Table 1.

	k_{Mg}^{Ca}	k_{Mg}^{Sr}	k_{Ca}^{Cu}
B. indica polysaccharide, deacetylated	1.1	1.0	14
Alginate fragment, 90 % L-guluronic acid	35	120	8

tigated and the results given in Table 1 show that no selectivity in exchange reactions involving Mg^{2+}, Ca^{2+}, and Sr^{2+} was observed, while a selectivity for Cu^{2+} compared to Ca^{2+} was found. This latter selectivity has previously been shown to be characteristic of polymers containing carboxyl groups.[12] The remarkable lack of selectivity of the L-guluronic acid residues of *B. indica* polysaccharide for alkaline earth ions is most probably caused by these residues occurring as isolated units as indicated by Parikh and Jones.[3] This is in agreement with observations by Kohn and Furda [13] who found that the selectivity of pectins in the potassium-calcium ion exchange rapidly decreased with increasing degree of esterification.

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Crystallographic and Other Studies of Bis(*N*-methylethylenediamine)-copper(II) Complexes

III. Bis(*N*-methylethylenediamine)-copper(II) Chloride

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Bis(*N*-methylethylenediamine)copper(II) bromide and iodide, both of which are triclinic have been prepared previously.[1] The bis(*N*-methylethylenediamine)copper-(II) chloride described below is triclinic also and its other properties are similar to those of the bromide and iodide.

Experimental. *N*-Methylethylenediamine (*N*-Meen) of practicum grade from Fluka AG was purified by distillation. The other chemicals were analytical reagents.

Preparation and analyses. 0.071 mole of copper(II) chloride dihydrate in 80 ml of methanol was added dropwise to 80 ml of mechanically stirred methanol containing 0.142 mole of *N*-Meen. A crude product was precipitated with ether and dried at room temperature. Recrystallizations were performed from ethanol containing about 10 % water. Copper was determined electroanalytically, chloride as silver chloride and *N*-methylethylenediamine by potentiometric titration. (Found: Cu 22.46; Cl 25.02; *N*-Meen 52.92. Calc.: Cu 22.48; Cl 25.08; *N*-Meen 52.44).

Measurements. Weissenberg photographs were taken around two axes with a Nonius

Table 1. Powder diffraction data for bis(*N*-Meen)copper(II) chloride. Internal standard CaF_2, $a=5.4630$ Å. Cu$K\alpha$ radiation.

h k l	$10^5\sin^2\theta$		*h k l*	$10^5\sin^2\theta$		*h k l*	$10^5\sin^2\theta$	
	obs.	calc.		obs.	calc.		obs.	calc.
1 0 0	945	945	0 2 0	7188	7182	3 $\bar{2}$ 2		13474
0 0 1	1524	1525	2 $\bar{1}$ 2	7521	7523	1 $\bar{3}$ 1	14284	14295
0 1 0	1795	1796	2 1 1	8039	8046	2 $\bar{1}$ $\bar{2}$		14298
1 0 1	2092	2091	2 $\bar{1}$ $\bar{1}$		8029	0 3 $\bar{1}$	14881	14880
1 $\bar{1}$ 0	2363	2357	2 $\bar{2}$ 1	8327	8326	2 2 1	15152	15134
1 $\bar{1}$ 1	2568	2568	3 0 0	8529	8508	4 0 1		15133
1 0 $\bar{1}$	2854	2850	1 $\bar{2}$ 2	8956	8962	4 0 0		15125
1 1 0	3126	3124	1 2 $\bar{1}$		8928	1 1 $\bar{3}$		15182
1 1 $\bar{1}$	4088	4093	0 2 $\bar{2}$	9534	9542	4 $\bar{1}$ 2	16578	16584
0 1 1	4249	4256	2 $\bar{2}$ 2	10266	10273	0 2 2	16990	17024
2 $\bar{1}$ 0	4811	4810	3 $\bar{1}$ 2	11101	11108	1 3 $\bar{1}$	17328	17354
1 $\bar{1}$ $\bar{1}$	5192	5197	1 $\bar{1}$ $\bar{2}$		11087	2 $\bar{3}$ 0	17620	17641
1 1 1		5205	1 $\bar{2}$ $\bar{1}$		11135	3 1 $\bar{2}$	17942	17959
1 $\bar{1}$ 2	5835	5829	3 1 0	11450	11454	1 $\bar{2}$ $\bar{2}$		17960
2 0 $\bar{1}$	6081	6065	2 2 0	12479	12497	3 $\bar{2}$ $\bar{1}$		17923
0 0 2		6100	0 1 $\bar{3}$	12709	12716	3 $\bar{3}$ 2	19448	19431
2 1 0	6335	6344	3 1 $\bar{1}$	13154	13181	4 0 3	24369	24301
1 $\bar{2}$ 1	6631	6636	2 $\bar{1}$ 3	13444	13455	2 $\bar{4}$ 0	29437	29443
						5 $\bar{2}$ 3		29408

Table 2. Crystal data for bis(*N*-Meen)copper(II) chloride.

