Formation and Solid State Structures of Highly Crystalline Guanidinium Salts of Sulfonated Tertiary Phosphanes

Ágnes Kathó,[a,*] Attila C. Bényei,[b] Ferenc Joó,[a,c] Mária Ságí[c]

[a] University of Debrecen, Institute of Physical Chemistry, POB 7, 4010 Debrecen, Hungary
Fax: (+36)-52-512-915, e-mail: katho@tigris.klte.hu
[b] University of Debrecen, Department of Chemistry, Laboratory of X-ray Diffraction, 4010 Debrecen, Hungary
[c] Hungarian Academy of Sciences, Research Group on Homogeneous Catalysis, 4010 Debrecen, Hungary

Received: November 7, 2001; Accepted: January 7, 2002

Abstract: Formation of highly crystalline guanidinium salts of sulfonated triphenylphosphane derivatives is demonstrated as a general method for obtaining samples suitable for single crystal X-ray structural characterization. The structures of sulfonated phosphane ligands **1** – **5** have been determined. Extensive hydrogen bond networks between guanidinium N-H donors and $-SO_3$ oxygens as acceptors and/or π-π interactions stabilize the structures.

Keywords: hydrogen bonds; phosphanes; water-soluble ligands; X-ray analysis

Water-soluble salts of sulfonated triphenylphosphanes such as sodium (3-diphenylphosphino)benzenesulfonate (*m*TPPMS) and 3,3′,3″-phosphanetryilbenzenesulfonate (*m*TPPTS) are widely used in aqueous homogeneous and biphasic reactions as ligands of transition metal containing catalysts.[1] However, only a dozen compounds of this class, i.e., sulfonated triphenylphosphane derivatives and their complexes have been characterized by X-ray diffraction according to the latest edition (October 2001 release) of Cambridge Structural Database.[2] The obvious reason for this lack of structural data is in that these ligands and complexes are notoriously hard to crystallize and in many cases the use of bulky cations (Cs^+, R_4N^+) or complexation of the alkali metal cation had to be used in order to obtain X-ray quality crystals. The *m*TPPMS ligand has been known since 1958, nevertheless, the structure of its $[(C_6H_5CH_2)NEt_3]^+$ salt has been reported only in 1997.[3] $K_3[Pd(mTPPMS)_3] \cdot 4\ H_2O$, the first sulfonated phosphane complex structurally characterized in the solid state, was crystallized from *t*-BuOH/EtOH/H_2O.[4] Crystals of the water-soluble analogue of Vaska's compound, *trans*-$Na_2[IrCl(CO)(mTPPMS)_2]$ could be obtained[5] only with encapsulation of Na^+ counterions in [2.2.1]-kryptofix. The *o*- and *p*-monosulfonated triphenylphosphanes are also known,[6] it was however only recently that the solid state structure of *p*TPPMS-Cs salt,[7] and that of $RPhP(C_6H_4\text{-}p\text{-}SO_3K) \cdot 1/2\ H_2O$ (R = mesitylene)[8] have been determined. The structure of the hydroxyalkylphosphonium salt, formed from benzaldehyde and *m*TPPMS has also been published.[9]

The scarcity of solid state structures is even more striking in the case of trisulfonated triphenylphosphane and its derivatives, since the catalyst of the Ruhrchemie-Rhone Poulenc industrial hydroformylation process: $Na_3[HRh(CO)(mTPPTS)_3]$ is based on such a ligand.[10] In fact, the structure of *m*TPPTS itself has not been determined earlier, in contrast to $P(C_6H_4\text{-}p\text{-}SO_3K)_3 \cdot KCl \cdot 1/2\ H_2O$.[11] $Na_3[W(CO)_5(mTPPTS)]$ could be crystallized with [2.2.1]-kryptofix,[12] however, attempts at the isolation of crystalline Ca, Ba, Sr, K, Rb, or Cs salts failed. The characterization of $Na_6[Co_2(CO)_6(mTPPTS)_2]$ was hampered by disorder of the sulfonate groups, sodium cations, and solvent molecules present in the crystal lattice.[13] The structure of $Cs_8[Au(TPPTS)_3]$ and that of the polymeric $\{Na_5[Cu(TPPTS)_2] \cdot 5\ H_2O \cdot 1/2\ EtOH\}_n$ have also been published.[14]

