Supplementary Information for
Trimethylglycine Complexes with Carboxylic Acids and HF: Solvation by Polar Aprotic Solvent

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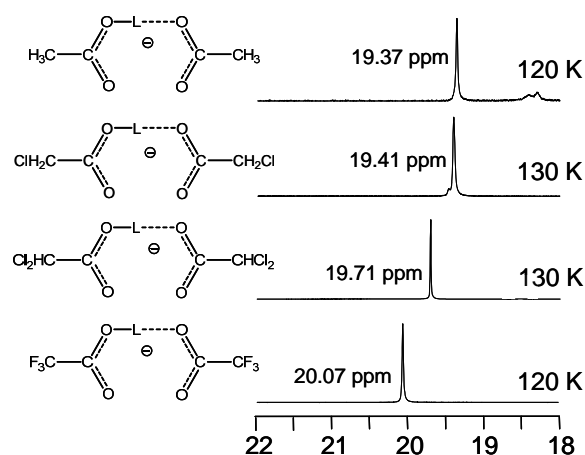[1] Institute of Chemistry and Biochemistry, Free University of Berlin, Germany

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Contents:

1. Additional ^{1}H NMR spectra used for the signal assignment..

Figure S1. Low-field parts of the ^{1}H NMR spectra of the sample containing excess of tetraethylammonium (TEA) carboxylate (from top to bottom: acetate, chloroacetate, dichloroacetate and trifluoroacetate) and the corresponding acid dissolved in CDF_3/CDF_2Cl at low temperature.

The chemical shifts of homo-conjugated anions of acetic, chroloracetic, and trifluoroacetic acids differ significantly from those shown in Figure 3a,b. This allows one to rule out the possibility that the signals reported in the paper belong to homo-conjugates of the acids. In case of complex **5**, which exhibits ^{1}H NMR chemical shift of the bridging proton close to that of homo-conjugated cation of trimethylglycine, the stoichiometry of the complex could be established using the integrated intensities of OHO, -CHCl$_2$, -CH$_2$- and –CH$_3$ proton signals, see Figure S2.
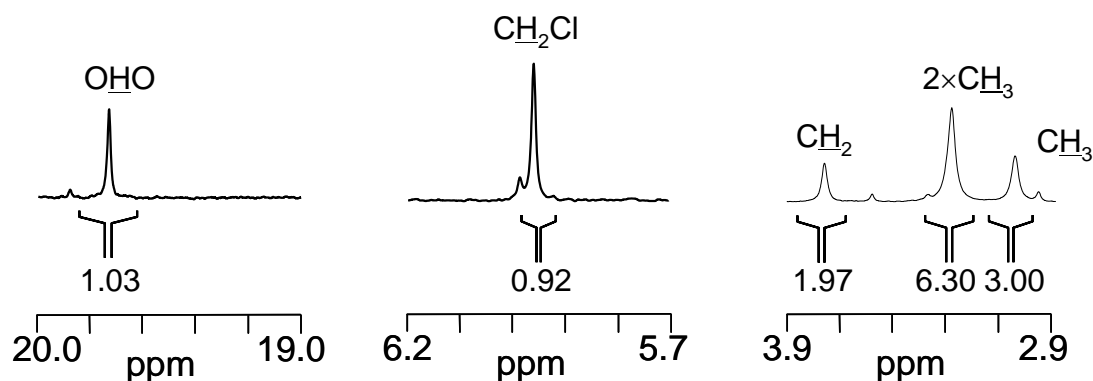
Figure S2. Integrated intensities of ^{1}H NMR signals of the sample containing complex **5**.

2. Temperature-dependent width of the ^{1}H NMR signal of $CHClF_2$ for the samples containing trimethylglycine with dichloroacetic acid (**5**) and HF (**6**).
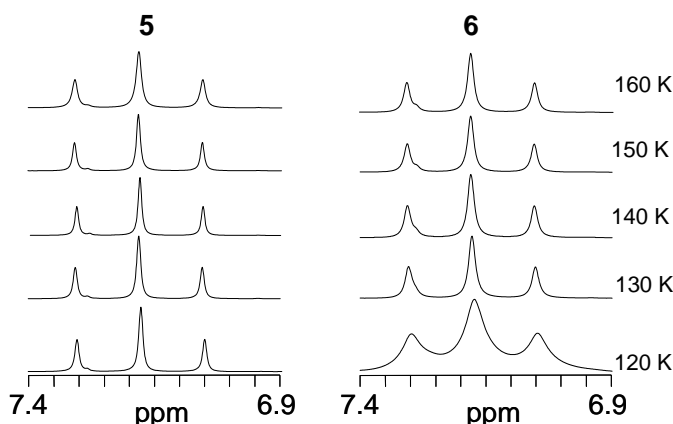
Figuse S3. Temperature-dependent width of the ^{1}H signal of the $CHClF_2$ component of the solvent for the samples containing trimethylglycine with dichloroacetic acid (**5**) and HF (**6**). The increase of the solvent signal width is due to the decrease of magnetic field homogeneity, which is because of the precipitation of the complex **6** on the sample tube walls.