$a=8.199\pm0.002$ Å	Space group: $P1$ (C_1^1, No.1) or $P\bar{1}$ (C_i^1, No. 2)
$b=6.124\pm0.001$ Å	
$c=6.656\pm0.002$ Å	F.W. $=282.69$
$\alpha=108.25\pm0.03°$	$D_{obs.}=1.53$ gcm^{-3}
$\beta=77.86\pm0.03°$	$D_{calc.}=1.53$ gcm^{-3}
$\gamma=101.66\pm0.02°$	$Z=1$
$V=307$ Å^3	$\mu_{eff}=1.85$ B.M.

Weissenberg camera and powder photographs with a focussing camera of the Guinier type. Calcium fluoride was used as internal standard. The thermogravimetric curve was recorded on a Chevenard thermobalance and the visible spectra were recorded with a Beckman DK-2A spectrophotometer. Infrared spectra of the compound in Nujol and hexachlorobutadiene mulls were measured on a Perkin-Elmer Model 125 spectrophotometer. The density of the compound was determined by the flotation method (carbon tetrachloride-chloroform mixtures). The magnetic susceptibility at room temperature was evaluated by the Gouy technique using Pascal's constants for diamagnetic corrections.[2,3]

Results. Approximate dimensions of the unit cell of the compound were estimated from equi-inclination Weissenberg photographs. The compound was concluded to be triclinic and its space group $P1$ (C_1^1, No. 1) or $P\bar{1}$ (C_i^1, No. 2).[4] Values read from Weissenberg photographs were used to index the powder photographs. More accurate values of the cell dimensions were then calculated from the uniquely indexed reflections by a least squares method. The reflections read from powder photographs and calculated values are shown in Table 1 and crystal data in Table 2.

In the thermogravimetric analysis of bis(*N*-Meen)copper(II) chloride, the weight begins to decrease above 220°C, when the first ligand begins to escape. Constant weight is reached just above 760°C, when all of a the chelate has been converted into cupric oxide.

The maxima in the electronic spectra of the compound in the solid state and in aqueous and methanolic solutions are located at 554 nm, 552 nm and 576 nm, respectively. The absorption maxima in the IR spectrum of bis(*N*-Meen)copper(II) chloride (4000–450 cm^{-1}) originate from the bound *N*-Meen as in the case of bis(*N*-Meen)copper(II) bromide and iodide.[1] The magnetic moment μ_{eff}, 1.85 B.M. at 23°C, is normal.

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The Solubility of Water in Mixtures of Organic Solvents

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Some years ago we started to investigate the extraction of water and acids by organic solvents.[1,2] It is found that monomeric water predominates in all solvents studied so far, but dimers and sometimes even trimers seem to be present in several systems.[3,4] NMR data seem to indicate weak interactions between solvent and water, as illustrated in the system benzene-water.[3] In order to get further information about solute-solvent interactions we have studied the solubility of water in the following binary mixtures: benzene-hexane, benzene-octane, benzene-carbon tetrachloride and toluene-carbon tetrachloride.

A part of the content in this paper has been communicated previously.[5]

Table 1. Purity of organic compounds as checked by VPC.

Compound	Purity %
Benzene	99.8
Toluene	99.4
Hexane	99.9
Octane	98.3
Carbon tetrachloride	99.95

We are indebted to Gösta Lindgren for carrying out these measurements.

Experimental. The purity of the organic solvents used was checked by VPC. The results are given in Table 1. Samples of solvent mixtures were shaken to equilibrium with pure water at 25°C, centrifuged and the organic phase analyzed for water according to a modification of the Karl Fischer method, as described elsewhere.[2]

Treatment of data. Since the interactions between water and solvent can be expected to be small, it is tempting to try to correlate the results with the solubility parameter, as already done for water and various organic compounds.[6a,7] In this approach the relation between the solubility of water and solubility parameter (δ) for a ternary mixture is [6b]

$$\log X_{H_2O} = -\frac{v_{H_2O}}{RT \ln 10}(\delta_{H_2O} - \delta_m)^2 = \\ = -1.321 \times 10^{-3}(\delta_{H_2O} - \delta_m)^2 \quad (1a)$$

or

$$\log \phi_{H_2O} = -1.321 \times 10^{-3}(\delta_{H_2O} - \delta_m)^2 \\ -\phi_2\left(\frac{1 - v_{H_2O}}{v_2}\right) - \phi_3\left(\frac{1 - v_{H_2O}}{v_3}\right) \quad (1b)$$

where (1b) tries to take into account the influence on the entropy of mixing of a difference in size of the molecules. X = mole fraction, ϕ = volume fraction; δ_{H_2O} is the solubility parameter of water, v = molar volume (variations in molar volume are neglected); δ_m is defined by