Independent of the degree of sulfonation, in most cases layered crystal structures were revealed by X-ray diffraction, in which networks of electrostatic and hydrogen bonds involving the $-SO_3^-$ groups, the Na^+, K^+ or Cs^+ cations, as well as water or ethanol present in the lattice seemed to play a fundamental role in the crystal architecture. This case closely resembles that of the solid state structure of guanidinium sulfonates. Ward et al. have isolated a large number of guanidinium alkyl- and arylsulfonates and studied their structure and host/guest complexation properties.[15] They have established that the $[CN_3H_6]^+$ (gua) cations perfectly match sterically with the sulfonate anions resulting in the formation of two-dimensional, quasi-hexagonal networks of strong hydrogen bonds and, therefore, most guanidinium sulfonates showed a strong tendency for crystallization. We inferred that such hydrogen bonding could be advantageous also for the crystallization of sulfonated phosphanes. Indeed, single crystals of guanidinium sulfonates of tertiary phosphanes and phosphane oxides have been obtained by simple procedures, and here we report the structures of *m*TPPMS(gua) (**1**), *o*TPPMS-

  1615-4150/02/3443+4-278 – 282 $ 17.50-.50/0

oxide(gua) (**2**), *m*TPPTSNa(gua)$_2 \cdot H_2O$ (**3**), *m*TPPTS-oxideNa_2(gua)$\cdot$1/2 (C_6H_{14})$\cdot$3 H_2O (**4**), and *m*TPPTS-(gua)$_3 \cdot$gua(NO_3) (**5**) as well as some details on the effect of the guanidinium salt on the catalytic activity. Our results suggest that formation of guanidinium salts can be a very effective tool to trap sulfonated phosphane ligands. Because of steric hindrance and limitations not all hydrogen bonding capability of possible donors has been utilized in the supramolecular assembly of the crystals which can be even an advantage in the design of new structures stabilized by such H-bond networks.

Sulfonated phosphanes are usually obtained as their alkali metal salts.[1–10]; A general method for the preparation of guanidinium salts involved the stirring under an inert atmosphere of a methanolic or an aqueous solution of alkali phosphane sulfonates with an equivalent amount of guanidinium chloride for 1 h, followed by evaporation to dryness. The residue was extracted at room temperature with methanol. Colourless crystals of **1 – 4** were obtained by layering hexane onto the filtered extracts. The main results of structure determination have been compiled in Table 1, an ORTEP view and numbering scheme of structures **1** and **3** are shown in Figure 1 while an ORTEP view of **2** is in the graphical abstract. To our knowledge, the structure of *o*TPPMS has not been reported earlier, and **3 – 5** are the first simple salts of *m*TPPTS structurally characterized in the solid state. Structures **3 – 5** also represent examples when the guanidinium salt of a sulfonated phosphane ligand co-crystallizes with another compound, i.e., **3** with one molecule of water, **4** with three molecules of water and one half molecule of hexane (disordered over special position), and **5** with one molecule of guanidinium nitrate. There are disordered -SO_3 groups in **3**, **4**, and **5** to fulfill as much hydrogen bonding capacity of donors as possible and hence to stabilize the crystal. Strong packing interaction between phenyl rings and electrostatic interaction with sodium ions provide an additional enforcement of the layered structures. Generally, the crystals were very soft and mechanically weak. Nevertheless, according to our preliminary results this crystallization method is applicable to crystallize sulfonated phosphane complexes, too.[16]

Results of X-Ray Analysis: The structures of **1**, **3**, and **5** are very similar to that of PPh_3 with an average C-P distance of 1.842 Å and C-P-C angle of 101°, the corresponding values of PPh_3 are 1.827 Å and 103°, respectively. The structures of **2** and **4** are similar to PPh_3 oxide with an average C-P distance of 1.798 Å, P-O distance of 1.443 Å, O-P-C angle of 113.0°, C-P-C angle of 105.7°; the corresponding values in PPh_3 oxide are 1.793 Å, 1.489 Å, 112.5° and 106.4°, respectively.[17] The electronic and steric properties of the sulfonate group can explain these small differences.

