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]

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

or

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

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

Table 2. The solubility parameter δ for water at 25°C computed from the solubility in various solvents.

Solvent	Solubility M	δ_{solv} Ref. 9	v_{solv} ml Ref. 9	δ_{H_2O} (1a)	δ_{H_2O} (1b)	Ref.
Benzene	0.034	9.2	89	23.0	23.9	8
Toluene	0.026	8.9	107	22.8	23.9	8
o-Xylene	0.021	9.0	121	23.0	24.2	8
m-Xylene	0.020	8.8	123	22.9	24.0	8
p-Xylene	0.025	8.8	124	22.6	23.8	8
Carbon tetrachloride	0.010	8.6	97	23.7	24.6	This work
Hexane	0.00_4	7.3	132	23.0	24.2	»
Octane	0.00_4	7.5	164	23.0	24.4	»

$$\delta_m = \phi_{H_2O}\delta_{H_2O} + \phi_2\delta_2 + \phi_3\delta_3 = \phi_2\delta_2 + \phi_3\delta_3 \quad (2)$$

The solubility of water is so small, that the first term in (2) is practically negligible.

We may now consider some binary systems. In Table 2 the solubility parameter of water has been computed from (1a) and (1b) for some systems studied by us.[2,8] The values for δ_{solv} and v_{solv} are those given by Hildebrand-Scott.[9]

From Table 2 it is evident that the solubility parameter differs on the two scales. Neither seems quite satisfactory. The mole fraction expression (1a) should be expected to work well for mixtures of benzene and aliphatic hydrocarbons. This is illustrated in Fig. 1 where the solubility of water in M (mole liter^{-1}) is plotted against $\phi_{C_6H_6}$ for the system $C_6H_6 - C_8H_{18} - H_2O$. The fulldrawn curve is

that computed from (1a) with $\delta_{H_2O} = 23.0$. It is seen that the fit to the experimental data is not entirely satisfactory for $\phi_{C_6H_6} < 0.5$ in spite of the good agreement for the binary systems. As expected a ternary system offers a more severe test than a binary one. For the sake of comparison the dashed curve in Fig. 1 is that computed from eqn. (1b) with $\delta_{H_2O} = 24.0$.

Of the solvents given in Table 2 carbon tetrachloride gives on both scales a δ_{H_2O} value that deviates very much from all the others. This implies a poor fit between theory and experiment and the dashed curve in Fig. 2 gives the solubility of water calculated from (1b) with $\delta_{H_2O} = 24.4$ (the average in the two solvents). Because of the quadratic term in eqn. (1) the choice of the value for the solubility parameter is important.
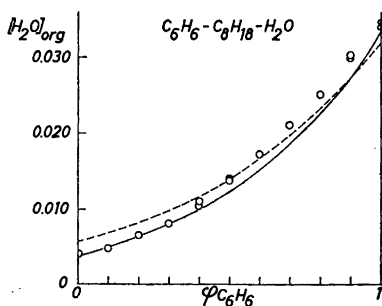

Fig. 1. $[H_2O]_{org}$ (M=mole liter^{-1}) plotted against $\phi_{C_6H_6}$ for the system C_6H_6-C_8H_{18}-H_2O. − − − calculated from eqn. (1a) with $\delta_{H_2O} = 23.0$; − − − calculated from eqn. (1b) with $\delta_{H_2O} = 24.0$.
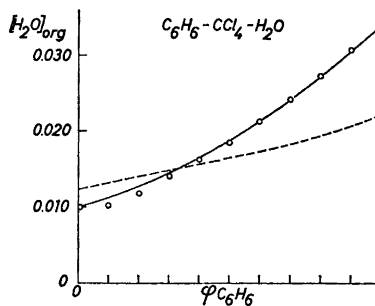
Fig. 2. $[H_2O]_{org}$ (M=mole liter^{-1}) plotted against $\phi_{C_6H_6}$ for the system C_6H_6-CCl_4-H_2O. − − − calculated from eqn. (1b) with $\delta_{H_2O} = 24.4$; − − − calculated from eqns. (1a) and (3).

A simple improvement of the fit can be obtained by computing δ_{H_2O} from the following expression:

$$\delta_{H_2O} = \phi_2 \delta_{H_2O(2)} + \phi_3 \delta_{H_2O(3)} \qquad (3)$$

where $\delta_{H_2O(2)}$ and $\delta_{H_2O(3)}$ refer to the values for δ_{H_2O} in the binary mixture. The fulldrawn curve in Fig. 2 has been computed from (1a) with δ_{H_2O} computed from (3). An excellent fit is obtained. By using (1b) instead of (1a) an equally good fit is obtained. For the sake of simplicity in computation (1a) is to be preferred.

Eqn. (3) implies that the interactions between water and a component in the mixture can be treated as if they are the same as in the pure solvent. This may be considered an indication that there are to a certain extent specific interactions between water and the two solvents. It is also possible that interactions between benzene and carbon tetrachloride partly are the reasons for the deviations. A 1:1 complex has been found to freeze out from this system [10] but this cannot be taken as a very strong argument in favor of its existence in solution. It is possible that an NMR study using water as a probe could elucidate on these points.

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The Diterpenoids of *Solidago missouriensis* Nutt.

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In a series [1] of investigations of the genus *Solidago* we have isolated from an ethyl acetate extract of the roots of *Solidago missouriensis* Nutt. several diterpenoids (Table 1).

One of these, m.p. 90—92°, $[\alpha]_D^{24} = -26°$ (CHCl$_3$), has physical and spectroscopic [2,3] properties similar to 13-epi-*enantio*-manoyloxide (*1*), and a related, new, further oxygenated compound is on spectroscopic grounds proved to be 3-oxo-13-epi-*enantio*-manoyloxide (*2*) (m.p. 90—91°, $[\alpha]_D^{23} -53°$ (CHCl$_3$)), (IR 1705 cm^{-1}). Its mass spectrum is similar to the mass spectrum of 3-oxo-manoyloxide.[3]

The strong peaks at *m/e* 206 and *m/e* 191 arising from the cleavage of bond C-9,C-11 and the C-8 oxide bond indicate that the keto group is in ring A or B.

The values obtained from the benzene-induced solvent shifts in the NMR spectrum of the 3-ketone [4] then accord only with a 3-keto group. [τ(benzene) — τ(CDCl$_3$) = + 0.25 (C-10 Me), +0.03 (C-8 Me), +0.04 (C-13 Me), +0.08 (C-4 axial Me) and −0.17 ppm (C-4 equatorial Me)]. Neither a C-1, 2,[5] 6,[6] nor 7 keto function would produce a solvent shift in a methyl group of −0.17 ppm. A further indication of a 3-keto function is the two proton multiplet at τ 7.5 in the NMR spectrum.[2] The *enantio* stereochemistry at C-13 follows from the position of the three vinylic protons (τ$_A$ 3.92, τ$_B$ 5.00, τ$_C$ 5.05, J_{AB}=18.0, J_{AC}=10.5, J_{BC}=1.3 Hz).[2]

The remaining diterpenoids (*3*, *4*, *5*) all have one feature in common, a UV spectrum [λ_{max} (EtOH) 234, 241, 250 nm] diagnostic of a heteroannular diene system.[7] They all show olefinic signals in the NMR spectrum. One broad and one narrow multiplet around τ 4.5 (1 H C-7) and 4.2 (1 H C-14). This suggests that the compounds are 7,13-abietadienes. One of them, the ketone *3* (IR 1712 cm^{-1}), on Wolff-Kishner reduction furnishes a hydrocarbon shown by GLC to be identical with 7,13-abietadiene (*10*) produced from abietic