudes (5 pages). Ordering information is given on any current masthead page.

(17) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(18) The structure of  $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_4$  was determined by single-crystal diffraction to obtain the corresponding Cu-Cl distances: space group  $B2_1/c$ ;  $a = 7.276$  (1),  $b = 7.380$  (1),  $c = 18.654$  (2) Å;  $\beta = 90.37$  (1) $^\circ$ . The ammonium hydrogen atoms are linked by H bonds to two axial Cl's and one equatorial Cl with N...Cl distances from 3.29 to 3.36 Å. The space group and lattice parameters are different from those reported in ref 9.

Contribution from the Department of Chemistry,  
University of Cincinnati, Cincinnati, Ohio 45221

## The Chemistry of [Co]Cobalamins: Equilibrium Constants and Energies of Formation of Species in Aqueous Solution

KENNETH A. RUBINSON,\* HEMAXINI V. PAREKH, EKEI ITABASHI, and HARRY B. MARK, JR.\*

Received May 21, 1982

A thermochemical analysis is carried out with use of electrochemical equilibrium data derived from spectroelectrochemical experiments on aquo[Co(III)]cobalamin in aqueous solutions. The [Co(II)]cobalamin species are more stable than their corresponding Co(III) or Co(I) species in the pH range 0-11. The oxidation-reduction reaction scheme of the [Co]cobalamins is explained by the pH-dependent redox potentials of the various species. These findings and, hence, the redox properties of methylcobalamin and coenzyme B<sub>12</sub> are explained by a simple  $\sigma$ -orbital model. The same theoretical model also can be used to explain the electronic mechanism for photolysis of the Co-C bond as well as the low-energy limit for the cleavage. The thermal cleavage of the Co-C bond is explained as well.

The function of the B<sub>12</sub> enzymes undoubtedly depends on the fundamental chemistry of the alkyl[Co]cobalamin reaction center. Our understanding of the enzymatic processes thus requires knowledge of the equilibrium thermochemical properties, which quantitate the effects of the benzimidazole base binding, of the cobalt oxidation state, and of the cobalt-carbon bond energy. These all can be obtained in principle from electrochemical equilibrium measurements. For these, the primary requirement for determining the Co-C equilibrium bonding properties is the measurement of a reversible equilibrium potential with known products.

Toward this end, using a polarographic technique, Birke and Kim have calculated that methyl[Co(III)]cobalamin's reversible reduction potential is  $-1.24 \text{ V}$  vs. SCE in neutral aqueous

solution in the presence of Triton X-100, a nonionic detergent used to prevent adsorption on the mercury electrode.<sup>1</sup> Coenzyme B<sub>12</sub> showed a similar value of  $-1.26 \text{ V}$ . An electrochemical half-wave potential value of about  $-1.5 \text{ V}$  is obtained when the methyl complex is reduced irreversibly at an Hg-Au minigrid electrode in neutral aqueous media in the absence of Triton X-100. In this case, the alkyl-cobalt bond breaks after a one-electron transfer to yield ethane and [Co(I)]cobalamin exclusively.<sup>2</sup>

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(2) Rubinson, K. A.; Itabashi, E.; Mark, H. B., Jr. *Inorg. Chem.* **1982**, *21*, 3571-3573.