According to the generally accepted graph set analysis[18] notation[19] of hydrogen bond patterns developed by Etter et al. in case of guanidinium sulfonate salts, the 'full' hexagonal network consists of $\mathbf{R_2^2(8)}$ and $\mathbf{R_6^3(12)}$ rings. This pattern means weaving, highly bent H-bond sheets or ribbons as seen in Figure 1 for the case of *m*TPPMS(gua). Other guanidinium salts form similarly

Table 1. Summary of crystallographic data for structures **1 – 5**.

Compound	**1**	**2**	**3**	**4**	**5**
Acronym	*m*TPPMS-(gua)	*o*TPPMS-oxide (gua)	*m*TPPTS(gua)$_2$-Na$\cdot H_2O$	*m*TPPTSoxide (gua)-$Na_2 \cdot$1/2 hexane$\cdot$3 H_2O	*m*TPPTS(gua)$_3$ guaNO_3
Formula	$C_{19}H_{20}N_3O_3PS$	$C_{19}H_{20}N_3O_4PS$	$C_{20}H_{26}N_6NaO_{10}PS_3$	$C_{22}H_{31}N_3Na_2O_{13}PS_3$	$C_{22}H_{36}N_{13}O_{12}PS_3$
M_w	401.41	417.41	660.61	718.63	801.79
Crystal system	orthorhombic	monoclinic	triclinic	monoclinic	triclinic
Space group	*Pca*21	*P*21/c	$P\bar{1}$	*P*21/c	$P\bar{1}$
Crystal size [mm^3]	0.4 × 0.25 × 0.2	0.55 × 0.42 × 0.35	0.41 × 0.12 × 0.1	0.3 × 0.25 × 0.22	0.45 × 0.4 × 0.3
a [Å]	19.3926(10)	11.286(5)	11/554(2)	8.5429(10)	12.515(2)
b [Å]	7.9529(10)	10.230(4)	11.861(2)	14.668(2)	14.257(2)
c [Å]	25.5575(10)	17.004(4)	12.483(2	23.7840(10)	14.344(2)
α [°]	90	90	82.8(1)	90	112.31(1)
β [°]	90	95.1(1)	89.11(12)	91.804(10)	115.53(1)
γ [°]	90	90	62.81(10)	90	97.82(1)
V [Å^3]	3941.7(6)	1955.5(12)	1507.9(4)	2978.8(5)	1994.3(5)
Z	8	4	2	4	2
D_{calc} [Mg m^{-3}]	1.353	1.418	1.455	1.602	1.335
θ_{max} [°]	27.0	27.0	25.1	25.3	26
Measured independent reflections $I > 2\sigma(I)$	3474	1479	3206	4082	2116
μ [mm^{-1}]	0.27	0.279	0.373	0.402	0.293
R [%]	7.3	6.9	5.57	6.56	7.03
R_w [%]	23.68	24.61	15.3	13.15	42.0
Data/parameter	11	16.38	13.3	13.92	16.0