3. Formation of homo-conjugated betaines *vs*. proton tautomerism.

   In the main text of the paper we have mentioned that in the sample containing a mixture of trifluoroacetic acid and trimethylglycine (betaine) the 1:1 complexes are virtually absent and the homo-conjugated cations of betaine are formed instead. Apparently, due to the high proton donating ability of trifluoroacetic acid it prefers to give the proton away and to become a counteranion to a homo-conjugated betaine cation. By analogy, this can help to explain the UV-Vis spectra publismhed previously by Dega-Szafran *et al*.,[1] who have studied the solution of pyridine betaine (Py$^+$BeCOO$^-$) and 2,6-dichloro-4-nitrophenol (DCNP-OH) in CH_2Cl_2 at room temperature. The UV-Vis spectrum consisted of two bands, which were virtually indistinguishable from the bands of free DCNP-OH and of the DCNP-O$^-$ Bu$_4$N$^+$ salt. This has been interpreted as tautomerism between "molecular" and "zwitterionic" forms of the complex, *i.e.* Py$^+$BeCOO$^-$···HO-DCNP and Py$^+$BeCOOH···$^-$O-DCNP. However, the UV absorption bands of H-bonded complexes of phenols and phenolates have been shown to differ significantly from those of "free" species.[2i] In order to resolve this discrepancy we propose here the alternative interpretation, based on the analogy with the case of complexes **1** and **2**. It is possible that in the experiment of Ref. 1 most of DCNP was not involved in the formation of H-bonded complexes, but existing either as free DCNP-OH or as DCNP-O$^-$, the latter being a counterion for a homo-conjugated pyridine betaine. One of the ways to check this hypothesis would be to measure NMR and UV-Vis spectra at low temperatures. The presence of low-field ^{1}H resonances can be used to identify the H-bonded species. This, however, lied outside the scope of this study.

[1] Z. Dega-Szafran, A. Komasa, M. Grundwald-Wyspiafiska, M. Szafran, G. Buczak and A. Katrusiak, *J. Mol. Struct.* 1997, **404**, 13-23.
[2] P.M. Tolstoy, B. Koeppe, G.S. Denisov and H.-H. Limbach, *Ang. Chem. Int. Ed.*, 2009, **48**, 5745-5747.

4. The complete set of *r*(OH) and *r*(HO) distances estimated from ^{1}H NMR chemical shifts for complexes **1-5** using H-bond correlations.

Table S1. Hydrogen bond geometries *r*(OH) and *r*(HO) estimated from ^{1}H NMR chemical shifts for complexes **1-5** using H-bond correlations (see text for details). The literature X-Ray data is given for comparison.

	T /K	*r*(OH) /Å	*r*(HO) /Å	*r*(OH) + *r*(HO) /Å	*r*(OO) /Å (X-ray)
1	293				2.457[a]
	160	1.1128	1.3239	2.4367	
	150	1.1164	1.3184	2.4348	
	140	1.1198	1.3133	2.4331	
	130	1.1232	1.3085	2.4317	
	120	1.1264	1.3040	2.4304	
2	293				2.565/2.488[b]
	160	1.3753	1.0821	2.4574	
	150	1.3766	1.0814	2.4580	
	140	1.3784	1.0804	2.4588	
	130	1.3801	1.0795	2.4596	
	120	1.3809	1.0791	2.4600	
3	160	1.0115	1.5551	2.5666	
	150	1.0127	1.5509	2.5636	
	140	1.0141	1.5457	2.5598	
	130	1.0153	1.5414	2.5567	
	120	1.0165	1.5375	2.5540	
4	160	1.0528	1.4358	2.4886	
	150	1.0560	1.4286	2.4846	
	140	1.0590	1.4218	2.4808	
	130	1.0620	1.4154	2.4774	
	120	1.0647	1.4095	2.4742	
5	160	1.1103	1.3277	2.4380	
	150	1.1131	1.3234	2.4365	
	140	1.1163	1.3186	2.4349	
	130	1.1190	1.3145	2.4335	
	120	1.1223	1.3098	2.4321	
		r(OH) /Å	*r*(HF) /Å	*r*(OH) + *r*(HF) /Å	*r*(OF) /Å (X-ray)
6	100				2.3788[c]
	160	1.3600	1.0367	2.3967	
	120	1.3435	1.0450	2.3885	

a – V.H. Rodrigues, J.A. Paixão, M.M.R.R. Costa and A. Matos Beja, *Acta Cryst.* 2001, **C57**, 213-215.
b – V.H. Rodrigues, J.A. Paixão, M.M.R.R. Costa and A. Matos Beja, *Acta Cryst.* 2001, **C57**, 761-763.
c – M. Szafran, Z. Dega-Szafran, R. Thaimattam and M. Jaskolski, *J. Mol. Struct.* 2004, **706**, 49-55, value corresponds to N-methylpiperidine betaine hydrofluoride.