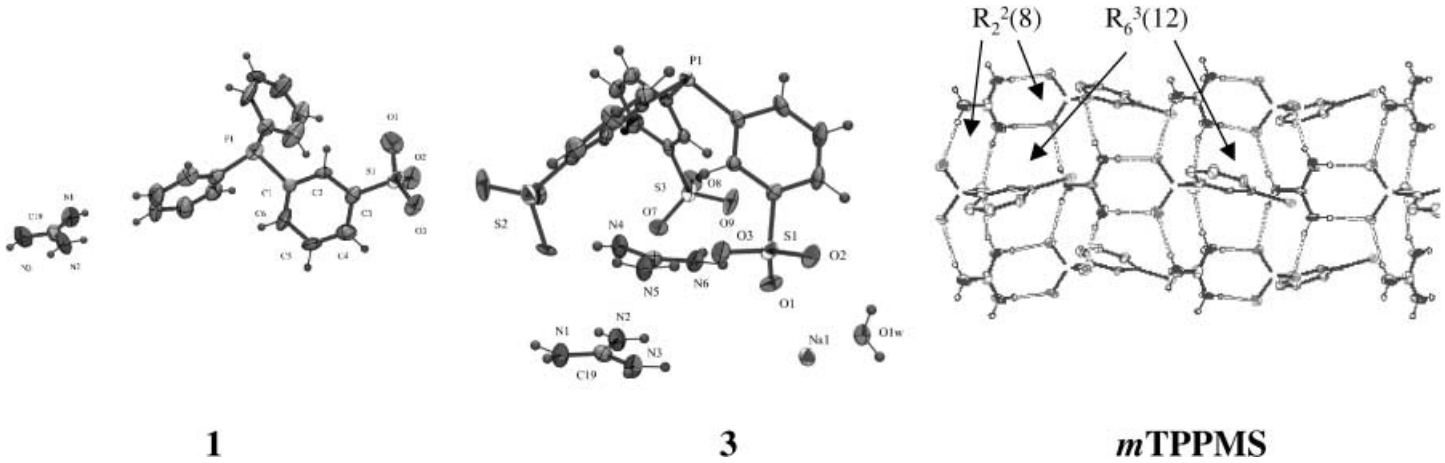

Figure 1. ORTEP view of **1** and **3** with partial numbering scheme and H-bond ribbon network normal to (001) in **1,** *m*TPPMS. The phosphane in *m*TPPMS is highly truncated for clarity.

highly ordered structures, i.e., rosettes in case of hydrogen carbonate ions.[20] However, both electronic and steric factors can influence the H-bond pattern also in guanidinium salts of organic sulfonates which in case of steric hindrance results in bilayer stacking with R groups connected to the sulfonate moiety either at the same side or in alternative fashion, at the opposite side of H-bond sheets. With suitable guest molecules pillared bilayer and pillared continuous single-layer stackings are formed. In the case of even bulkier substituents and/or electronic interactions, it is well probable that not all possible hydrogen bonds are formed as a consequence of packing interactions. Exactly this was the result of our investigation, too. The 'full' $\mathbf{R_2^2(8)}$ and $\mathbf{R_6^3(12)}$ network is formed in the case of *m*TPPMS(gua) **1** with $\theta_{ir} = 107°$ where θ_{ir} is the interribon dihedral angle representing the puckering of H-bond sheets. The other extreme is **4**, where an infinite three dimensional network is formed with the participation of solvent water molecules and sodium ions; bulky phenyl rings destroy gua-SO_3 ribbons but their π-π interactions stabilize the overall structure. These systems offer the unique possibility to compare the strength of different packing interactions with quantum mechanical calculations, too, provided that further X-ray structures will be available. The result of such interactions most probably will be several polymorphs. Indeed, we have observed crystals with different unit cell parameters but unfortunately, their quality was not satisfactory to perform structural analysis.

Solid state structures may not always represent the species present in solution. In our case, the catalytic hydrogenation properties of $[RuCl_2(m\text{TPPMS})_2]$ were found to be independent of the cation of the sulfonated phosphane ligand (Figure 2). In particular, the rate of hydrogenation of crotonic acid (0.02 M) catalyzed by $[RuCl_2(m\text{TPPMS})_2]$ (5×10^{-4} M) in aqueous solution (pH = 3.30 ± 0.05) at T = 333 K (Figure 2) was found to be the same ($t_{1/2} = 15$ min) in the absence and in the presence of guanidinium chloride in the 0.002 – 0.010 M concentration range ([gua]/[Ru] = 4 – 100). Having all components in low absolute concentrations, we can assume complete dissociation of both strong electrolytes ($ArSO_3Na$ and gua × Cl), accordingly no specific interaction of the sulfonated phosphane ligand and the guanidinium cation is expected in this slightly acidic solution. More gua × Cl, however, led to a slight inhibition of catalysis ([gua × Cl] = 0.075 M, $t_{1/2}$ = 18 min; [gua × Cl] = 0.100 M, $t_{1/2}$ = 27 min). One can expect even less effect from gua × NO_3 in catalytic systems due to the non-coordinating nature of nitrate ion.

In conclusion, guanidinium salts of sulfonated phosphanes and their metal complexes offer a unique possibility to combine results of structural chemistry in describing and perhaps designing new supramolecular assemblies, to calculate their energies with that of organometallics and to utilize their stability to trap transition metal complexes which are very difficult or impossible to crystallize in the form of salts. Our simple procedure provides a general method of establishing solid state structures of these important ligands in

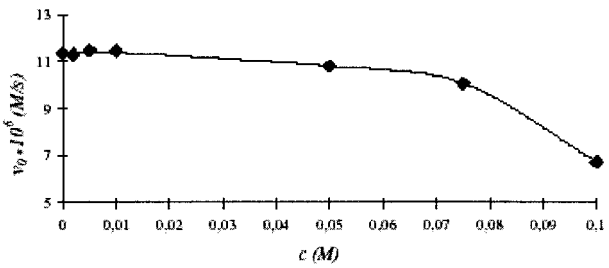

Figure 2. The effect of guanidine × HCl on the hydrogenation of crotonic acid catalyzed by $[RuCl_2(m\text{TPPMS})_2]$. [crotonic acid] = 2×10^{-2} M, $[RuCl_2(m\text{TPPMS})_2] = 5 \times 10^{-4}$ M, p_{H2} = 0.1 MPa, t = 60 °C.

organometallic catalysis. As exemplified by the case of $[RuCl_2(m\text{TPPMS})_2]$, replacement of alkali metal cation by guanidinium does not change the catalytic properties of water-soluble transition metal complexes carrying sulfonated phosphane ligands.

Experimental Section

General Remarks

Reagent grade chemicals were used as supplied. Sulfonated phosphanes and $[RuCl_2(m\text{TPPMS})_2]$ were prepared according to literature methods.[1,6,10] Purity of these known compounds was routinely checked by FT-IR spectroscopy (Perkin Elmer Paragon 1000 PC), HPLC (Waters), and ^1H and ^{31}P NMR spectroscopy (Bruker AM 360, D_2O, room temperature, referenced to residual H_2O and external 85% H_3PO_4, respectively). Catalytic hydrogenation of crotonic acid was followed by measuring gas uptake in a conventional gas-burette of constant pressure.[21]

Representative Procedure for the Synthesis of Guanidinium Salts of Sulfonated Phosphanes 1 – 4

To a solution of *m*TPPMS-Na (1 g, 2.5 mmol) in methanol (10 mL) guanidinium chloride (0.25 g, 2.5 mmol) was added in methanol (2.5 mL) under Ar. The mixture was stirred for an hour and the solvent was removed under reduced pressure. The residue was extracted with methanol (3 mL). Crystals were obtained by layering hexane onto filtered methanol solutions. ^{31}P NMR: $\delta = -3.9$ ppm, identical to that of *m*TPPMS-Na.

Guanidinum Salt of *m*TPPTS (5)

*m*TPPTS-Na (0.62 g, 1 mmol) in water (1 mL) and guanidinium nitrate (0.26 g, 2.1 mmol) in water (2 mL) were stirred under Ar for 20 min. Absolute ethanol was added (16 mL) and the mixture was stored in a refrigerator. 50 min later a white precipitate was obtained. Most of the supernatant was removed with the aid of a syringe and added to another flask containing ethanol (4 mL). The mixture became cloudy in minutes and in a few hours white crystals were deposited on the wall of the flask These were collected by filtration and washed thoroughly with cold ethanol. ^{31}P NMR: $\delta = -5.1$ ppm, identical to that of *m*TPPTS-Na.

X-Ray Analysis

X-ray data[22] were recorded at 293 K using an Enraf Nonius Mach3 diffractometer, Mo-Kα radiation, $\ddot{e} = 0.71073$ Å with graphite monochromator, ω-2θ motion. Structures were solved using the SIR-92 software[23] and refined on F^2 using the SHELX-97 program,[24] publication material was prepared with the WINGX-97 suite.[25] Structures were analyzed using the PLATON program.[26] Hydrogens were usually placed into ideal positions, however in some cases guanidinium hydrogens could be found at the differential electron density maps. These badly behaving hydrogens caused a remaining shift in the refinement. Structure **1** shows pseudo-symmetry with an 83% fit and a 2 e^- Å^{-3} peak close to the phosphorus atom in the reported non-centrosymetric space group. Crystals were generally weakly diffracting.

Acknowledgements

*This work was supported by the Hungarian Research Foundation (OTKA 29934 and D25136) and by the Ministry of Education (FKFP 0416). The authors are grateful to Drs. F. Riddell and Ph. Lightfoot (Univ. St. Andrews, Scotland) for their invaluable help in setting up the X-ray laboratory in Debrecen and to Prof. G. Oehme (IFOK, Rostock) for a gift of o*TPPMS. *A.C.B. is grateful for the Hungarian Academy of Sciences for Bolyai Postdoctoral Fellowship.*

References and Notes

[1] F. Joó, *Aqueous Organometallic Catalysis*, Kluwer, Dordrecht, **2001**; B. Cornils, W. A. Herrmann, (Eds.), *Aqueous-Phase Organometallic Catalysis*, Wiley-VCH, Weinheim, **1998**; F. Joó, Á. Kathó, *J. Mol. Catal. A.* **1997**, *116*, 3; F. Joó, J. Kovács, Á. Kathó, A. C. Bényei, T. Decuir, D. J. Darensbourg, *Inorg. Synth.* **1998**, *32*, 1.

[2] F. H. Allen, O. Kennard, *Chemical Design Automation News* **1993**, *8*, 1.

[3] S. Ahrland, J. Chatt, N. R. Davies, A. A. Williams, *J. Chem. Soc.* **1958**, 264; P. J. Roman, D. P. Paterniti, R. F. See, M. R. Churchill, J. D. Atwood, *Organometallics* **1997**, *16*, 1484.

[4] A. L. Casalnuovo, J. C. Calabrese, *J. Am. Chem. Soc.* **1990**, *112*, 4324.

[5] J. Kovács, T. D. Todd, J. H. Reibenspies, F. Joó, D. J. Darensbourg, *Organometallics* **2000**, *19*, 3963.

[6] J. A. van Doorn, E. Drent, P. W. N. van Leeuwen, N. Meijboom, A. B. van Oort, R. L. Wife, (Shell Int. Research), *European Patent* EP 0280380, **1988**; *Chem. Abstr.* **1980**, *110*, 58296g; H. Schindlbauer, *Monatsh. Chem.* **1965**, *96*, 2051; T. I. Wallow, F. E. Goodson, B. M. Novak, *Organometallics* **1996**, *15*, 3708.

[7] G. Papp, J. Kovács, A. C. Bényei, G. Laurenczy, L. Nádasdi, F. Joó, *Can. J. Chem*. **2001**, *79*, 635.

[8] F. Bitterer, O. Herd, A. Hessler, M. Kühnel, K. Rettig, O. Stelzer, W. S. Sheldrick, S. Nagel, N. Rösch, *Inorg. Chem.* **1996**, *35*, 4103.

[9] D. J. Darensbourg, F. Joó, Á. Kathó, N. White, A. C. Bényei, J. H. Riebenspies, *Inorg. Chem.* **1994**, *33*, 175.

[10] E. Kuntz, *CHEMTECH*, **1987**, *17*, 570; B. Cornils, W. A. Herrmann, (Eds.), *Applied Homogeneous Catalysis with Organometallic Compounds*, VCH, Weinheim, **1996**; B. Cornils, *Top. Curr. Chem*. **1999**, *206*, 133; J. Herwig, R. Fischer, in *Rhodium Catalyzed Hydroformylation*, (Eds.: P. W. N. M. van Leeuwen, C. Claver), Kluwer, Dordrecht, **2000**, pp. 189.

[11] O. Herd, K. P. Langhans, O. Stelzer, N. Weferling, W. S. Sheldrick, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1058.

[12] D. J. Darensbourg, C. Bischoff, J. H. Reibenspies, *Inorg. Chem.* **1991**, *30*, 1144.
[13] T. Bartik, B. Bartik, B. E. Hanson, K. H. Whitmire, I. Guo, *Inorg. Chem.* **1993**, *32*, 5833.
[14] J. P. Fackler, T. A. Grant, B. E. Hanson, R. J. Staples, *Gold Bull.* **1999**, *32*, 20; F. Tisato, F. Refosco, G. Bandoli, G. Pilloni, B. Corain, *Inorg. Chem.* **2001**, *40*, 1394.
[15] V. A. Russell, M. C. Etter, M. D. Ward, *J. Am. Chem. Soc.* **1994**, *116*, 1941; K. T. Holman, A. M. Pivovar, J. A. Swift, M. D. Ward, *Acc. Chem. Res.* **2001**, *34*, 107, and references cited therein.
[16] For preliminary publications on [{PdCl(**1**)}$_2$], see: A. Cs. Bényei, Á. Kathó, F. Joó, *Abstr. 19th Eur. Crystallographic Meeting*, (Nancy, France), s9.m1.p4, **2000**; Á. Kathó, A. Cs. Bényei, F. Joó, *Abstr. 12th Int. Symp. Hom. Catal.* (Stockholm, Sweden), **2000**, P119.
[17] J. J. Daly , *J. Chem. Soc*. **1964**, 3799; C. P. Brock, W. B. Schweizer, J. D. Dunitz, *J. Am. Chem. Soc.* **1985**, *107*, 6964; F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, G. Orpen, R. Taylor, *J. Chem. Soc. Perkin Trans. 2* **1987**, S1.
[18] M. C. Etter, *Acc. Chem. Res.* **1990**, *23*, 120; J. Bernstein, R. E. Davis, L. Shimoni, N. L. Chang, *Angew. Chem. Int. Ed. Engl*. **1995**, *34*, 1555.
[19] The hydrogen bond patter is described as $\mathbf{G_d^a(n)}$ where **G** stands for a designator letter (**C** for chains, **R** for rings, **S** for intramolecular pattern and **D** for other finite pattern), **d** is the number of H-donors while **a** is the number of acceptor atoms and **n** the total number of atoms in the pattern, for example, in the ring.
[20] T. C. W. Mak, F. Xue, *J. Am. Chem. Soc*. **2000**, *122*, 9860.
[21] Z. Tóth, F. Joó, M. T. Beck, *Magy. Kém. Foly.* **1980**, *86*, 20; Z. Tóth, F. Joó, M. T. Beck, *Inorg. Chim. Acta* **1980**, *42*, 153.
[22] Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-163227-163230 and 173673. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code +44-(1223)-336-033; e-mail: deposit@ccdc.cam.ac.uk].
[23] A. Altomare, G. Cascarano, G. Giacovazzo, A. Guagliardi, *J. Appl. Cryst*. **1993**, *26*, 343.
[24] G. M. Sheldrick, *SHELXL-97*, Universität Göttingen, Germany, **1997**.
[25] L. J. Farugia, *WINGX-97 system*, University of Glasgow, U. K., **1996**.
[26] A. L. Spek, *Acta Cryst*. **1990**, *A46*, C34.